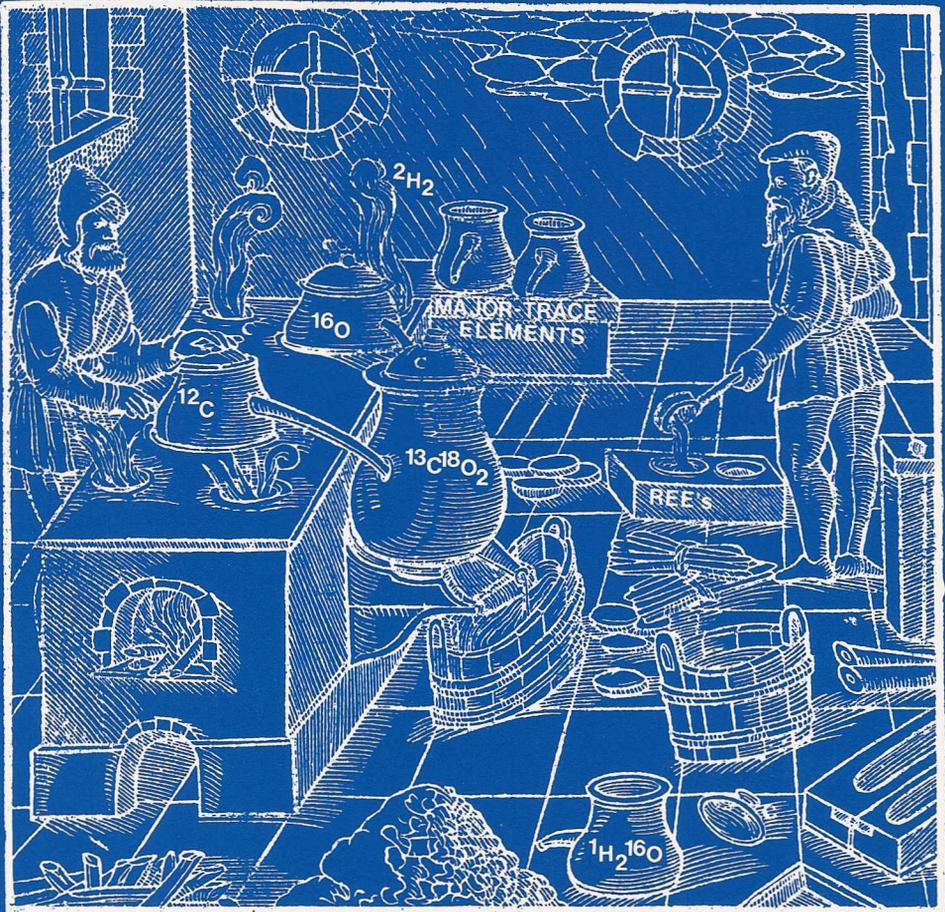


STABLE ISOTOPE (C, O, H), MAJOR- AND TRACE  
ELEMENT STUDIES ON HYDROTHERMAL  
ALTERATION AND RELATED ORE MINERALIZATION  
IN THE VOLCANO-SEDIMENTARY BELT OF  
BERGSLAGEN, SWEDEN.



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BERGSLAGEN, SWEDEN.

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SEDIMENTARY BELT OF BERGSLAGEN, SWEDEN.**

**STABIELE ISOTOPEN (C, O, H), HOOFD- EN SPORE- ELEMENTEN  
ONDERZOEKINGEN VAN HYDROTHERMALE OMZETTINGEN EN  
GERELATEERDE ERTSMINERALIZATIES IN DE  
VULKANOSEDIMENTAIRE GORDEL VAN BERGSLAGEN,  
ZWEDEN.**

(met een samenvatting in het nederlands)

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**Aan Regien, Bart, Lies  
Mijn ouders  
Marten**

Ai-je fait mieux ?  
Ai-je eu enfin le bonheur de *réaliser ce livre* ....attendu?  
Le public jugera;  
tout ce que je puis dire,  
c'est que j'ai fait autre chose que ce que l'on a fait jusqu'ici.

Le livre de cuisine  
*par*: Jules Gouffé  
Librairie Hachette et C<sup>ie</sup>  
Paris, France  
1884

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## PREFACE

This study originally started as part of a M.Sc. project, comprising mapping of an area in western Bergslagen, central Sweden, and studying hydrothermal alteration zones near the village of Hjulsjö. This work formed part of a large project of the former Geological Institute of the University of Amsterdam, which sadly enough had to be closed for financial/political reasons. This project had the aim of mapping in the western Bergslagen region, and studying specific problems in the geochemical, petrological, mineralogical, and especially the ore geology fields. Leader of the project was Prof. Dr. I.S. Oen.

This Ph.D. thesis started at the Geological Institute of the University of Amsterdam, under supervision of Prof. Dr. I.S. Oen. Subjects of study were hydrothermal alteration systems and related mineralizations. It was already clear that unraveling the alteration history could not be done separately from the volcanogenic, volcano-sedimentary, tectonic, metamorphic, and igneous development of the region. This was the reason for studying the regional development of Bergslagen, leading to a number of publications which are included in this thesis.

In 1987 a CNRS-CIES grant for a studentship at the "Centre de Recherches Pétrographiques et Géochimiques" (CRPG), Vandoeuvre-lès-Nancy, France, was awarded to the author, enabling him to learn the principles of stable isotope analyses under supervision of Dr. S.M.F. Sheppard. Work was done on C and O isotopes on carbonates, O and H isotopes on silicates and H isotopes on fluid inclusions. Upon returning to the Netherlands after a 16 months stay in France, the research continued at the Institute of Earth Sciences at the State University of Utrecht, studying O and H isotopes in silicates, under supervision of Dr. R. Kreulen and Prof. Dr. R.D. Schuiling.

Study on the alteration history of the region concentrated on geochemical methods. Chemical analyses by X-ray fluorescence (XRF) and neutron activation (INAA) techniques were included.

The results of the study on the hydrothermal alteration systems of W. Bergslagen and a discussion on the Proterozoic Bergslagen region are presented in this thesis.

## SAMENVATTING

De 1.90 - 1.86 Ga oude vulkanosedimentaire gordel van West Bergslagen, centraal Zweden, is een onderdeel van het Svecofennische domein, dat op zijn beurt weer deel uitmaakt van het Baltische Schild. De gordel van West Bergslagen omvat een pakket van meer dan 10 km dikte dat bestaat uit felsische vulkanieten en een meer dan 2 km dik pakket van vulkanoclastische sedimenten. De vulkanieten bevatten carbonaat-, chert- en ijzer-oxide lensen. De supracrustale gesteenten worden geïntrudeerd door diabaas gangen en platen en door graniet plutonen.

De supracrustale gesteenten zijn scheefgesteld in een sub-verticale stand. Foliaties volgen doorgaans de gelaagdheid en zijn ook ontwikkeld in schisteuze schuif- en breuk zones. Lineaties staan eveneens steil en liggen in een foliatie vlak. De gesteenten van de West Bergslagen gordel zijn metamorf en hebben een mineraal-associatie die duidt op groenschist of laag amphiboliet facies.

Hydrothermale omzettingen en daaraan gerelateerde ertsafzettingen komen veelvuldig in West Bergslagen voor, en worden in dit proefschrift bestudeerd. De doelstelling van deze studie was om de werking van hydrothermale processen in de Proterozoïsche korst van West Bergslagen te begrijpen. Onderwerpen als: de oorsprong van de hydrothermale vloeistoffen, de uitwisseling tussen deze vloeistoffen en mineralen in het gesteente, mobiliteit van elementen tijdens de hydrothermale processen, de mate waarin deze elementen worden verwijderd of toegevoegd aan het gesteente, en de relatie tussen de hydrothermale vloeistoffen en de ertsvorming, komen aan de orde. Een belangrijke doelstelling was verder om de invloed van zeewater bij de hydrothermale processen, en de samenstelling van dit vroeg Proterozoïsch zeewater, in vergelijking met het huidige zeewater, vast te stellen.

Een overzicht van modellen voor de ontwikkeling van de korst van de Bergslagen gordel wordt in paragraaf 2 van het eerste hoofdstuk gegeven. De twee basismodellen zijn: 1) een eiland-boog - subductie model en 2) een continentale slenk model. Na een discussie van de verschillende modellen, zoals deze in de literatuur beschreven zijn, wordt een keuze voor het continentale slenk model gemaakt. De aanname van een zeebekken aan de rand van het continent gedurende de vorming van de slenk is in het model opgenomen. In dezelfde paragraaf wordt een poging gedaan de ontwikkeling van het West Bergslagen gebied en de omliggende provincies te plaatsen in een plaat-tektonisch model. Dit is een erg algemeen en speculatief model en moet als een introductie voor de andere hoofdstukken worden beschouwd. Tenslotte wordt een mogelijke geologische ontwikkeling van de Oostzee (Baltische zee) besproken.

Het continentale slenk-model van Oen en medewerkers wordt in hoofdstuk 2 uitgebreid met een model van koepel-vormige tektoniek, waarin getracht wordt om de verticale stand van de gesteentepakketten in het gebied van West Bergslagen te verklaren. Graniet intrusie en het wegzakken van zwaardere gesteentepakketten in trog-vormige zones worden beschouwd als de belangrijkste oorzaak voor de verticale stand van de supracrustale gesteenten van West Bergslagen.

Na deze algemene inleiding worden de petrografische, geochemische en stabiele isotopen studies van de hydrothermale omzettingsprocessen in de korst van West Bergslagen gepresenteerd. In hoofdstuk 3 wordt een korte inleiding gegeven over de verschillende hydrothermale omzettingen en ertsafzettingen in de gordel van West Bergslagen.

In hoofdstukken 4 en 5 wordt een petrologische en chemische studie van de omzettingszones van Hjulsjö gepresenteerd. Deze Hjulsjö zones vormen een serie van pijpvormige kanalen waardoor hydrothermale vloeistoffen werden getransporteerd. Zij snijden door de primaire structuren van de supracrustale gesteenten. Deze omzettingszones worden gerelateerd aan de ijzer-oxide en carbonaat horizon van Sirsjöberg - Ösjöberg, en aan een intrusief-complex van granitische samenstelling, dat de warmte voor het hydrothermale systeem kan hebben geleverd. Deze gelaagde Sirsjöberg - Ösjöberg afzettingen zijn waarschijnlijk als exhalatieve afzettingen op de zeebodem gevormd. Tijdens een latere fase zijn deze afzettingen gedeformeerd en (gedeeltelijk) chemisch omgezet door metamorfe processen en door hydrothermale skarn vorming.

Er zijn aanwijzingen gevonden voor hoge mobiliteit van bepaalde elementen, in het bijzonder zeldzame aarden (REE), veroorzaakt door hoge water/gesteente ratio's in het hydrothermaal systeem. Een relatie tussen mobiliteit van elementen, mineralogie, en vorm van de omzettingszones wordt aangetoond. Voorts wordt getoond dat de chemische samenstelling van het gesteente in de omzettingszones van Hjulsjö door de vloeistoffase wordt gecontroleerd

Een conclusie is dat in de meest omgezette delen van de zones veel elementen uit het gesteente werden opgelost door de hydrothermale vloeistoffen. Deze elementen werden naar de oppervlakte (zeebodem) getransporteerd, of afgezet in een ander deel van de aardkorst. De REE's in de gesteenten van de omzettingszones vertonen een heel karakteristiek gedrag: met toenemende graad van omzetting worden de lichte-REE's aanzienlijk verlaagd in concentratie, terwijl de zware-REE's geen of slechts een lichte afname vertonen. Eu neemt sterk af en laat een sterke negatieve anomalie zien.

Een hoge Mg-aanrijking is waargenomen in het gesteente en geeft een sterke aanwijzing dat de hydrothermale vloeistoffen in de Hjulsjö zones bestonden uit opgewarmd zeewater. Onder voorbehoud wordt een samenstelling gegeven van zware-REE's in vroeg Proterozoïsch zeewater. Berekeningen, gepresenteerd in hoofdstuk 6, gebaseerd op thermodynamische gegevens

van Jasinski (elders gepubliceerd), voorspellen het gedrag van mineralen bij interactie van een felsisch gesteente met een zeewater bevattend hydrothermaal systeem. Een model dat de stabiliteit beschrijft van de gevormde omzettingsmineralen wordt getoond in een diagram van temperatuur tegen  $aK/aNa$ . De mineralogie in dit diagram komt redelijk overeen met de mineralogie die in de Hjulsjö omzettingszones wordt gevonden.

Analyse van stabiele isotopen in mineralen en gesteenten was een belangrijk hulpmiddel om de hydrothermale omzettingen en de daarmee gerelateerde ertsafzettingen van het West Bergslagen gebied te bestuderen. In hoofdstuk 7 wordt een inleiding gegeven en een beschrijving van de verschillende analyse technieken. Mineraal - water en mineraal - mineraal isotopen fractionaties zijn van groot belang voor de interpretatie van de gegevens en worden kort besproken. Hoofdstuk 7 wordt afgesloten met een beschrijving van de preparatie methode zoals deze is uitgevoerd aan monsters bestemd voor stabiele isotopen analyses.

Koolstof en zuurstof isotopen werden gemeten aan calcieten en dolomieten van gelaagde carbonaten en carbonaat aders en concentraties in W ± Mo, Fe - Mn oxide en Zn - Pb sulfide skarns. Koolstof isotopen ( $\delta^{13}C$  rond 0‰) van de gelaagde carbonaten wijzen op afzetting op een zeebodem. Zuurstof isotopen laten twee groepen van gelaagde carbonaten zien: een groep met enigszins lage tot normale carbonaat  $\delta^{18}O$  waarden (12 tot 19‰) vertegenwoordigt onveranderde sedimentaire carbonaten, en een tweede groep met  $\delta^{18}O$  waarden tussen 6 en 11‰. Deze laatste groep is gerelateerd aan exhalatieve ijzer-oxide afzettingen, en de lage  $\delta^{18}O$  waarden werden waarschijnlijk veroorzaakt door uitwisseling van de carbonaten met heet zeewater ( $300^\circ \pm 50^\circ C$ ), of met meteorisch water onder lagere temperaturen. Carbonaten in de skarns geven zowel lage  $\delta^{13}C$  (-2 tot -8‰) als lage  $\delta^{18}O$  (6 tot 12‰) waarden. Deze waarden zijn karakteristiek voor carbonaten in skarn mineralisaties, en liggen in de buurt van de isotopen waarden van magmatisch carbonaat. Een mogelijke onderverdeling in groepen van Fe - Mn en W - Mo skarn-gerelateerde carbonaten aan de hand van isotopen samenstelling wordt als mogelijkheid naar voren gebracht. Echter blijkt deze verdeling niet te worden gevonden bij analyse van H en O isotopen aan silikaat mineralen in dezelfde skarns, zoals in hoofdstuk 9 wordt aangegeven.

Waterstof en zuurstof isotopen analyses van silikaat mineralen in de skarn mineralisaties van West Bergslagen worden in hoofdstuk 9 besproken. De isotopen samenstellingen van vloeistoffen die in evenwicht zijn met de gehydrateerde skarn mineralen zijn berekend. Proterozoïsch zeewater, of eventueel meteorisch water met hoge  $\delta^{18}O$  en  $\delta D$  waarden (geografische

ligging van het Baltische Schild tussen  $0^\circ$  -  $30^\circ$  N tijdens het vroege Proterozoïcum) zijn de meest waarschijnlijke bron van de skarnvormende hydrothermale vloeistoffen.

De berekende  $\delta D$  waarden van deze vloeistoffen hebben een grote spreiding (-5 tot -80‰) terwijl  $\delta^{18}O$  waarden een relatief kleine spreiding vertonen (4 tot 7‰). De hoogste  $\delta D$  waarden (-5 tot -20‰) liggen dicht bij die van het huidige zeewater en zijn een aanwijzing voor een vergelijkbare waterstof isotopen samenstelling van modern en vroeg Proterozoïsch zeewater. De spreiding in waterstof isotopen is, met enig voorbehoud, verklaard door uitwisseling van silikaat mineralen met het huidige meteorische water ( $\delta D = -82‰$ ;  $\delta^{18}O = -11.5$ ) aan de oppervlakte. Een verschil van meer dan 10‰ in  $\delta D$  over een afstand van slechts 10 cm in een groot amfiboliet-blok afkomstig van een storthoop bij een oude mijn, laat duidelijk de invloed van verwerking zien. Een zelfde verschil in  $\delta D$  wordt gevonden als men verweerde monsters en verse monsters van eenzelfde skarn vergelijkt. Ook is de hoeveelheid water in verweerde monsters vergeleken met die in verse monsters. Phlogopieten in verweerde monsters laten verlaagde  $\delta D$  waarden zien bij toename van het water gehalte. Amfibolen geven een minder duidelijk beeld; verweerde monsters tonen een zeer kleine spreiding in water gehalten, terwijl juist in verse monsters een grote spreiding in water gehalten wordt gevonden. Mogelijk is dit het gevolg van de aanwezigheid van wisselende hoeveelheden F en Cl in het amfibool-rooster.

Een model van waterstof uitwisseling tussen mineralen en meteorisch water bij lage temperaturen aan het aardoppervlak wordt als meest waarschijnlijke verklaring gegeven voor het patroon van de waterstof isotopen in de skarns van West Bergslagen. Er is echter nog aanvullende studie nodig om dit model met meer zekerheid te kunnen verdedigen.

Hoofdstuk 10 laat zien hoe op grote schaal zuurstof isotopen uitwisseling plaatsvond tussen carbonaten, cherts, ijzer-oxides en de hete hydrothermale oplossingen die ook verantwoordelijk waren voor exhalatieve processen op de zeebodem. Archeïsche en vroeg tot midden Proterozoïsche kalken en cherts zijn voornamelijk bekend uit groensteen gordels, welke bekend staan om hun vulkanische activiteit. Aanwijzing voor grootschalige hydrothermale systemen en uitvloeit van hete vloeistoffen zijn de grote gelaagde sulfidische-oxidische mineralizaties op de zeebodem. Een model van kleine door hydrothermale activiteit opgewarmde zeebekkens, in plaats van warme open oceanen, is in overeenstemming met: 1) een min of meer gelijkblijvende  $\delta^{18}O$  waarde van het zeewater van het Archeïcum tot heden, 2) de regelmatige trend van lagere  $\delta^{18}O$  waarden in carbonaten en cherts met

toenemende ouderdom, 3) de temperatuur van de atmosfeer in het Archeïcum en het Proterozoïcum, die niet drastisch verschillend was van de huidige temperatuur, 4) de aanwezigheid van uitgebreide ijskappen in het Proterozoïcum. Het hier gepresenteerde model geeft mogelijk een oplossing voor het dilemma van de  $\delta^{18}\text{O}$  afname in carbonaten en cherts met hun geologische ouderdom. Twee gangbare interpretaties zijn dat of de  $\delta^{18}\text{O}$  van het zeewater toenam van het Archeïcum tot heden terwijl de temperatuur aan de oppervlakte van de aarde niet drastisch veranderde, of dat de  $\delta^{18}\text{O}$  van zeewater gelijk bleef, gebufferd door de omzettingsprocessen onder de zeebodem, en dat de temperatuur aan het aardoppervlak vroeger hoger was dan nu. Een alternatieve verklaring is dat bij gelijkblijvende  $\delta^{18}\text{O}$  van zeewater en bij temperaturen vergelijkbaar met de huidige, de carbonaten en cherts hebben uitgewisseld met grondwater nadat ze waren afgezet, waarbij de oudste afgezette mineralen het meest hebben uitgewisseld. Deze laatste verklaring wordt als te toevallig beschouwd, omdat een gelijkmatige uitwisseling voor verschillende afzettingen verspreid over de hele wereld en over bijna de gehele geologische geschiedenis niet erg waarschijnlijk is.

Na voorafgaande petrologische en chemische studies van de hydrothermale omzettingen in West Bergslagen, wordt in hoofdstuk 11 een benadering met stabiele isotopen gepresenteerd. Verschillende typen van hydrothermale omzettingen zijn onderzocht: de relatief diepe Hjulsjö omzettingszones, de relatief ondiepe Fogdhyttan omzettingszone, en verschillende omzettingen in graniet intrusies.

Isotopen waarden van de vloeistoffen, die in evenwicht waren met de silikaten van de Hjulsjö omzettingszones, zijn berekend, en zijn vergelijkbaar met de vloeistoffen die bij de skarn vorming aanwezig waren. De aanwijzingen voor een zeewater oorsprong van deze vloeistoffen is echter wat minder duidelijk, ook al door de kleine spreiding in  $\delta\text{D}$  waarden. De Fogdhyttan zone geeft een vloeistof isotopen compositie die vergelijkbaar is met modern zeewater in een vroege fase van de ontwikkeling van de omzettingszone. Deze samenstelling verschuift naar een samenstelling die overeenkomt met die van de Hjulsjö zones en de skarn-vormende vloeistoffen die eerder werden besproken.

Zeewater sijpelt vanuit de zeebodem in de korst bij lage temperaturen. Dit water wordt opgewarmd naarmate het dieper komt, en concentreert zich bij nadering van de hittebron (graniet intrusies). De vloeistoffen wisselen zowel chemisch als isotopisch uit met het gesteente. Ondanks de hoge water/gesteente ratio's in de Hjulsjö zones kan de vloeistof een behoorlijke verandering hebben ondergaan bij uitwisseling in voorafgaande delen van het hydrothermale systeem, bij lagere temperatuur en kleinere water/gesteente ratio's, alvorens de Hjulsjö zones te bereiken.

De ertsvormende processen in West Bergslagen, besproken in hoofdstuk 12, worden toegeschreven aan hydrothermale omzettingsprocessen in de korst. De hydrothermale vloeistoffen worden door hun uitwisseling met het gesteente aangerijkt in bepaalde elementen, die verder in het systeem weer kunnen worden neergeslagen door decompressie of chemische reactie met het gesteente. Reactie kan bijvoorbeeld optreden als een vloeistof, die in chemisch evenwicht is met felsisch gesteente, een carbonaat lens of een diabaas gang of plaat bereikt. Een algemeen overzicht van de verschillende ertsmineralisaties in West Bergslagen wordt gepresenteerd in een schematische voorstelling in hoofdstuk 12.

In de appendix, tenslotte, worden de bestudeerde skarns uitvoeriger beschreven.

## SUMMARY

The 1.90 - 1.86 Ga volcano-sedimentary belt of West Bergslagen, central Sweden, is situated in the Svecofennian domain, which forms part of the Baltic Shield. The West Bergslagen belt comprizes more than 10 km of felsic volcanics and over 2 km of volcanoclastic sediments. Carbonate, chert and iron-oxide lenses are intercalated in cthe volcanics. The supracrustal rocks were intruded by diabase dykes and sills and by granitic plutons. The supracrustal rocks have been tilted into a sub-vertical position. Foliation follows approximately the bedding planes, or is developed in schistose shear or fault zones. Lineations are generally steeply dipping and positioned in foliation planes. The rocks of the West Bergslagen belt are metamorphosed to greenschist or lower amphibolite mineral parageneses.

Hydrothermal alterations and related ore mineralizations occur in the West Bergslagen belt, and are studied in this thesis. The aims of the study were to understand the working of the hydrothermal systems operative in the Proterozoic crust of West Bergslagen, and include topics such as: hydrothermal fluid genesis, interaction between rock minerals and fluids, mobility of elements in the systems and estimates of mass in/decrease during the processes, and relation of hydrothermal fluids with the different ore forming processes. An important aim was to determine the amount of involvement of sea water in the hydrothermal processes, and to evaluate the Early Proterozoic chemical and isotopic composition of sea water compared with present sea water.

A review of models for the crustal development of the Bergslagen belt is given in section 2 of chapter 1, basically coming down to a controversy between on one hand arc-based models and on the other a rifting model. Discussing the different models from the literature, a choice is made for an aborted continental rift model as proposed by Oen and coworkers. This model includes the assumption of a sea basin at a continental margin during the rifting stage. In the same section an attempt is made to place the crustal development of the West Bergslagen region, and surrounding domains, in a plate tectonic model. This is a very generalized and speculative model and must be seen as an introduction to the following chapters.

Finally, a possible development of the Baltic Sea is discussed. A rifting model is tentatively proposed for the Baltic Sea.

The West Bergslagen rifting-model of Oen and coworkers was extended to include a model of diapirism, attempting to explain the vertical trend of tectonics in the West Bergslagen region, and is presented in chapter 2. Granitic diapirism and gravity subsidence of relatively dense sediments in trough-shaped zones are thought to cause the sub-vertical position of the supracrustal rocks in West Bergslagen.

Petrographic, chemical and stable isotope studies on hydrothermal alteration processes in the West Bergslagen crust are presented. Chapter 3 gives a short introduction to different types of hydrothermal alteration and ore mineralizations in the West Bergslagen belt.

In chapters 4 and 5, a petrological and chemical study is presented on the Hjulsjö alteration zones, which form a group of conduits cutting through the primary structures of the supracrustal rocks. These alteration zones are related to a nearby intrusive complex of granitic composition, thought to provide the heat for the hydrothermal system, and to the Sirsjöberg - Ösjöberg Fe-ore and carbonate horizon. The Sirsjöberg - Ösjöberg stratiform mineralizations most probably were formed as exhalative deposits on a sea floor. Later, the stratiform deposits were deformed and (partly) changed chemically by metamorphism and by hydrothermal skarn alteration. Evidence is found for high element mobility, specifically rare earth elements (REEs), in a high water/rock hydrothermal system. Relationships between element mobility, mineralogy, and shape of the conduit zones are shown. Evidence is presented indicating control of the chemistry of the Hjulsjö zones by hydrothermal fluids.

The conclusion is reached that most elements were leached from the rocks in the most altered parts of the alteration zones by the hydrothermal fluids and transported either to the surface (sea floor), or trapped in the crust at another place. REEs in the rocks show a very characteristic behaviour; with increasing alteration a considerable decrease of LREEs (light-REEs), weak or no decrease of HREEs (heavy-REEs) and a very strong decrease of Eu, leading to strong negative Eu-anomalies, is found.

The high-Mg enrichment of the rocks strongly suggests a sea water origin of the hydrothermal fluids in the Hjulsjö zones. A HREE composition of sea water for Early Proterozoic ages is tentatively proposed.

In chapter 6 calculations are made based on thermodynamic data of Jasinski (published elsewhere), for mineral behaviour in a sea water hydrothermal system with rocks of felsic composition. A model explaining the stability of alteration minerals formed in a felsic rock - sea water interaction system, shown by a temperature versus  $a_K/a_{Na}$  diagram, fits well with the mineralogy of the Hjulsjö alteration zones.

Stable isotope analysis was a major tool to study the hydrothermal alterations and ore mineralizations of the West Bergslagen region. In chapter 7, an introduction is given in stable isotope (C, O, H) analysis. Descriptions of the methods and analytical extraction lines are given. Mineral-water, or mineral-mineral isotopic fractionations are important for this analytical technique which are briefly discussed. Chapter 7 concludes with a description of sample preparation for stable isotope analysis.

Carbon and oxygen isotope values of calcites and dolomites were obtained from stratabound carbonates and carbonate veins and clots in W ± Mo, Fe -

Mn oxide and Zn - Pb sulphide skarns. Carbon isotopes ( $\delta^{13}\text{C}$  around 0‰) of stratabound carbonates imply a marine environment of carbonate deposition. Oxygen isotopes show two groups of stratabound carbonates: one with low to normal carbonate  $\delta^{18}\text{O}$  values (12 to 19‰), representing marine deposited carbonates, and a second group of carbonates with  $\delta^{18}\text{O}$  values between 6 to 11‰. The last group is related to exhalative iron-oxide deposits and the  $^{18}\text{O}$ -depletion most probably occurred during exchange with sea water at temperatures of  $300 \pm 50^\circ\text{C}$ , or meteoric waters if temperatures were lower. The skarn related isotopic values of carbonates show both low  $\delta^{13}\text{C}$  values (-2 to -8‰) and  $\delta^{18}\text{O}$  values (6 to 12‰). These isotopic values are characteristic for carbonates in skarn mineralizations and are near magmatic carbonate isotopic values. A possible isotopic sub-division in groups of Fe - Mn and W - Mo skarn-related carbonates is proposed. However, this sub-division was not confirmed by H and O isotope analysis of silicate minerals from the same skarns, described in chapter 9.

Hydrous and non-hydrous silicate minerals from skarn mineralizations in West Bergslagen were analysed for H and O, and O isotopes respectively, as shown in chapter 9. A selection of a group of skarns was made from which carbonates were analysed. Fluids in equilibrium with the hydrous minerals at assumed temperatures of skarn formation were calculated. It is concluded that the skarn forming fluids most probably were Proterozoic sea water, or alternatively meteoric water with high  $^{18}\text{O}$  and D values, based on the low-latitude geographical position of the Baltic Shield in Early Proterozoic times from paleomagnetic reconstructions.

Calculated hydrogen values of these fluids shows a wide range of values (-5 to -80‰), while oxygen only shows a narrow range (4 to 7‰). The highest  $\delta\text{D}$  values (-5 to -20‰) are close to the present sea water field and show evidence for an Early Proterozoic hydrogen composition of sea water, similar to or slightly lower than the present value. This hydrogen shift is tentatively explained by exchange of silicate minerals with modern meteoric water ( $\delta\text{D} = -82‰$ ;  $\delta^{18}\text{O} = -11.5‰$ ) at surface conditions. A difference in

$\delta\text{D}$  of more than 10‰ in amphiboles in a large amphibolite block from an old mine dump over a distance of only 10 cm, clearly shows the influence of weathering on the rocks. The same trend in different hydrogen values is found if strongly weathered samples are compared with fresh-looking samples from the same skarns. Water contents in weathered minerals are compared with those in fresh samples. Phlogopites show a decrease in hydrogen values with increase in water contents for weathered samples. Amphiboles, however, show a less clear pattern. Weathered samples show a very narrow range of water contents, while a wide scatter of water content values is shown by fresh samples. Probably, widely different F or Cl contents in the fresh amphiboles are the cause of this scatter in water

contents. A hydrogen exchange model is tentatively proposed; additional study on low temperature hydrogen exchange is needed.

A post-depositional decrease in carbonate, cherts or iron oxides  $^{18}\text{O}$  is proposed in chapter 10, based on the decrease of oxygen isotopic values in carbonates by warm fluids at exhalative sites on the sea floor as explained in chapter 8. Carbonate and chert samples of Archean and Early to Middle Proterozoic ages were collected in greenstone belts, which are known for their extensive volcanic processes. Evidence for the existence of extensive hydrothermal systems, discharging hot fluids, is provided by large stratiform sulphide and oxide mineralizations on the sea floor. Heating of restricted marine basins instead of global warm conditions is in accordance with: a steady  $\delta^{18}\text{O}$  value of sea water from Archean ages till present, the decrease of  $\delta^{18}\text{O}$  values of carbonates and cherts with geological age, atmospheric temperature conditions in Archean and Proterozoic ages which were not drastically different from modern temperature conditions, and the existence of extensive glaciations of Proterozoic age. The model presented here provides a solution to the contradiction in interpretations of the  $\delta^{18}\text{O}$  decrease in carbonates and cherts with their geological age. Either sea water  $\delta^{18}\text{O}$  increased from Archean till present and the Earth's surface temperatures did not change drastically, or sea water  $\delta^{18}\text{O}$  values, buffered by sea floor exchange processes, did not change with the Earth's history, but surface temperatures were higher in the past. An alternative explanation is unchanged  $\delta^{18}\text{O}$  values of sea water and the Earth's surface temperatures comparable with present ones, while the carbonates and cherts were exchanged with groundwaters, oldest rocks exchanged most. This last explanation is considered to be too coincidental, since conditions for different deposits must have been drastically different during Earth history to have exchanged with groundwater in such a regular trend.

Hydrothermal alterations in West Bergslagen are studied in chapter 11, after earlier petrographic and chemical studies, using a stable isotope approach. Different types of hydrothermal alteration were selected. The relatively deep level Hjulsjö conduit type alteration zones, described in detail above, the relatively shallow Fogdhyttan alteration zone, and sharply bordered and pervasive hydrothermal alterations in granites are discussed.

Calculated fluids for the Hjulsjö zone silicates are comparable with the skarn forming fluids discussed above, although a sea water source is less clear in this case, also because a relatively narrow  $\delta\text{D}$  range which may also be interpreted as a magmatic fluid, if we neglect the skarn-forming fluids. The Fogdhyttan zone shows a fluid composition comparable with present sea water, which changes at later stages to a fluid composition which is

comparable with the Hjulsjö zones and skarn fluids composition. Fluids circulating through granites are also comparable with these fluids, or show a magmatic fluid isotopic composition (for the Reboda pegmatite muscovite). An evolution of sea water is proposed, seeping down from the sea floor at low temperatures, heating of the fluids while moving downwards, and concentration of the fluids in funnel-shaped channels, with decreasing distance to the heat source (granitic diapirs). The fluids exchange with the host rocks in both chemical and isotopic sense. Despite the high water/rock ratio's the fluid of sea water origin may have shifted considerably in oxygen isotopic values before reaching the Hjulsjö zones. This is caused by low temperature and low water/rock ratio fluid rock exchange at shallower levels of the hydrothermal system.

In West Bergslagen ore forming mineralizations are related to the hydrothermal alteration processes. The hydrothermal fluids, during their exchange with the rocks, are enriched in specific major and trace elements, which may be trapped at sites where decompression occurs or when the fluid is in disequilibrium with the country rocks. This may happen when fluids pass a carbonate horizon or mafic dykes or sills. A general review of different ore mineralization types in West Bergslagen is presented in a cartoon.

Descriptions of skarns studied in this thesis are given in an appendix

## Chapter 1

### 1.1 - INTRODUCTION

This study concentrates on the western part of the Bergslagen region. Where appropriate, discussions about, or references to other parts of the Bergslagen region or the Baltic Shield are made. The regional geology is presented in the form of an overview.

Extended geological descriptions will not be given here, since it is outside the scope of this thesis. Parts of this introduction are repeated in the introductions of publications represented in this thesis by chapters 2, 4-6 and 8-10, a partial overlap which unfortunately is unavoidable in a thesis of this form.

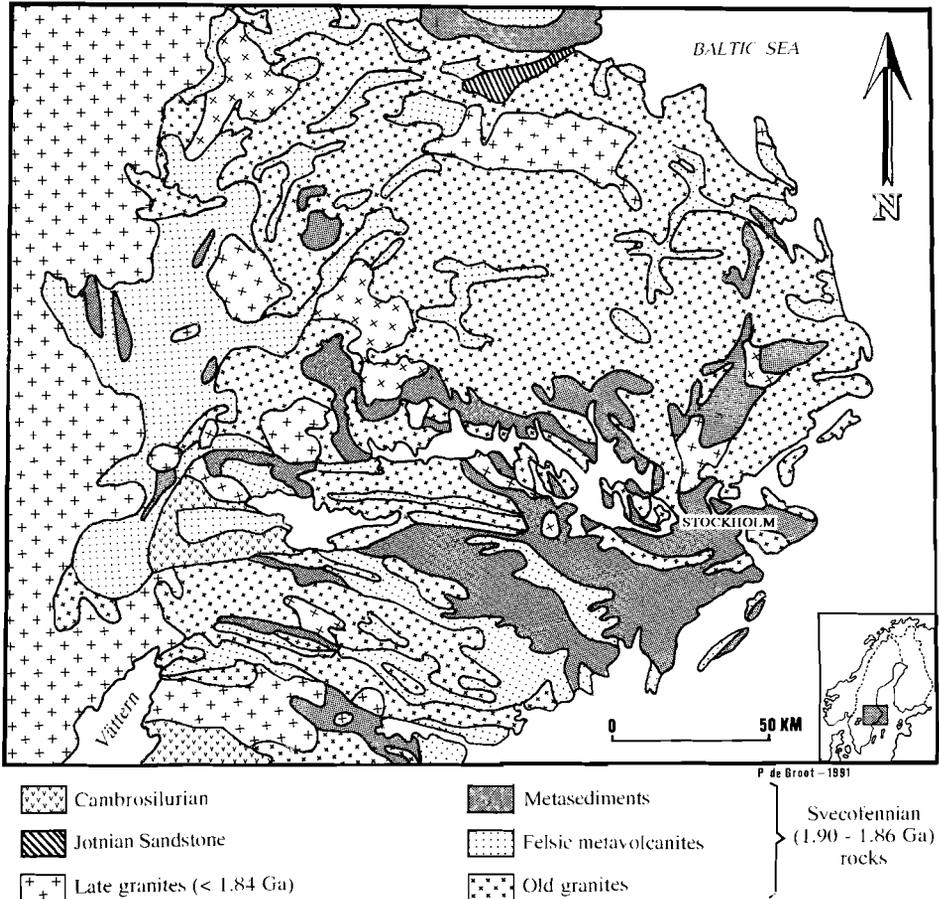
#### Geological synopsis

The 1.90 - 1.86 Ga volcano-sedimentary ensialic belt of Bergslagen is situated in South Central Sweden, West of Stockholm (Fig. 1), and forms part of the Svecofennian domain of the Baltic Shield. In West Bergslagen the belt comprises a sequence of felsic volcanics which is over 10 km thick, and volcanic-derived sediments, including conglomerates at higher stratigraphic levels, of at least 2 km thick. The volcanics contain intercalations of carbonates (calcite and dolomite), cherts, and iron  $\pm$  manganese oxide and base metal sulphide stratiform deposits (Sundius, 1923; Magnusson, 1925, 1970; Gavelin, 1976; Oen et al., 1982; Van der Velden et al., 1982; Baker, 1985a; Lundström, 1987, 1988; Oen, 1987; Kuipers, 1987; Lagerblad, 1988; Van Meerten, 1988).

The felsic volcanics are represented by lava flows, pyroclastic flows and ignimbrites, air and water transported volcano-sediments, and mass flows comprising remobilized volcano-sediments. Bedding and primary (volcano) sedimentary structures are preserved at some places. Bedding is characterized by thin layers of different grain-size and mineral composition. Sometimes bedding is shown at the weathered surface by the different grade of erosion of the separate layers, or by colouration of different layers, layers.

Flow banding on a macroscopic and microscopic scale is also preserved in the rocks. This banding is easily confused with the ignimbritic flow banding, and additional criteria are needed to decide on the banding type. Glomeroporphyritic structures are well preserved in some of the flow banded volcanics. Spherulitic structures, volcano-lithic fragments, lapilli, shards, fiamme structures, perlitic structures, and embayments in quartz are common features in rocks of this volcano-sedimentary belt.

Plutonic and a few vein-type granitic intrusions, and intrusions of mafic dykes and sills occurred during the 1.90 - 1.86 Ga development of the Bergslagen volcano-sedimentary belt (Stephansson, 1975; Wilson, 1980,



**Figure 1.** Geological map of the Bergslagen region, central Sweden (after Lundström, 1988).

1982; Oen and Verschure, 1985; Baker, 1985a; Baker and Drucker, 1988). Younger granitic intrusions after 1.7 Ga are also recognized.

Despite the increasing number of radiogenic datings, no uniform opinion exists over the number of generations. Oen and Verschure (1985) consider a division of granitic intrusions in two major generations; an older generation of 1.9 - 1.8 Ga and a younger generation of 1.7 - 1.6 Ga. This two-fold division in granitic intrusion is followed in this study.

Shallow intrusion or dome shaped extrusions of rhyolitic composition are found in some places, usually called quartz-porphyrries (Sundius, 1923, 1968; Welin et al., 1980; De Groot, 1985). They are compact bodies of very fine grained quartz-feldspar matrix with quartz and, now altered, feldspar phenocrysts.

A minor volume of intermediate in- and extrusives is present (e.g. Frietsch, 1982; Lagerblad, 1988). Intermediate intrusives are described as hybrid melts by Hellingwerf and Oen (1986) and Andersson (1991), while a few extrusives of intermediate composition are found in more easterly regions of the Bergslagen belt and the related southern Finnish belt (Lundquist, 1962; Gavelin, 1976; Gorbatshev, 1969; Simonen, 1980). Rare occurrences of spilitized basaltic extrusions are described in the region (e.g. Geijer and Magnusson, 1944; Koark, 1962; Oen et al., 1982; Hellingwerf, 1984; Oen et al., 1986; Oen, 1987).

The felsic volcanics of the West Bergslagen region are mostly tilted to a (sub-)vertical position. A foliation is parallel to, or at a low angle to the bedding. Lineations formed by elongated minerals or rock fragments in a near vertical position are situated in the plane of foliation.

Low temperature and low pressure metamorphism of upper greenschist facies to lower amphibolite facies mineral parageneses affected the volcanics regionally. The metamorphic grade, starting from the lowest grade in the Grythyttan - Hällefors - Hjulsjö area, increases both in western as in eastern directions to the present borders of the belt, but never exceeds upper amphibolite grade in the western Bergslagen region. Around some of the granitic diapirs the metamorphic grade increases in a concentric pattern. The increase or decrease of metamorphic grade of the rocks is not related to the position in the stratigraphic sequence.

Joint systems in 4 general directions: E-W, N40-50E, N130-140E and N340-350E, are developed in different intensities in the region. Fault zones and diabase dyke swarms often follow these directions. Channels of hydrothermal fluids were generally determined by these joint and fault zone orientations.

Folding on different scales is described for several parts of the western Bergslagen belt. Carlon and Bleeker (1988) recognized at least two phases of folding in the eastern part of western Bergslagen. Stålhös (1981, 1984) explains the vertical position of the eastern Bergslagen regions by two phases of approximately simultaneous compressive folding at oblique angle to each other.

Small scale folding, at a scale of cm to tens of m, is ubiquitous through the area and may, besides tectonic folding, be explained as flow folding in rhyolitic lavas or ignimbrites.

Numerous faults crosscut the region, although direct evidence for faults is rare. Most of the faults are located by means of indirect field evidence and interpretation.

In western Bergslagen the apparent lack of clastic sediments in the more than 10 km thick volcanic pile is remarkable. In the eastern Bergslagen regions, however, sedimentation started with clastic sediments, followed by one or more, mostly thin volcano-sedimentary layer(s), and was capped by clastic sediments. From eastern to western regions in the belt the volume of clastic sediments decreases in favor of the volcano-sediments (e.g. Gavelin, 1976; Lundström, 1987, 1988). In the eastern Bergslagen regions the

metamorphic grade is reaching upper amphibolite facies mineral parageneses, and is higher than in the western Bergslagen regions.

Intensive fluid - rock interactions occurred during and after deposition of the rocks. In West Bergslagen the supracrustal sequence was deposited in marine basins. Sea floor and sub-sea floor metasomatism altered the supracrustal rocks, and to some extent the intrusive rocks of the belt.

Hydrothermal fluid circulation systems in the 1.9 - 1.8 Ga Svecofennian crust of West Bergslagen were initiated by the heat of coeval magmatic intrusive bodies, most commonly granitic intrusions. Pervasive type, conduit zone type, and channeling fracture zone type fluid circulation systems are recognized in the West Bergslagen region. Intensive chemical exchange of fluids with the crustal rocks changes the chemical and isotopic signature of both the rocks and the fluids. Exhalative mineralizations (Fe-, Mn- oxide deposits, stratiform massive sulfide deposits) and replacement and reaction mineralizations (Fe-, Mn- oxide or base metal sulfide skarns; W- and/or Mo- bearing) which can be stratiform or irregular in form caused by remobilization and/or tectonism, are related to these hydrothermal systems. Mineral parageneses of the alteration zones and related (ore) mineralized sites are generally of higher grade (higher temperature) than the regional metamorphic grade. The fact that these zones and related mineralizations are not formed primarily by metamorphic processes, although probably influenced, but by hydrothermal/metasomatic processes must be stressed.

For those who are interested to read more about the geology of the Bergslagen region, the classical works of Sundius (1923) and Magnusson (1925) are providing very good descriptive studies. Descriptions with more modern interpretations of the geology are available in special issues of following magazines: *Geologische Rundschau* (Vol. 71, 1982), *Precambrian Research* (Vol. 35, 382 p., 1987), *Geological Society Special Publication No.33* (T.C. Pharaoh, R.D. Beckinsale and D. Rickard (eds.), *Geochemistry and Mineralization of Proterozoic Volcanic Suites*, Blackwell Sci. Publ., 1987) and *Geologie en Mijnbouw* (Vol. 67, pp. 121-478, 1988). Special issues about the relation of the Baltic Shield with the Precambrian Shields in Scotland, Ireland, Greenland and northern America are: *Geol. Assoc. of Canada, Special Paper 38* (581 p., 1990) and *Precambrian Research*, which is in preparation and will most probably appear this year.

## 1.2 - CONSIDERATIONS ON THE PLATE TECTONIC HISTORY OF BERGSLAGEN.

The historical economic interest in the Bergslagen region, shown by its mining activities, raised the need for a better knowledge of the regional geology. In the middle of the last century geological mapping started, while at the same time the knowledge of the sub-surface geology from inside the mine operations increased. This information created a base to attempt explaining the geological development of the Bergslagen region. After the introduction of plate tectonics, new models were developed to incorporate the geological data from field, geochemical and geophysical methods.

### **Plate tectonic models**

A first model based on plate tectonic theory was produced by Hietanen (1975). She compared the magmatic evolution of the Bergslagen and southern Finnish regions with that of the northern Sierra Nevada in California, and recognizing a magmatic-volcanic calc-alkaline trend, explained these regions as being formed in a volcanic arc setting. Löfgren (1979) presented an island arc model based on a continuous magmatic-volcanic suite from basaltic to rhyolitic composition representing a calc-alkaline trend. Loberg (1980) presented a subduction related volcanic arc model. He showed clearly the bimodal magmatic-volcanic character of the belt instead of the incorrect continuous trend of Löfgren (1979), and stated that alteration processes almost certainly influenced the rock compositions and complicate, or even invalidate the use of major element chemistry in determining the original nature of the rocks. Nevertheless he used a calc-alkaline trend as basis for an island arc setting for the magmatic-volcanic rocks of the belt.

Oen et al. (1982) and Oen (1987) proposed a continental rift setting for the western Bergslagen region. Baker (1985a) supported this theory and De Groot et al. (1988; chapter 2 of this thesis) extended the model by the introduction of diapirism and gravity tectonism.

Vivallo and Rickard (1984) introduced an andinotype active continental margin setting, including processes of subsidence, rifting and compression respectively; a model followed, but poorly argumented by Kresten (1985), and supported by Lindh (1987). Although alteration of the volcanic rocks was distinguished (Vivallo and Rickard, 1984; Vivallo, 1984, 1985a), a calc-alkaline trend in these volcanic rocks was assumed to be a primary magmatic one, and the assumption of non-marine, terrigenous conditions for the eastern Bergslagen as opposed to marine conditions of the western Bergslagen region (e.g. Rickard, 1987; Parr and Rickard, 1987; Parr, 1988) is fundamental to this model.

Park (1985) proposed a series of island arcs forming the Svecofennian domain, in which the Bergslagen belt is represented by the Örebro arc. These arcs, making a wide angle with the older Karelian continental block in

the East, are thought to fit on this Karelian block along the Laahe - Ladoga lineament with a series of wrench faults.

A model proposed by Beunk and Valbracht (1992), following the Russian explanation for the Archean greenstone belts of the Baltic Shield (Berkovskiy et al., 1989), compares the Bergslagen region with the Basin and Range Province in western United States, and places an arc, comparable with the Sunda arc (e.g. Hamilton, 1988), south of the present southern Swedish Baltic Sea coast, in fact in the middle of the Baltic Sea where no reliable geological evidence can be obtained. An oceanic spreading zone is assumed to occur between these "Basin and Range" and "Sunda arc" type terranes, although no oceanic crust is registered in these regions of the Svecofennian domain.

### **Arc - subduction versus continental rifting models**

Basically two genetic models, a variety of arc and subduction models versus a continental rift model for the Bergslagen crustal development are reviewed above. The major part of these models conflict with each other and with the geological and geochemical data of the belt and critical comment about the reliability and quality of these models needs to be given.

First of all, many of the models are mostly based on what is assumed to be a primary magmatic calc-alkaline trend. Elements such as Na, Ca, K, Si, or alternatively including Mg, Fe, used to estimate such a trend are highly mobile in alteration processes leading to greenschist or amphibolite mineral parageneses in the volcano-sedimentary rocks of marine basins (e.g. Honnorez, 1981; Hajash and Chandler, 1981; Alt and Honnorez, 1984; Alt et al., 1985, 1986) of which the Bergslagen belt is an example. Therefore this trend cannot be considered to be primary magmatic without a discussion of the effects of alteration processes. The intrusive rocks of the belt are also strongly affected by the regional alteration processes, which occurred in the belt (granites: Baker, 1985a, 1985b; Baker and Drucker, 1988, diabase dykes and sills: Hellingwerf and Oen, 1986). The alteration processes affecting the Bergslagen belt are extensively discussed in chapters 3-6 and 11.

### **Why arc models are rejected - a discussion**

Island arc settings in Bergslagen are not supported by evidence, like the presence of ophiolites or blueschist zones, although the dominantly marine conditions of the belt could be supportive. On the contrary, the place and type of sediment deposition increasing towards the east in the belt is very unlikely for an island arc setting (e.g. Vivallo and Rickard, 1984; Lundström, 1987; Rickard, 1988).

An andinotype active margin model (e.g. Vivallo and Rickard, 1984) is contradictory to the dominantly marine circumstances in the volcano-sedimentary basins as evidenced by marine  $\delta^{13}\text{C}$  values of stratabound carbonate horizons or lenses (De Groot and Sheppard, 1988: collection of

carbonates from western Bergslagen, including samples from the more eastern Ställdalen region; Schidlowski et al., 1975: samples from the eastern Bergslagen Sala region; Gebeyehu, samples from the eastern Bergslagen Garpenberg region, in prep.), and is not supported by the lack of any evidence for weathering surfaces or clastic sediments typical for the erosion of mountains expected in an andinotype setting.

In addition, Vivallo (1985b) proposes seafloor exhalative processes for the Garpenberg mineralizations, contradicting the terrestrial continental margin conditions of an Andean margin as proposed by Parr and Rickard (1987) and Parr (1988) for an area in the same region.

All subduction related models also should present accretionary sedimentary prisms at the ocean side of the arc or continental margin, which theoretically could be represented by the E-W oriented sedimentary series in the southern part of eastern Bergslagen. Compressional stresses in these sedimentary series, however, caused folding with N-S oriented axial planes, with folds verging to the East (e.g. Stålhös, 1981, 1984). Accretionary prisms in this part of the Bergslagen belt should have a major compressional direction towards the North.

Comparison with a Basin and Range setting is debatable. Basin and Range and the Bergslagen belts both are thought to be situated within a continental plate; in both belts the volcanism is proposed to be initiated by tensional processes and magmatism is bimodal. However differences are notified too: the volume of clastic sediments is far bigger in the Basin and Range belt compared with the Bergslagen belt and also the stacking of clastics interlayered with volcanics, as seen in the Basin and Range belt is uncommon for the Bergslagen belt. Also the tectonics were not quite the same: the Basin and Range belt shows an approximately horizontal structure while the Bergslagen belt is dominated by vertical tectonics. Depending on the preference of comparing only a selection of phenomena or to include the complete set of data, one may decide if this comparison is valid or not.

### **Arguments for a continental rift model**

This leaves us with tensional or rifting processes, thought to be coupled with the extensive and voluminous magmatism (e.g. Oen et al., 1982). Tensional processes operating in the belt are generally accepted nowadays, however not the setting in which these tensional processes occurred. Rifting of a pre-existing continent (Oen et al., 1982; Oen, 1987), in an arc or back arc configuration (Loberg, 1980; Park, 1985), or in an andean type active margin (Vivallo and Rickard, 1984) are proposed. Since the last two settings were considered less probable by arguments given above, the rifting of a pre-existing continental crust is accepted as the most reasonable explanation and is discussed here further. Tensional processes in the crust are expressed by the intrusion of basaltic dykes and sills during the late Svecofennian stages in the metavolcanics and in coeval older granites.

Support for the pre-existence of a (continental?) crust is found in the enormous volume of felsic (rhyolitic) volcanics and granitic intrusions

compared with the small volume of mafic (basaltic) intrusives and extrusives and nearly complete absence of intermediate products (Oen et al., 1982; Van der Velden et al., 1982; Frietsch, 1982; Vivallo and Rickard, 1984; Baker, 1985a; Lundström, 1988; De Groot et al., 1988/chapter 2). Gaál and Gorbatshev (1987) reason that a continental crust must have existed and is present below the volcanics of the Bergslagen belt.

### **The basement question**

Unfortunately no basement to the belt has ever been found (e.g. Lundström, 1987; Baker, 1985a; Baker et al. 1988; De Groot et al., 1988/chapter 2). This is in fact the case for all the volcano-sedimentary belts in the Svecofennian domain, making it impossible to obtain direct information about the composition of a pre-existing crust. Only a combination of evidence from rocks which are presently exposed at the surface can give us information about this pre-existing crust.

### **A two phase development of the Svecofennian crust**

A two phase model of crustal development of the Svecofennian domain was presented by Baker et al. (1988). This model describes formation of a pre-Svecofennian primitive plate, probably by a series of oceanic arcs, of mafic to intermediate chemical composition, followed, after an interval of 0.2 - 0.5 Ga, by the Svecofennian "orogeny" during which the crustal plate at lower levels ( $\pm 12$  km depth) is melted, reworking the crustal plate into a volcano-sedimentary sequence containing granitic plutons. Short term reworking of newly-formed continental crust in volcano-sedimentary belts is an increasingly accepted phenomenon (e.g. Kröner, 1991; Miller and Saleeby, 1991; Bowring and Grotzinger, 1992; Lucas et al., 1992), in combination with the relatively short term reworking of the crust in the two phase model (Baker et al., 1988).

The Sm-Nd isotopic systematics of the Bergslagen rocks produce  $T_{DM}$ -ages of 2.1 to 2.4 Ga (Valbracht, 1991), which are interpreted as evidence for the existence of an Early Proterozoic basement, or alternatively mixing of crustal material of Svecofennian and Archean ages. This last alternative is less probable because of the big distance of Archean crust from the West Bergslagen region.

Rock dating is based on radiogenic techniques (Rb-Sr, U-Pb<sub>zircon</sub>, U-Pb<sub>zircon</sub>-SHRIMP, K-Ar, Pb-Pb) of whole rocks or minerals and yield ages between 1.90 - 1.86 Ga for the Svecofennian volcano-sedimentary and intrusive rocks of the Bergslagen belt (see Welin, 1992, for a compilation of datings).

Crustal residence times of 200 to 500 Ma for the West Bergslagen crust after the formation of a primitive crustal slab must be sufficient to include the subsequent reworking of this crust by a later tectonic event, as proposed by the two phase model (Baker et al., 1988). This second stage reworking of the primitive crust in the two phase model could include underplating or

mantle plume processes, initiating tensional stresses in the upper crust and melting of the lower crust.

A Pb isotopic study on ore minerals in Bergslagen (Gebeyehu and Vivallo, 1991) supports the existence of a pre-Svecofennian crust which is reworked during the Svecofennian period, leading to a two stage model of crustal development. Valbracht (1991) presents also a model, based on a Sm-Nd and Sr isotopic study on mafic rocks of the western Bergslagen region, of a two stage crustal development. A pre-existing crust is underplated and melted in its lower levels. The melts rise to the surface causing the intensive volcanism and plutonism of the Bergslagen belt.

The Svecofennian Tampere schist belt in southern Finland (Nironen, 1989) shows the same radiogenic isotopic systematics (e.g. Huhma, 1986) as the Bergslagen belt and most probably had a comparable crustal development.

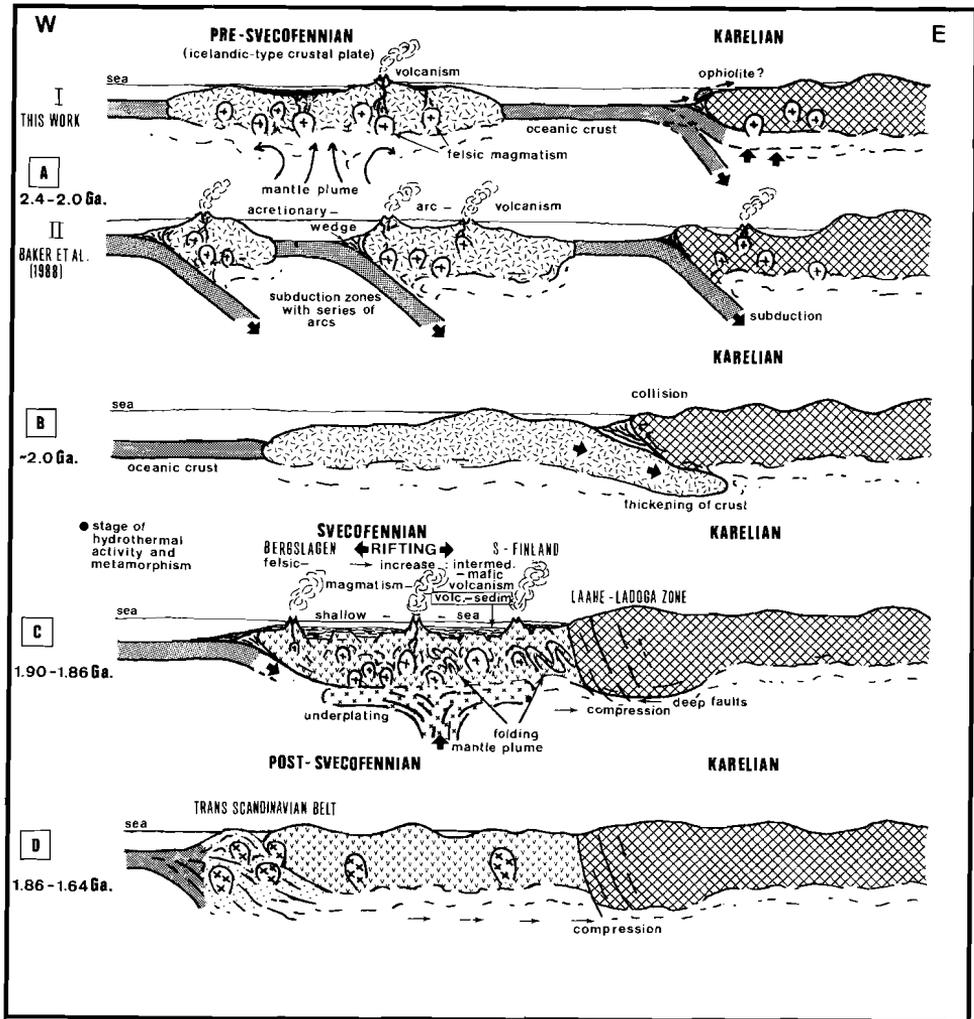
Formation of the first phase continental crust, of possibly primitive composition, is presented as a series of subduction zones by Baker et al. (1988). Whether this really was the process leading to this crustal formation is debatable, and many other models can be brought forward, depending on the scientists' taste or belief in actualistic explanations or not.

### **Facts about the Bergslagen belt**

Whichever the processes for development of the Svecofennian crust were, evidence exists for:

- dominantly marine basin conditions (Mg-enrichment in altered rocks: Baker and De Groot, 1983/chapter 4;  $\delta^{13}\text{C}$  values for stratabound carbonate lenses: De Groot and Sheppard, 1988/chapter 8);
- shallow conditions for at least some part of the basins (stromatolites: Boekschoten et al., 1988; wave-base ripples: Roep and Linthout, 1989; Gorbatshev, 1969);
- a prevailing ensialic composition of the volcanism-magmatism (e.g. Oen et al., 1982; Van der Velden et al, 1982; Lagerblad and Gorbatshev, 1985; Lagerblad, 1988);
- a low grade of metamorphism (greenschist to lower amphibolite phase) of the belt (e.g. Helmers, 1984; Rickard, 1988);
- the absence of clastic sediments or weathering surfaces in the thick pile of felsic volcanics in West Bergslagen.
- extensive fluid-rock alteration processes (e.g. Baker and De Groot, 1983/chapter 4; Lagerblad and Gorbatshev, 1985; De Groot and Baker, 1992/chapter 5).

In addition it may be concluded that no mountain-building on the continental crust occurred close to the marine basins because of the absence of clastic sediments typical for such a setting.



**Figure 2.** The development of the Svecofennian domain shown in a set of schematic sections. A- Development of a pre-Svecofennian proto (primitive) crust; two alternative possibilities are envisaged I: mantle plume magmatism forming a (micro-)plate with an Icelandic type of crust, and II: a series of subduction zones and island arcs amalgamated to a protocrust. B- Collision of the pre-Svecofennian proto-plate with the Karelian crustal domain along the Laahe - Ladoga zone. C- Continued motion of the oceanic plate West of the pre-Svecofennian proto-plate leads to subduction or underthrusting of this oceanic plate under the pre-Svecofennian plate. A mantle plume is underplating the Svecofennian crust. Tensional/rifting processes and intensive magmatism/volcanism are result of this (caption continued on page 11)

### **A speculative model of Svecofennian domain crustal formation and evolution**

From the above evidence a scenario can be constructed of a sea-basin marginal to the continent or a continent surrounded basin which is not closed to the open ocean. A marginal basin environment for the western part of the Bergslagen belt was originally proposed by Boström et al. (1979), Vivallo and Rickard (1984), Gorbatshev and Gaál (1987), Gaál and Gorbatshev (1987), Rickard (1987, 1988), and Lundström (1987, 1988). Gorbatshev (1969) also assumes the existence of a shelf sea near a continent for the Mälaren - Hjälmaren basin (E of Örebro).

A primitive plate could have been formed between 2.4 - 2.0 Ga ago close to the front of a Karelian coast by arc-accretionary processes as proposed by Baker et al. (1988), or alternatively by plateau-forming on an oceanic plate, eventually leading to Iceland-type continental crust (see Kröner, 1991, and Kröner and Layer, 1992)(Fig. 2a). This primitive pre-Svecofennian continent moved by plate tectonic activity to the Karelian coast, where it collided against the continental margin before about 2.0 Ga (Fig. 2b). An oceanic crust could underthrust the Karelian crust or subduct prior to this collision. An advancing oceanic plate possibly explain ophiolite oceanic crustal fragments emplaced in the Karelian crust. An underplating event could activate the 2.25 - 2.0 Ga magmatic and tectonic activity in the Karelian domain (Fig. 2a). Baker et al. (1988) also propose a collision of the primitive pre-Svecofennian plate with the Karelian (+ Lapponian) continent at about 2.1 - 1.9 Ga, with subsequent reworking of this Karelian crust (see Fig. 6 in Baker et al., 1988).

It can be concluded from the increasing volume of clastic sediments in eastern regions of the Svecofennian domain towards the Karelian domain (e.g. Gavelin, 1967; Simonen, 1980; Lundström, 1987, 1988), that a coastline marked the boundary of the Svecofennian and Karelian domains in middle Finland. Collision of the pre-Svecofennian crustal plate against the Karelian continent could occur along this coast, now represented by the Laahe-Ladoga zone which shows an abnormal crustal thickness (Luosto et al., 1990; Fig. 2b-e). A high metamorphic grade near this zone (up to granulite grade) and high strain shear zones in the southern Finnish belt are supportive of this collision model (e.g. Simonen, 1980; Gaál, 1982; Schreurs and Westra, 1985; Ploegsma and Westra, 1990).

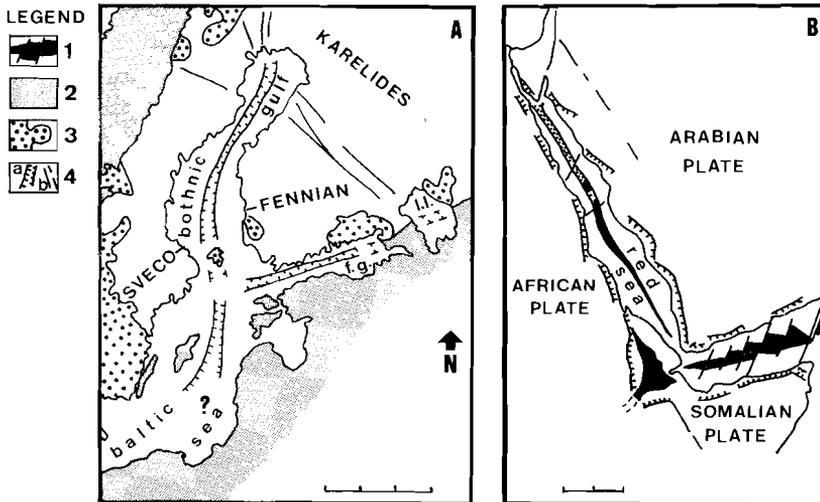
The pre-Svecofennian plate docked against the Karelian continent, while the

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(caption of Figure 2 continued)

underplating event. The pre-Svecofennian protoplate is reworked completely in the Svecofennian plate. Underplating activity by a mantle plume leads to compressive events in the eastern Svecofennian domain with crustal folding. D- Blocked eastern motion of the oceanic plate leads to compression of this crust against the Svecofennian crust, to thickening of the crust and to magmatic intrusion. The Trans- Scandinavian Belt could be formed by reworking of the Svecofennian crust and compressed oceanic crust at the western compressive site of the Svecofennian domain.

oceanic plate behind the pre-Svecofennian plate continued its easterly motion. This possibly led to underthrusting of the pre-Svecofennian continental plate by the oceanic plate. Mantle plume underplating caused tensional stresses in the pre-Svecofennian plate (rifting) and initiation of the Svecofennian reworking of the primitive continental plate, starting from about 1.9 Ga (melting followed by magmatism and volcanism; 1.90 - 1.86 Ga)(Fig. 2c).



**Figure 3.** Comparison of assumed post-Svecofennian rifting in the Baltic Sea region with recent rifting in the Red Sea region. A- The Baltic Sea including the Bothnic Gulf and the Finnish Gulf (f.g.) and Lake Ladoga (l.l.). A proposed rift-pattern is drawn in the sea. Scale-bar in lower right corner is 300 km. B- The Red Sea Rift (map after Malkin and Shemenda, 1991). Scale-bar in lower left corner is 400 km. A right angle junction between rifts is present in both rift systems. Legend: 1- oceanic basaltic crust formed in rift with transform faults [Red Sea region]. 2- post - 1.64 Ga crustal rocks (Caledonian and Phanerozoic platform cover)[Baltic Sea region]. 3- 1.75 - 1.20 Ga granitic intrusions [Baltic Sea region]. 4a- rift fault scarps. 4b- faults.

Pressure by the oceanic plate at the western side and blocking of the continental plate at the side of the Karelian continent in the East may explain the compressional events at later stages in the development of the Svecofennian crust eventually causing the compressional folding as is common in the eastern regions of the Bergslagen belt (Stålhös, 1981, 1984; Carlon and Bleeker, 1988). If, at a later stage during the Gothian event, also this oceanic plate in the West is blocked, stresses build up on this oceanic side of the Svecofennian plate, possibly represented by the subsequent activity in the Trans-Scandinavian Belt (about 1.74 - 1.64 Ga)(Fig. 2d). Rapakivi granitic intrusions of Gothian age inside the Svecofennian crust could represent a reactivation of deep fault systems, relieving stresses from

the blocked motion of the oceanic plate at the western border of the Svecofennian domain.

### **The Baltic Sea - a rifting model**

A still unanswered question is the development of the Baltic Sea, which in fact is neglected by nearly all geologists explaining the crustal development of the Baltic Shield. Simonen (1980; page 14, Fig. 5) shows that the basaltic crust in the Baltic Sea area is several km thicker than in the rest of the Baltic Shield. The basaltic composition of the crust of this basin may point to a rifting event of the Baltic Sea comparable with the Red Sea rift (e.g. Malkin and Shemenda, 1991)(Fig. 3). Rifting was abandoned before an ocean could form, leaving a basin more or less in its present form. The basaltic crust is covered by a sedimentary layer of probably considerable thickness, eventually leading to the increased thickness of the present crust (A thick sedimentary layer is found in the Bothnic Gulf N of the Åhland islands; C. Ehlers, pers. com.).

This rifting event must have occurred after the Svecofennian event (1.90 - 1.86 Ga), based on the continuity of the Bergslagen and southern Finnish volcano-sedimentary belts. A more specific dating is not possible at present.

The model presented above is very speculative, lacking detail, and only tentatively tries to explain the crustal development - accretionary history of the Svecofennian domain, and specifically the Bergslagen region.

### **Some general remarks about Precambrian crustal evolution**

Most models explaining Early to Middle Proterozoic crustal development are based on actualistic plate tectonic processes. Explanations based on changing plate tectonic processes from Archean to modern times are advocated by Harris et al. (1987), Kröner (1991) and Kröner and Layer (1992). They suggest that underplating instead of subduction was the dominant process in Archean and early Proterozoic times. During an intermediate period (Middle to Late Proterozoic?) underplating processes shift to subduction processes, and "mixed" evidence for both processes may be represented as recently reported by Kröner (1991).

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## Chapter 2

### Evidence for gravity subsidence and granite diapirism in the 1.8–1.9 Ga Proterozoic succession of W. Bergslagen, Sweden

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*Key words:* Proterozoic, ensialic rifting, tectonic development, granite diapirism, gravity subsidence, Bergslagen, Sweden

#### Abstract

Western Bergslagen, Central Sweden contains a number of large scale features including long, narrow, synformal, sediment-filled basins, separated by wide intervening areas of felsic metavolcanics in which anticlinal structures are absent. Synvolcanic granites intrude the felsic metavolcanics. Bedding, foliation and mineral lineations are sub-parallel both where bedding is sub-vertical or more rarely sub-horizontal. These features, taken in their geological context, are consistent with a dynamic system in which granite diapirism and gravity tectonic processes operated. Previous models (Oen et al., 1982; Oen, 1987) emphasize the continental rift setting of Bergslagen. We propose the following four stage tectono-magmatic model to account for the structure of the area:

*Phase 1:* A primary crust forming event at about 2.1 Ga.

*Phase 2:* Subsequent attenuation produced rifting accompanied by melting of the lower crust to give large scale felsic volcanism, contained predominantly in sinking grabens of a wider rift structure. Granite diapirism was initiated.

*Phase 3:* Tectonic inversion followed, with an uplift of the graben floors, and a higher emplacement of the granite diapirs. At the same time a second generation of rift basins evolved on the flanks of the updomed areas, to be filled with debris derived from the felsic volcanics. A gravity instability developed as the heavier sediments filled the grabens, contributing to the overall tectonic process.

*Phase 4:* A younger event of granitic magmatism.

The development of the sediment filled rift basins is the surficial expression of the deeper gravity tectonic system.

#### Introduction

The available geological information on the ore province of Bergslagen, Central Sweden has been used to support various interpretations of a geotectonic setting, including an orogenic model with synformal depressions caused by folding (Sundius,

1923; Magnusson, 1925, 1970), back-arc and subduction related models (e.g. Hietanen, 1975), a continental rift/aulacogene model (Oen et al., 1982; Oen, 1987), and an active, Andean type, continental margin model (Vivallo & Rickard, 1984). No detailed structural analysis has been published on W. Bergslagen and structural consider-

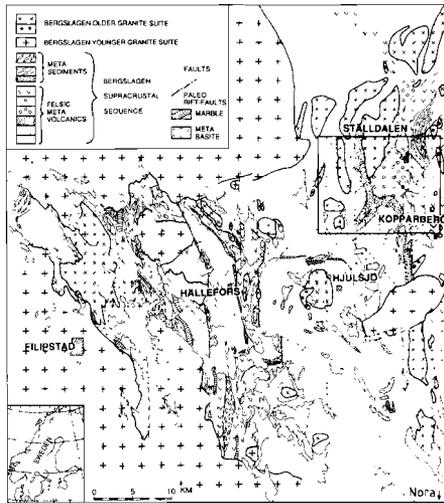


Fig. 1. Geological sketch map of western Bergslagen, compiled from Oen et al. (1982) and Baker (1985), with additional material from Lundström (1983) and Helmers (1984). Inset shows location of Fig. 3.

ations are often ignored in making geological interpretations. Previous structural investigations in Central Sweden include those of Stephansson (1975) and Stålhös (1984). Lundström & Papunen (1986) note that while two phases of deformation are generally invoked, a one-stage model is now favoured, due to constraints placed on the time available for deformation by radiometric dating. This paper summarizes the structural features of W. Bergslagen (Fig. 1), in the light of the continental rift model of Oen et al. (1982) and Oen (1987), and extends the rift model by introducing the concept of granite diapirism and gravity tectonic processes which gradually replace the epeirogenic tectonism of the rift stage.

### Geological synopsis

The 1.8–1.9 Ga Bergslagen Supracrustal Sequence, comprises a >10 km thick pile of felsic metavolcanics in which metasediments appear in the higher levels, predominating at the top of the sequence

(Fig. 1). In W. Bergslagen the Bergslagen Supracrustal Sequence (BSS) is divided into three lithostratigraphic groups.

*The Lower Leptite Group* comprises large ignimbritic flows, possibly laterally transitional into sub-volcanic domes and intrusions (Van Meerten 1987, personal communication) in which limestone and/or ore horizons are either absent or thin and discontinuous.

*The Middle Leptite Group*, unconformably overlying the Lower Leptite Group in the area N of Hjulsjö (Fig. 1), is also composed predominantly of felsic pyroclastics, but contains large limestone and iron ore horizons.

*The Upper Leptite – Hällefrinta and Slate Group* contains a lower unit of felsic pyroclastics which pass upwards into tuffite, overlain by a sulphide-bearing black shale unit. This unit is overlain in turn by quartzitic grey shales, immature sediments derived by the reworking of the underlying pyroclastics. Lenses of coarse conglomerate are present in this upper group but are not part of a single stratigraphic unit, rather mark local unconformities. Mafic intrusives and spilites are developed towards the close of the felsic magmatism.

Submarine deposition of the felsic volcanics is supported by marine carbon isotope values ( $\delta C^{13} \approx 0 \pm 1\%$ ) for marble intercalations in the BSS (De Groot & Sheppard, in press).

Felsic metavolcanics in the Yxsjöberg area have been dated at 1.9 Ga (U-Pb; Åberg & Fredriksson, 1984), while the metasediments yield an age of 1.86 Ga (Sm-Nd; Miller et al., 1986). Granite intrusions can be divided broadly into two groups, the Bergslagen Older Granite Suite (Oen, 1987) with ages of 1.9–1.88 Ga (U-Pb; Welin et al., 1980; Åberg et al., 1983a, b; Welin, 1987; Rb-Sr: Oen et al., 1984), and the Bergslagen Younger Granite Suite with ages of 1.78–1.6 Ga (Welin et al., 1977; Oen, 1982, 1983; Åberg & Bjurstedt, 1986). The Bergslagen Older Granite Suite comprises largely syn-volcanic intrusions (Baker, 1985; Oen, 1987) coeval with the main period of felsic volcanism. A minor phase of Hyttisjö mafic magmatism occurred at around 1.84 Ga (Oen & Wiklander, 1982) coinciding with the peak of metamorphism and compressive deformation (Moorman et al., 1982).

### A continental setting for W. Bergslagen

Oen et al. (1982), Oen & Verschure (1982), and Oen (1987) developed a model of continental rifting to account for the geological phenomena seen in W. Bergslagen. Arguments supporting this model are summarized by Baker (1985). Oen et al. (1982) equate the Lower Leptite Group with an early volcanic stage, prior to an initial rift stage and rift stage marked by the Middle Leptite- and Upper Leptite-Hällefrinta and Slate Groups, respectively. Nd-Sm data from this area (Beunk et al., 1985; Miller et al., 1986) are in agreement with the findings of Wilson et al. (1985) in suggesting that the crustal precursor to the 1.8–1.9 Ga BSS had an age of about 2.1 Ga. This led Baker (1985) to suggest that rifting was affecting a 2.1 Ga basement and encompassed the whole BSS development, including the Lower Leptite Group assigned by Oen et al. (1982) to the initial volcanic stage. Chemical evidence (Vivallo & Rickard, 1984; Baker, 1985; Johansson & Rickard, 1985) indicate that this crust must have had an intermediate to felsic composition. In common with Archean and Proterozoic mobile zones, no older basement has, as yet, been found in the Bergslagen region. One striking feature of W. Bergslagen is the strong bimodality between the felsic metavolcanics and mafic rocks (Van der Velden et al., 1982; Vivallo & Rickard, 1984; Lagerblad & Gorbatshev, 1985) shown by Martin & Piwinski (1972) to be a characteristic of magmatism in extensional regimes. In the model of Oen et al. (1982) compressive tectonism caused deformation (flattening, shear folding) and low pressure metamorphism of greenschist to amphibolite grade in a post rift stage. Several phases of metamorphism related to granite intrusions have been suggested by Helmers (1984). High-grade metamorphism is confined to the aureole of the Horrsjö granite (e.g. Linthout, 1983). Sub-seafloor metamorphism and related hydrothermal alteration resulting from the syn- and post-volcanic plutonism, resulted in an annealing recrystallization in the felsic volcanics. This was preserved and enhanced during subsequent tectonic processes.

### Structural aspects of West Bergslagen

W. Bergslagen comprises a number of long, narrow synformal structures, made up of meta-sediment units, flanked by large thicknesses of felsic supracrustal rocks. These felsic supracrustals are cut off or enclosed by massifs of the Bergslagen Older Granite Suite (e.g. east of Nora, Lundström, 1983), or cut off by younger (1.7 Ga) granites. The absence of large scale isoclinal folds, the presence of homoclinal successions within the synformal structures, and the occurrence of discordancies at the base of several formations, suggest these structures are basins. In addition a number of paleofaults have been recognised in the field (see Fig. 1), located between the volcanic units and upper meta-sedimentary units, marked by mafic intrusive breccias. Two sets of faults, one N-S, the other NE-SW and NW-SE, cross the BSS and granites. W. Bergslagen is characterized by a predominance of sub-vertical to vertical structures in the supracrustal sequence (Fig. 2). Sub-vertical bedding which strikes N140E in the north of the area bends to an E-W strike south of Järnboås (see Fig. 2). A predominant NE-SW strike is present east of a N-S trending fault zone running from Nora to Kopparberg (see Fig. 1) (Lundström, 1983). The foliation ( $S_1$ ) is generally sub-vertical to vertical and makes a very low angle (usually less than  $10^\circ$ ) with the bedding. A later, open low angle kinking ( $S_2$ ) has affected the  $S_1$  foliation in the rocks NE of Hjulsjö. Extension lineations are formed in the  $S_1$  plane by amphiboles, nests of biotite, elongated quartz grains or lenses, and stretched quartz pebbles, lithic fragments and lapilli. In the rare cases where the bedding is sub-horizontal, the  $S_1$  foliation and lineations are also sub-horizontal. This can be seen in the Gåsborn area (Fig. 1), where numerous F-rich pegmatites, thought to originate from an underlying granite pluton, cut the felsic supracrustals (Damman, 1987 personal communication). Structures of this type have been described in the diapirism models of Ramberg (1967, 1981), Talbot (1974), and gravity tectonic models of Dixon & Summers (1983). Evidence for a combined gravity and diapirism tectonism comes from the septum-like structure at Ställdalen (see Fig. 1). The geolog-

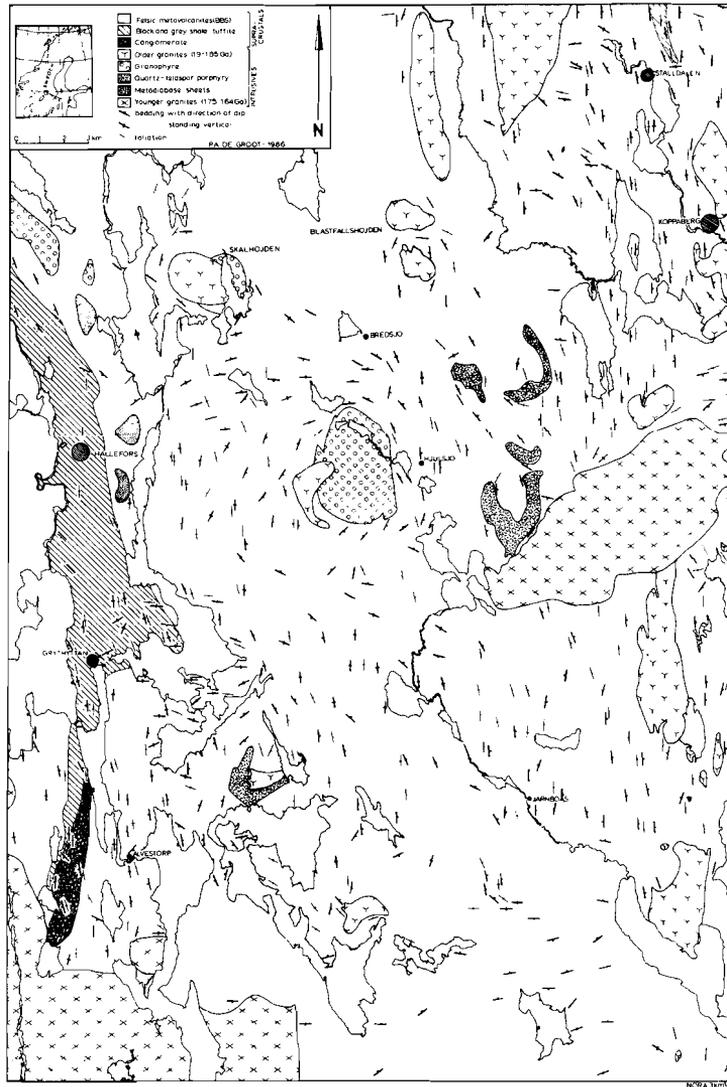
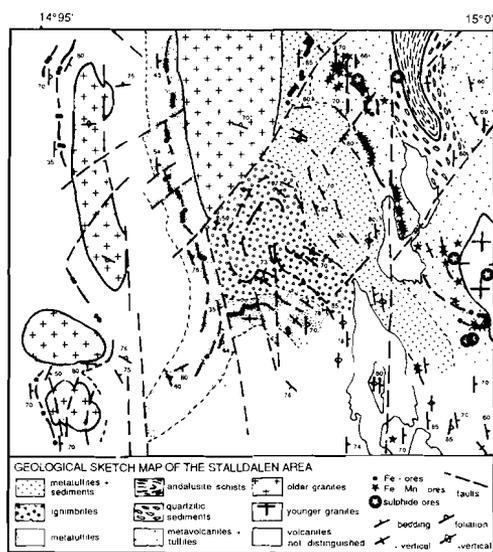


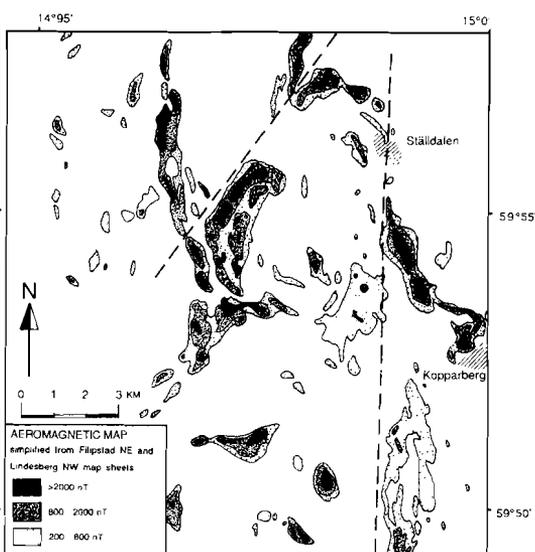
Fig. 2. Structural map of the Hällefors-Kopparberg-Nora area, showing bedding and foliation, and position of shales, metabasites, meta-conglomerates and granites from the Bergslagen Older and Younger Granite Suites.



A

Fig. 3a. Geological sketch map of the Stålldalen area, showing the septum-like structure, enhanced by the stratigraphic iron ore marker horizons.

ical relationships of the area W of Stålldalen are given in Figure 3a, which shows a stratigraphic sequence younging from SW-NE, and a number of granite intrusions from the Bergslagen Older Granite Suite. A detailed description of the stratigraphy of this area is given by Parr (in press). The lowest stratigraphic unit comprises well banded metatuffites, and includes calcareous metasediments and a sedimentary exhalative iron ore horizon, marked by a series of iron ore mines. This is overlain by a unit of coarse ignimbrites and includes pyroclastic flows, with occasional lapilli or crystal tuffs, and an iron ore horizon in the north (Fig. 3a). A unit of metatuffites with metasediments follows, and is in turn overlain by a unit of metavolcanites and tuffites which contain carbonate beds and lenses and two Fe-Mn volcano-exhalative ore horizons. These units of banded metatuffites and metasediments can be correlated with the Upper Leptite-Hälleflinta and Slate Group of Oen et al. (1982), or the Usken Formation of Lund-



B

Fig. 3b. Sketch map of the main magnetic features interpreted from the aeromagnetic maps Filipstad 11E NE and Lindsberg 11F NW (Lundström, 1983).

ström (1983). A unit of quartzitic metasediments is overlain by andalusite-bearing metasediments which form the synformal, trough-like structure in the E of the map area (Fig. 3a). The area is cut by a N-S set of faults, and a NE-SW set of faults (Fig. 3a) reflecting the pattern developed across the whole region (see Fig. 1), but they do not obscure the geological relationships. The volcano-exhalative ore horizons form clear stratigraphic markers in the area, confirming the bedding measurements in the supracrustals. The structure of the area is seen particularly well on the aeromagnetic maps (Fig. 3b). The iron ore horizon in the lowest metasedimentary unit runs south between two older granites before bending sharply SW towards the Bastfallshöjden granite. The horizon then folds back along itself (see magnetic map, Fig. 3b) to run E-W before bending again to run south. The stratigraphically highest ore horizon, located in the metavolcanite and tuffite unit (Fig. 3a), shows a hinge-like structure located along the NE-SW axis

of the structure shown by the lower ore horizon. Figure 3a also shows that the bedding in the supracrustals, where close to the older granites, runs parallel to the contacts with the granite massifs, even following the contacts in between the two small Bastfallshöjden plutons (Fig. 3a; Melkert, 1987, personal communication). The fold structure defined by the lower iron ore horizon, comprises three bedding directions (N-S, NE-SW and NW-SE), which meet under angles of about 120°, with bedding dips varying between 35° and vertical, mostly more than 65°. This, and the apparently sub-vertical fold axis and axial plane is an unlikely product of orogenic folding as required by the classic structural interpretation of Bergslagen (e.g. Magnusson, 1970). The structure is, however, compatible with the subsidence structures produced in diapirism and gravity tectonic experiments (e.g. Talbot, 1974; Ramberg, 1971, 1981; Dixon & Summers, 1983, 1985). It is our contention that the septum-like structure at Ställdalen, taken together with the subparallel bedding/older granite contact relationships, are consistent with gravity controlled tectonic processes in this region. This coalescence of three bedding directions (N-S, NE-SW, E-W) is not unique to the Ställdalen area. A similar structure is also present just NE of Hällefors (Fig. 1). While this structure was previously interpreted in terms of local disconformities (e.g. Oen et al., 1982), the structure is not inconsistent with a gravity tectonic interpretation.

#### **The tectonic development of W. Bergslagen**

W. Bergslagen is an elongate zone in the crust characterized by predominantly felsic igneous activity, low to high temperature and low pressure metamorphism, and minor migmatization (e.g. NE of Filipstad). The tectono-magmatic development of this area, including a consideration of the roles of tensional and gravity determined tectonism, can be divided into the following four stages (Table 1, Fig. 4).

##### *Phase 1: primary crust forming event*

An initial phase comprises the formation of pri-

mary crust from the mantle at about 2.1 Ga; an inference based on an interpretation of Sm-Nd data (Beunk et al., 1985; Miller et al., 1986).

##### *Phase 2: attenuation, rifting, volcanism and diapirism*

In the second phase low density asthenospheric mantle diapirism causes tensional stresses in the crust resulting in attenuation and rifting (e.g. Ramberg, 1978; and Fig. 4a). Subsidence of the lower crust (Fig. 4b) developed a series of grabens, while melting of the lower crust, presumably caused by underplating with mafic magma, produced magma of a relative homogeneous composition. An immense volume of felsic magmatism resulted, developing a volcanic pile of several km's thickness. The massive, uninterrupted outpourings of felsic magma indicate a rapid sinking of the crust, and melting of material to be vented as fissure eruptions or through individual volcanoes (Fig. 4b). The sinking of the graben basements within the developing rift zone ensured the containment of the felsic eruptions in the multiple rift grabens, though topographic highs were also covered (e.g. Fig. 4c). Granite diapirism was initiated at this stage, with the deeper seated intrusions being emplaced into the lower levels of the developing volcanic pile in the grabens. The freezing granite magma chambers, which had fed the rhyolitic volcanoes became, in a later stage, the granitic diapirs. Isotopic age data on the older granites suggest Phase 2 started at about 1.9 Ga, and continued until after 1.88 Ga (Welin et al., 1980; Welin, 1987).

##### *Phase 3: uplift, sedimentation and gravity subsidence*

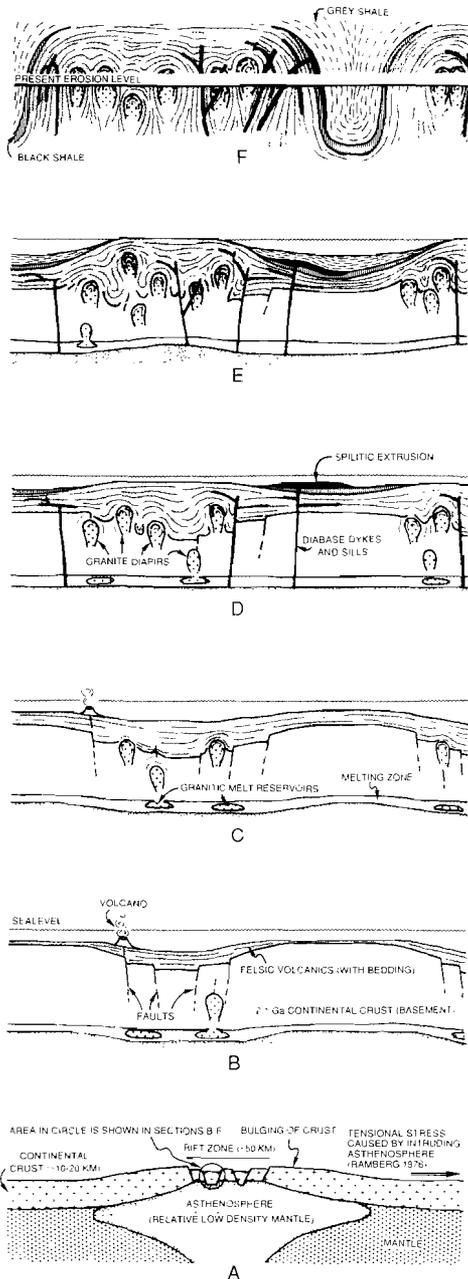
Phase 3 starts with a clear change in tectonic and magmatic evolution, and is heralded by the incoming of more tuffitic rocks towards the top of the stratigraphic sequence, and a period of volcanic quiescence marked by the black, graphitic and pyritiferous shales. Mafic magmatism is mostly developed during this period, where crosscutting dykes and sills have their extrusive, spilitized equivalents located in, or just under the black shales. This period of crustal relaxation, between sinking of the graben floors and uplift, in which the mafic mag-

matism occurs, marks the change to an inversion stage (Fig. 4d). While the graben floors now apparently rose, new grabens were initiated on the flanks of these rising blocks. The original grabens inverted to horsts. Although there was still sporadic felsic

volcanism, the tendency was to erosion of the felsic supracrustals on the rising horsts, to allow the deposition of sediments (black and grey shales) in the newly formed, downfaulted basins (Fig. 4d). This period is, in part, the initiation of a gravity flow

Table 1. Four stage model, and geochronological relationships for the evolution of the W. Bergslagen ensialic belt, modified from Oen et al. (1982).

Ga.			Period associated with later orogenic events
1.64–	Younger granite suite: – Dala-Järna granite – Fellingsbro granite – Värmland-Småland granite (Oen and Verschure, 1985b)	<i>Phase 4:</i> Younger granite intrusions ± contact metamorphism ± deformation	
1.74–			Gravity flow tectonics
?	?	<i>Phase 3:</i> Gravity flow tectonics + metamorphism + 2nd phase granite intrusion (W-Mo association) + continued sub-seafloor alteration processes	
? –	–W-Mo granites – 2nd phase granites		
1.84–	– metamorphism period of gravity flow tectonics	Grey shale deposition (minor felsic volcanism) Isostatic processes Black shale deposition	
1.86–	– initiation of gravity flow tectonics – uplift of volcanics by isostatic re-adjustment processes, erosion, deposition of grey shales – minor felsic volcanism – period of quiescence; formation of black shales – diabase sheet and dyke intrusion – extrusion and spilitization of basalt (pillow lava's)	Mafic magmatism (sheets and dykes – spilites)	
1.88–	– solidification of 1st phase granites (e.g. Horrsjö, Gillershöjden granite, Hjulsjö granophyre)		Rifting
		<i>Phase 2:</i> Sub-seafloor alteration processes (e.g. Hjulsjö hydrothermal system + associated sedimentary exhalative Fe (Mn) ore deposits on the seafloor) Felsic magmatism (volcanics + 1st phase granites)	
1.90–	– start of felsic volcanism and diapirism – anatexis of 2.1 Ga. crust		Primary crust formation
2.1 –	----- formation of crust  from mantle	<i>Phase 1:</i> Formation of oldest crust	



← Fig. 4. Proposed evolutionary model for the main structures of W. Bergslagen; A. sketch showing initiation of tensional regime in the lower crust through asthenospheric mantle diapirism (after Ramberg, 1978). Section runs W-E; B. initial volcanic phase, with large eruptions of felsic material; C. sinking of graben floor allows containment of felsic extrusiva predominantly within the grabens. Granitic diapirism is initiated; D. start of inversion phase, with an elevation of the original graben floor and emplacement of granite batholiths, while sedimentary basins start to develop in the intervening areas. Mafic magmatism accompanies this period of crustal relaxation; E. granite diapirism accompanied by the initiation of gravity subsidence in the sedimentary basins leads to the development of subvertical bedding and foliation, and sub-parallel contact relationships with the granites; F. completion of the diapirism - gravity subsidence process develops the structural features currently seen in W. Bergslagen, for which vertical rather than lateral (orogenic) forces were responsible.

system, and is equivalent to the main rifting stage of Oen et al. (1982). As the sediments fill the trough-like depressions between the rising horsts, the troughs themselves, with their heavier sediments add to the crustal instability, and their sinking lends a clear character to the deformational style (e.g. Kuipers, 1987). The diapirism initiated during phase 2 with the emplacement of granite bodies was enhanced in phase 3, during which the sub-vertical stand of the bedding, with sub-parallelism of foliation and lineation was achieved through gravity tectonics (Fig. 4e). Lateral constraints apparently prevented further growth in the rift (e.g. Illies, 1981), which thus developed the characteristic vertical structures seen in W. Bergslagen. A sub-vertical parallel layering, with sub-parallel foliation and lineation is typical of the sediment filled basins, and is predicted by the experiments of Dixon & Summers (1983) for trough-like basins at depth. Granite intrusions often have sub-parallel contacts with the felsic metavolcanics, which are developed as septum-like structures (e.g. Stålldalen, see Fig. 3) between the granites, similar to the models of Ramberg (1967, 1981). In this model there is no necessity of assuming a regional compressive phase in the crust to develop the structural elements observed in W. Bergslagen, although compression cannot be totally ruled out. Deformation of the type seen here or in Archean gneisses is not in itself evidence of crustal short-

ening (Carey, 1954). Gravity flow (Rayleigh-Taylor type processes) and diapirism (temperature gradient dependent) remove the need for the previously assumed Svecofennian orogeny in western Bergslagen.

*Phase 4: younger granitic magmatism.*

Phase 4 comprises a 1.74–1.64 Ga period of renewed granitic igneous activity after a period of relative quiescence. This phase will not be discussed here, since it post dates the period of gravity tectonics under consideration. It led to the development of the Bergslagen Younger Granite Suite (Oen, 1987), part of the Trans-Scandinavian granite belt. The later  $S_2$  foliation is probably developed at this stage.

### Discussion

Large scale structures in Bergslagen include long, narrow, synformal, sediment-filled basins separated by large areas of felsic supracrustals in which antiformal structures are absent, but in which volcano-plutonic complexes with sub-circular structures are developed. The layering and foliation in these felsic supracrustals folds around the granites, while the foliation in the marginal zones of the granite runs parallel to the contact with the felsic supracrustals forming structures comparable to mantled gneiss domes (Eskola, 1948). Variations in specific gravity (SG) have been measured (Table 2). The difference in SG measured in rock samples is similar to that to be expected between the sediments and felsic pyroclastics. The sediments are clearly heavier than the felsic volcanics or the gran-

ites, which have approximately similar SGs. The relatively heavier sediments deposited onto felsic volcanics with a lower SG provide a gravity instability in the crust. In addition the volcanogenic sediments, even if originally less dense than some of the sialic crystalline basement, become more dense by burial compaction, diagenesis, and metamorphic effects, the slightly metamorphosed equivalents of most sediments being denser than most acid gneisses (Clark, 1966; Talbot, 1974). This instability is thought to complement the granite diapirism and contribute significantly to the sinking of the heavy sediments into the underlying felsic supracrustals and eventually the continental basement in a way as described by Ramberg (1971, 1981) and Dixon & Summers (1983, 1985), controlled by density contrasts (Rayleigh-Taylor instabilities). This process contrasts with simple granite diapirism, where temperature differences drive a convective process (Weyeremars, 1987, personal communication).

### Conclusions

The rifting model of Oen et al. (1982) is expanded to include and suggest an explanation for the structural features encountered in W. Bergslagen. A four-phase crustal – tectonic evolution is envisaged. The first phase is an initial crust forming event at about 2.1 Ga. Phase 2 is the melting of the lower part of this initial crust, probably caused by underplating by mafic magma during a phase of crustal attenuation. A >10 km thickness of felsic volcanics developed, contained in grabens in the opening rift structure. The intrusion of granite plu-

Table 2. Numbers (N), averages, standard deviations (SD), and ranges of specific gravities (SG), in granites, felsic pyroclastics and metasediments from W. Bergslagen. (granite values from Baker, 1985).

Rock	N	SG average	SD	SG range
Granite	6	2.622	–	2.603–2.632
Felsic pyroclastics	73	2.646	0.036	2.550–2.740
Basin sediments	12	2.749	0.035	2.679–2.794

tons and initiation of diapirism is coeval with the rifting and volcanism. Granite diapirism occurred chiefly in phase 3, in a convective system controlled by temperature differences, contrasting with the Rayleigh-Taylor instability type process. Phase 4 comprises a younger phase of granitic magmatism.

We consider the whole volcanic phase to be rift related, not just the higher parts of the stratigraphic sequence, while the sedimentary stage culminating the sequence is considered to be the surficial expression of the gravity tectonic system, which engulfs the whole pile.

While this model does not explain all the structural complexities of W. Bergslagen it attempts to provide a chronological reconstruction of the main tectonic events, which should serve as a basis for future investigations.

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## Chapter 3

### HYDROTHERMAL SYSTEMS AND ORE MINERALIZATION - AN INTRODUCTION

Early workers quickly recognized the occurrence of alteration processes in the Bergslagen belt (e.g. Johansson, 1911; Lindroth, 1922; Sundius, 1923; Magnusson, 1925; Geijer, 1936; Geijer and Magnusson, 1944), although their ideas on these processes were drastically different from what is thought nowadays. Isochemical metamorphic processes and overprinting by metasomatism caused by fluids moving as a front in advance of intruding plutons were their explanation for the alterations.

Since it is known that fluids derived from the earth's surface (meteoric water or sea water) circulate deep into the crust - down to depths of 5 or even 10 km - explanations involving alteration by fluids derived from the surface and heated by intrusives are considered.

The rocks of the Bergslagen belt were affected by interaction with fluids to very different degrees, depending on permeabilities of the rocks and temperatures of both rocks and fluids. Fluid-rock exchange caused weak to strong chemical rearrangements of the rocks and fluids. Most supracrustal and intrusive rocks suffered a regional alteration at low water/rock ratio, which now generally is ascribed to a sub-sea floor alteration process (Schermerhorn, 1978; Oen et al., 1982; Baker and De Groot, 1983/chapter 4; Helmers, 1984; Lagerblad and Gorbatshev, 1985; Lagerblad, 1988; De Groot and Baker, 1992/chapter 5).  $\delta^{13}\text{C}$  values of stratabound carbonates gave evidence for marine circumstances in the Bergslagen region (De Groot and Sheppard, 1988/chapter 8) while the Mg-enrichment of the rocks during alteration almost certainly derived from a sea water source (Baker and De Groot, 1983/chapter 4). This regional alteration of the Bergslagen belt is comparable with oceanic alteration processes (see also section 1.2; Baker and De Groot, 1983/chapter 4; De Groot and Baker, 1992/chapter 5). However, the chemical difference between basaltic oceanic crust and the Bergslagen felsic sea floor leads to differences in chemical exchange and alteration mineralogy in both types of crust.

Hydrothermal systems which are active at higher temperatures deeper in the crust of the Bergslagen belt are restricted to conduit zones, channelling the fluids through the crust, generally in the direction of the surface and away from the heat sources, which were the intruding granitic plutons. These deeper and relatively warm (300 - 500°C) hydrothermal processes are related to exhalative (Fe  $\pm$  Mn oxides, base metal sulphides of VMS-type), skarn (Fe ( $\pm$ Mn), W, Mo, base metals, Ag and minor Ni, Co), and epigenetic (Pb - Zn stratiform sulphide deposits) mineralizations in the West Bergslagen belt.

An extensive study was carried out on the Hjulsjö hydrothermal alteration zones. The chemistry of these Hjulsjö zones is discussed in chapters 4 and

5, and the alteration mineralogy is discussed in chapter 6 based on a model of sea water derived fluids and thermodynamic calculations.

A stable isotopic study (C, O) on stratabound marbles and carbonates formed during skarn mineralization is presented in chapter 8.

Oxygen and hydrogen isotope data of silicate minerals from the Hjulsjö and Fogdhyttan alteration zones are discussed in sections 11.1/2. Alteration of granitic intrusions are briefly discussed in section 11.3.

Proterozoic sea water, which certainly was an important source for the hydrothermal systems in Bergslagen, is discussed in chapters 4, 9 and 10. A short summary of Proterozoic sea water is given in section 11.4.

Different types of ore mineralization in Bergslagen and their relation to hydrothermal processes are discussed in chapter 12.

Descriptions of selected skarn mineralizations, their geological setting, mineralogy and stable isotopic values are given in an appendix. Chapter 9 is a stable isotopic study (O, H) on silicate minerals in these skarns.

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## Chapter 4

### Proterozoic Seawater – Felsic Volcanics Interaction W. Bergslagen, Sweden. Evidence for High REE Mobility and Implications for 1.8 Ga Seawater Compositions

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**Abstract.** Mg enrichment in diffusely bounded, schistose alteration zones occurring in Proterozoic submarine felsic volcanics NE of Hjulsjö, W. Bergslagen is shown to result from felsic rock-seawater interaction in a sub-seafloor hydrothermal system. The alteration is apparently in two stages, feldspar being altered first to a kaolinite-type clay which is then replaced by Mg-chlorite.

Major and trace element data are presented for the schist and sheridanite (chlorite). Relative to the least altered felsic volcanics, and for negligible volume change, the schist shows strong addition of Mg and to a lesser extent Si; K, Al and Rb are apparently conserved, while most other elements are strongly depleted, including the REEs which are removed for ~75%, indicating a high degree of mobility.

The chlorite, with its HREE enriched pattern, is considered to have equilibrated with the hydrothermal fluid, which consisted predominantly of seawater. Comparison with modern seawater leads to the tentative conclusion that the Proterozoic seawater HREE composition was not drastically different from that of modern seawater.

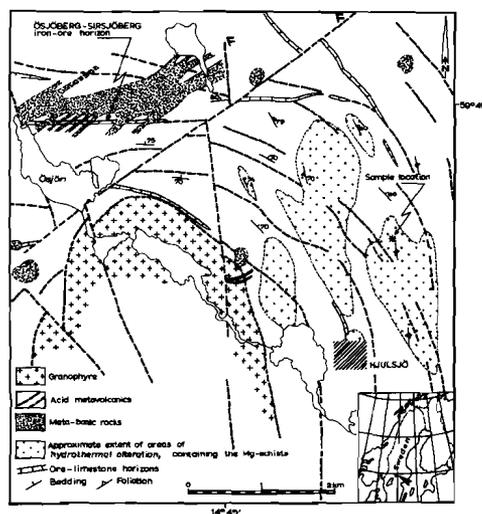
#### Introduction

Chlorite-mica-quartz schists, extensively developed in the Hjulsjö area, West Bergslagen, Sweden, form discordant and discontinuous NNW-SSE trending, often lensoid zones, in an E-W to NNW-SSE striking succession of acid metavolcanics. Relative to the metavolcanics the schist zones contain high amounts of MgO (up to ~7 wt%). Similar Mg-rich schist zones in W. Bergslagen are often found as concordant or subconcordant layers or lenses which have been formerly interpreted as metamorphosed, possibly metasomatically altered sediments (Magnusson 1970; Koark et al. 1979). The Mg-rich schistose zones developed NE of Hjulsjö are the most altered parts of larger zones of hydrothermal alteration (Fig. 1), and are ideally suited for investigation, showing only low grade greenschist facies metamorphism; similar zones further to the East are generally metamorphosed under amphibolite facies conditions to cordierite schists.

Detailed petrographic examination reveals that these Mg-rich schists are progressively altered metavolcanics, the

original pyroclastic texture being gradually blurred as re-crystallization and chemical alteration increase through the zones of hydrothermal alteration towards the cores, where the highest MgO values are recorded. South of the Hjulsjö area, and East of Grythyttan, alteration on an outcrop scale shows unaltered metavolcanic remnants preserved in Mg-rich schists (Linthout, pers. comm.). This paper details the major and trace element chemistry of the chlorite, a sheridanite, the main carrier of MgO.

Oen et al. (1982) have developed a geological model for West Bergslagen whereby the formation and metamorphism of iron, manganese and sulphide deposits, and associated skarns and magnesium-metasomatic alteration zones, "sköls", and schistose and shear zones has involved widespread exhalative-sedimentary and sub-seafloor hydrothermal metamorphic processes operating during the different stages of deposition and consolidation of the Bergslagen Supracrustal Series 1.9–1.8 Ga ago (see also Moorman



**Fig. 1.** Geological map of the area around Hjulsjö (modified from Baker, unpubl. work) showing the approximate extent of areas of hydrothermal alteration which include the schistose zones

	Lithostratigraphic units	Intrusive rocks	Setting	
BERGSLAGEN SUPRACRUSTAL SERIES	1.6 Ga	Younger granites (Filipstad, Grängen, Dala)	Regional subsidence	
	1.7 Ga			
	1.8 Ga	Hyttsjö gabbro- tonalite suite	Post rift stage: main phase of tectonic compression & regional metamorphism	
	Conglomerates			meta-splilites, meta- basic flows, sheets and dykes
	Upper Leptite-Hälleflinta Slate Group felsic metavolcanics overlain by tuffites, greywackes, black slates, grey slates			
Middle Leptite Group felsic metavolcanics, thick marbles calcareous and siliceous iron formations (BIFs), Fe-, Mn-, sulphide skarns and ores	older granites, granophyres, felsic porphyry dykes	Initial rift stage		
Lower Leptite Group felsic metavolcanics, minor marbles, skarns and Fe-ores				
1.9 Ga	Unknown, probably gneissic Archean basement	Early volcanic stage		

Fig. 2. Stratigraphic table for the Filipstad-Grythyttan-Hjulsjö region, modified from Oen and Verschure (1982)

et al. 1982). Chemical modelling for the enrichment in magnesium in the Mg-rich schistose zones in Bergslagen is presented here, in which Mg-chlorite, or an Mg-bearing clay, is thought to have formed through the interaction of seawater with the metavolcanics in structurally controlled areas of high hydrothermal activity, probably associated with high level felsic intrusive complexes, which will have served as heat sources (Arnórsson et al. 1978). Enrichment and depletion factors for the Mg-rich schist relative to the average composition for the chemically least altered metavolcanics show that most elements have been removed during the hydrothermal alteration, including the REEs, Ti, and Y. Assuming the alteration products have partially equilibrated with the hydrothermal fluid, then the preferential retention of some elements by the chlorite leads to important conclusions concerning the initial composition of the seawater.

#### Geological Setting

The Proterozoic Bergslagen Supracrustal Series, as defined by Oen et al. (1982), comprises three lithostratigraphic groups, in which the lower and middle groups, composed of predominantly submarine acid metavolcanics with subordinate metasediments, are overlain by an upper group in which metasediments increase and dominate, the succession terminating with black and grey slates and a conglomerate (Fig. 2).

The Mg-rich schistose zones under discussion here form the cores to larger hydrothermal alteration zones, and are found in the lower group, which in the Hjulsjö area forms part of a major subcircular volcano-plutonic complex, the subvertical metavolcanic beds striking generally parallel to, and younging away from, the margins of a central core of intrusive granitic rocks (Fig. 1). The metavolcanics comprise a thick succession of pyroclastic flows with occasional airfall tuffs, in which primary structures such as fiamme, pumice fragments, and shards are well preserved. Carbonate deposits and banded iron formations, virtually absent from this lower group, are extensively developed in the middle group which discordantly overlies the lower group to the North.

Deformation is only slight in the metavolcanics, a macroscopic foliation being seldom visible in airfall tuffs, though in the flow banded rocks the primary texture tends to be accentuated when this runs parallel to the foliation direction.

The discordant lensoid zones near Hjulsjö form part of a series of larger Mg-rich schistose belts which extend SSE for at least 40 km, running parallel to the general foliation, the proposed axis of rifting, and trend of the sedimentary rift basins (Oen et al. 1982).

The greyish white Mg-rich schists have diffuse contacts with the country rocks, grading through the wider zones of hydrothermal alteration into the metavolcanics. The schists are the most deformed rocks of the area, but while

there is some evidence for brittle displacement along these structurally weak zones, evidence for lateral displacement of the country rocks via slip in the zones is often lacking.

Details of the chemical and petrographic variations in and across the zones will be presented later (De Groot and Baker, in prep.). Oen et al. (1982) and Moorman et al. (1982) have indicated that in the Hjulsjö area shear and schistose zones, skarn zones, and early rift stage metabasic dykes are mutually intersecting and coeval features that predate the post-rifting, major phase of compression. They conclude that the metamorphism of basic dykes, skarn formation and shear and schistose zone development are all related to sub-seafloor metamorphic processes operating during the development of the Supracrustal volcano-sedimentary sequence 1.9–1.8 Ga ago (Fig. 2).

#### Analytical Techniques

One sample from the core of a schistose zone was selected from a sequence of chemically analysed samples and used for mineral separation and analysis. The chlorite was extracted magnetically from a crushed and sieved sample, in the grain size range 71–125  $\mu\text{m}$ . Three 200 mg samples of chlorite, together with the whole rock were analysed for Sc, Cr, Co, Sb, Cs, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, and U by INAA using the Inter-university Reactor Institute (IRI) facilities in Delft. The weighted average is shown in Table 2, together with the average of 20 measurements of MAG-1 and the values of Flanagan (1976), McLennan and Taylor (1980), and Potts et al. (1981) for comparison. Major elements were measured using standard XRF techniques, and the trace elements Ni, Cu, Zn, Ga, Rb, Sr, Y, Nb and Pb in whole rock-samples using the XRF techniques developed by ViéleSage et al. (1979). EMP raster analyses were obtained using the Cambridge Microscan 9 automated microprobe of the ZWO-WACOM working group, operating at 20–25 Kv, using silicate standards: raw data were corrected using the mark 9 on line ZAF Computer Program.  $\text{Fe}^{2+}$  was determined by titration. XRD powder patterns were recorded with an Enraf Nonius Guinier camera using  $\text{CoK}\alpha_1$  radiation and corundum as an internal standard.

#### Petrography of the Altered Rocks

The low-grade Mg-schists, derived from hydrothermally altered felsic pyroclastics show progressive increase in deformation towards the cores of the zones, where blasts of greyish-green chlorite and an undulose mica foliation develop, the chlorite weakly orientated in the plane of the foliation. With the exception of a few relict H.T. quartz pseudomorphs, the original pyroclastic texture is obliterated as the foliation develops. A foliation develops preferentially in these rocks, the abundant phyllosilicates providing an easy passage for stress release, while the quartz-rich matrix shows little sign of deformation. A younger kinking is locally superimposed on the foliation.

Chlorite forming 20% of the rock, is developed as ragged poikiloblasts up to 2 mm long, containing quartz and rutile inclusions (Fig. 3a). Where they cross the foliation they are sometimes kinked, implying later slip along the foliation. The chlorite has the following optical properties:

pleochroism $\alpha \approx \beta$ very light green	$\gamma$ = colourless
refractive indices $\alpha = 1.584$	$\gamma = 1.594$
birefringence 0.0095	$+2v = 5^\circ$

Chlorite is also developed in the matrix, forming fine grained intergrowths and irregular aggregates with muscovite.

Muscovite grows across the chlorite poikiloblasts, or is intergrown along (001). It also forms occasional rims (<0.05 mm) around the chlorite blasts. Muscovite is also developed in the matrix, occurring both as individual, parallel orientated grains (0.75 mm), and together with the chlorite in the fine grained aggregates.

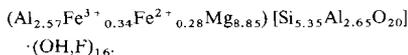
Quartz is present as relict HT-quartz pseudomorphs, forming 10% of the rock, both recrystallized to aggregates of new grains, or preserved as relatively strain free grains with undulose extinction. Quartz is the dominant matrix mineral, where a foam texture is developed, though a form preferred orientation is weakly present.

Accessory minerals are rutile and colourless tourmaline, the latter sometimes widely developed (up to 10%), and an important constituent in an Mg-rich schistose zone near Annehill, 20 km SE of Hjulsjö (Louwaars 1977).

Examination of thin sections from the Hjulsjö and Annehill schistose zones reveals the progressive alteration and replacement of alkali feldspars. The first stage (Fig. 3b) is hydrolysis of the feldspar, and its replacement by an extremely fine grained clay aggregate, while the old feldspar cleavage planes, particularly (010) are preserved and defined by fine-grained growths of sericite. The clay is colourless or very light brown, and almost isotropic. Identification has proved difficult, but XRD analysis suggests that it is composed of a kaolinite group mineral, possibly meta-halloysite (W. Drucker, pers. comm.). An illite-type clay has also been found, lacking the sericite bands. The second stage of alteration is replacement of the clay by Mg-chlorite, and where this stage has been exceptionally well preserved (Fig. 3c) the sericite still delineates the old (010) feldspar cleavage. In some cases total alteration to sericite has been observed, with no chlorite developed.

#### Mineralogy of the Chlorite and Associated Minerals

Representative microprobe analyses from the Hjulsjö zone are compiled in Table 1, with feldspar, clay mineral and chlorite analyses from the Annehill zone. The average structural formula of the chlorite, including 1.71 wt% FeO (wet chemical det.) is:



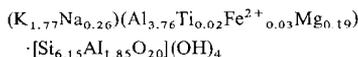
Only trace amounts of Ca, Ti, Mn, K, Na, and Cr were detected (less than 0.7 wt% of oxides); F varied irregularly (0.20–0.86% wt% element), and Cl was below the detection limit. The chlorite falls in the sheridanite field of Hey (1954) agreeing with the XRD determination of Tiersma (1974) for chlorite from a similar zone to the East. The following lattice parameters have been obtained by least squares refinement from XRD powder data of the 71–125  $\mu\text{m}$  fraction:

$$a = 5.317 \text{ \AA} (0.002) \quad \beta = 97.29^\circ (0.10),$$

$$b = 9.220 \text{ \AA} (0.002)$$

$$c = 14.298 \text{ \AA} (0.006) \quad (\text{standard deviation in brackets})$$

The muscovite deviates only slightly from the ideal composition, with an average structural formula of:



The uniformity in muscovite and chlorite composition is shown by the Si–Al–(Fe+Mg) plot (Fig. 4). Also

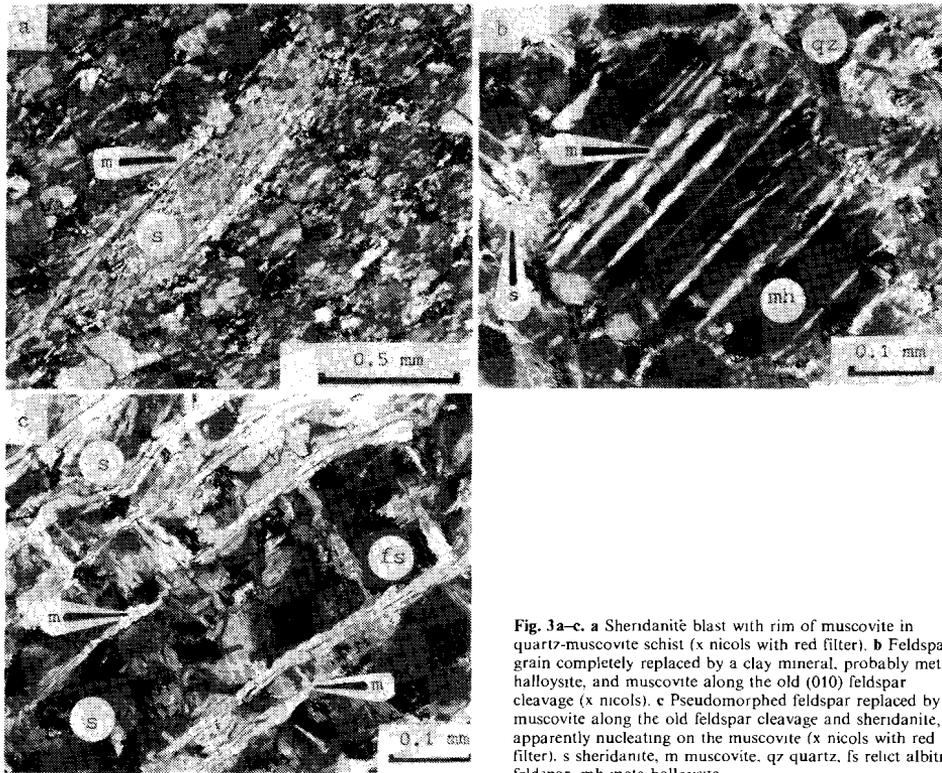


Fig. 3a-c. a Sherdanite blast with rim of muscovite in quartz-muscovite schist (x nicols with red filter). b Feldspar grain completely replaced by a clay mineral, probably meta-halloysite, and muscovite along the old (010) feldspar cleavage (x nicols). c Pseudomorphed feldspar replaced by muscovite along the old feldspar cleavage and sherdanite, apparently nucleating on the muscovite (x nicols with red filter). s sherdanite, m muscovite, qz quartz, fs relict albitic feldspar, mh meta-halloysite

shown for comparison is the field occupied by Mg-chlorites from hydrothermal alteration zones associated with the submarine volcanogenic Kuroko ore deposits of Japan (Shirozu et al. 1975).

The composition of the albite VSA (Fig. 3c) is typical for the rare relict grains found in these rocks. Different MgO contents have been measured in the clay minerals (1.87–5.52 wt%), but it is not yet clear if this represents a progressive increase. The high K<sub>2</sub>O content of the illite-type clays ROA and ROB suggests that these may represent altered potassium feldspar, rather than albite. The chlorite CHF developing at the expense of feldspar in Fig. 3c contains slightly more Fe than the other chlorites in Table 1.

#### Trace Element Chemistry

Trace element data for the chlorite, whole rock schist, and average of the least altered metavolcanics are given in Table 2.

Relative to the whole rock the chlorite is enriched in Cr, Zn, Sb, Ta, Th, U, and HREEs, somewhat depleted in Sc, Co, La, Ce and Hf, the other elements remaining more or less constant. The chondrite normalised REE plots for the chlorite and the whole rock are shown in Fig. 5.

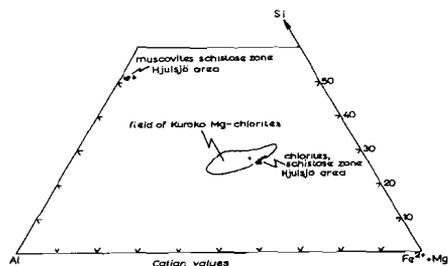
The chlorite has a slightly lower sum of REEs. The whole rock is LREE enriched and HREE depleted with respect to the chlorite, but the slope of the HREEs is almost identical for the whole rock and the chlorite. Alderton et al. (1980) report a convex upwards REE pattern for hydrothermally developed tourmaline and the presence of this mineral as an accessory phase may account for the steeper HREE pattern in the whole rock schist. Eu values are similar in the whole rock and chlorite.

Relative to the average of the metavolcanics both the whole rock and the chlorite from the schistose zone are depleted in LREEs, though the slope of the whole rock from the schistose zone parallels that of the metavolcanics. The chlorite is HREE enriched relative to the least altered metavolcanics. Clearly under the conditions of hydrothermal alteration the REE were *highly mobile*, approximately 75% of the total REE content being lost in the formation of the schist from the metavolcanics. Alderton et al. (1980) noted a similar case of HREE enrichment in a chlorite from an alteration zone in the Carnmenellis granite, SW England. There the HREE pattern is steeper ( $Lu_n/Tb_n = 2.9$ , contrasting with 1.5 for this chlorite); further the Carnmenellis chlorite is depleted in Th and strongly enriched in Sc and Ta, whereas the chlorite from the schistose alteration

**Table 1.** Cation values from microprobe analyses: slide Bj 550; coexisting muscovite and chlorite (CLB, CLC, CLF, CLH), individual chlorite blasts (CLA, CLD, CLE), partial analyses of tourmaline (dravite) (TMA, TMB); slide Gp 1L5: kaolinite group mineral, probably meta-halloysite (HAL); slide Gp 1L4; albitic feldspar (VSA), illite-type clays (ROA, ROB), chlorite (CHF), tourmaline (dravite) (TMC)

	CLA	CLB	CLC	CLD	CLE	CLF	CLH						
Chlorites, cations assuming 28 (O)													
Si	5.390	5.224	5.569	5.346	5.331	5.275	5.460						
Al <sup>IV</sup>	2.610	2.776	2.431	2.664	2.669	2.725	2.540						
Al <sup>VI</sup>	2.521	2.734	2.500	2.530	2.681	2.735	2.611						
Fe <sup>2+</sup>	0.525	0.494	0.471	0.509	0.498	0.493	0.532						
Mg	8.999	8.793	8.994	9.028	8.815	8.766	8.822						
Coexisting Muscovites, cations assuming 22 (O)													
Si		6.113	6.182			6.089	6.170						
Al <sup>IV</sup>		1.886	1.817			1.910	1.829						
Al <sup>VI</sup>		3.781	3.773			3.738	3.662						
Ti		0.029	—			0.061	—						
Fe <sup>2+</sup>		0.033	0.035			0.027	0.040						
Mg		0.153	0.205			0.173	0.377						
Na		0.347	0.207			0.286	0.201						
K		1.695	1.807			1.762	1.802						
	TMA	TMB	TMC	VSA	HAL		ROB	ROA	CHF				
Cations assuming: —	20 (O)*			32 (O)	14 (O)		22 (O)		28 (O)				
Si	5.865	5.991	6.173	5.931	3.851		6.521	7.245	5.425				
Al <sup>IV</sup>	6.000	6.000	6.000	2.052	3.936		1.479	0.755	2.575				
Al <sup>VI</sup>	0.427	0.700	0.366	—	—		3.414	2.783	2.764				
Ti	0.029	0.005	0.015	—	—		0.080	0.065	—				
Fe <sup>2+</sup>	0.087	0.076	0.285	—	0.053		0.144	0.275	0.955				
Mg	2.507	2.105	1.943	—	0.245		0.569	1.108	8.185				
Ca	0.136	0.048	0.039	0.032	0.037		0.008	0.008	—				
Na	0.680	0.781	0.608	1.866	0.011		0.064	—	—				
K	—	—	0.020	0.686	0.117		1.650	1.553	—				

\* Assuming (BO<sub>3</sub>)<sub>3</sub>



**Fig. 4.** Coexisting Mg-chlorites and muscovites from the schistose alteration zones, Hjulsjö area (cation ratios), with field of Kuroko Mg-chlorites for comparison (data from Shirozu et al. 1975)

zone shows only a slight Ta enrichment and is Sc depleted. The whole rock data of Alderton et al. (1980) indicate that their chlorite is Fe-rich, in contrast with the Mg-rich sherdanite from Hjulsjö.

### Mass Balance Calculations

The submarine eruption of the felsic volcanic rocks will have allowed an initial chemical exchange between the rock and seawater, in particular involving Na, K and Ca, so that

all volcanics, especially those with extreme Na or K values cannot be regarded as having a primary major element chemistry. The whole rock schist is compared to the average of 13 metavolcanics chosen as being chemically the least altered.

The formation of Mg-rich hydrous phases in the schistose zone may have involved some volume increase, and thus in considering the mass balance relationships it is essential to determine in how far the alteration process has involved a volume change.

Gresens (1967) developed the following general equation to take account of both mass balance and volume during metasomatism:

$$\Delta X_n = 100 \left[ \{F_v X_n^\beta (P^\beta/P^\alpha)\} - X_n^\alpha \right]$$

where

$\Delta X_n$  = loss or gain in grams of element  $n$  in producing rock  $\beta$  from rock  $\alpha$ .

$X_n^{\beta,\alpha}$  = weight fraction of element  $N$  in altered ( $\beta$ ) and unaltered ( $\alpha$ ) rock.

$P^{\beta,\alpha}$  = specific gravities of altered and unaltered rock.

$F_v$  = ratio between initial and final volumes of rock mass.

By plotting gains and losses for the different elements as a function of volume change, a composition-volume (c/v)

**Table 2.** Major and trace element data for the sheridanite, whole rock schist and average of the least altered metavolcanics together with the average of 20 measurements of MAG-1 and the values of ▲ Flanagan (1976), † McLennan and Taylor (1980), and □ Potts et al. (1981) for comparison. Major element data for sheridanite from microprobe analyses. \* Seawater values from Elderfield and Greaves (1982)

wt%	Chlorite from schistose zone	Whole rock schist n=1	Ave unaltered rocks					
			n=13	std dev				
SiO <sub>2</sub>	27.55	77.4	76.54	(1.67)				
TiO <sub>2</sub>	0.02	0.108	0.149	(0.029)				
Al <sub>2</sub> O <sub>3</sub>	22.84	11.55	11.89	(0.51)				
Fe <sub>2</sub> O <sub>3</sub>	1.53	0.46	1.518	(0.514)				
FeO	1.71	—	—	—				
MnO	—	—	0.006	(0.005)				
MgO	30.60	4.6	0.562	(0.352)				
CaO	0.03	0.41	0.753	(0.44)				
Na <sub>2</sub> O	0.04	0.2	4.367	(1.93)				
K <sub>2</sub> O	0.07	2.3	2.331	(1.45)				
P <sub>2</sub> O <sub>5</sub>	n.d.	0.015	0.24	(0.008)				
Total	84.40	97.11						
ppm								
Sc	2.40	4.159	5.05	(1.09)				
Cr	5.90	4.68	4.48	(1.39)				
Co	2.33	5.258	10.39	(2.83)				
Ni	—	3.54	3.76	(0.79)				
Cu	40.54	5.00	6.29	(1.09)				
Zn	32.40	10.80	12.72	(3.52)				
Ga	32.94	14.80	15.58	(1.33)				
As	0.70	0.81	—	—				
Rb	—	49.40	49.65	(28.82)				
Sr	—	1.94	62.03	(33.04)				
Y	—	32.10	51.35	(11.06)				
Zr	166.98	207.00	198.75	(24.71)				
Nb	—	11.20	10.99	(1.09)				
Sb	1.031	0.915	—	—				
Cs	0.565	0.712	1.05	(0.83)	Seawater * × 10 <sup>6</sup>	1.34	(0.30)	0.88 ▲
Ba	nd	nd	873.60	(264.0)		9.58	(0.53)	9.45 †
La	7.987	13.17	56.30	(30.4)	33.80	45.78	(7.29)	41.80 □
Ce	16.062	27.23	98.00	(54.61)	26.44	85.20	(2.08)	87.60 □
Sm	3.197	3.11	9.77	(5.42)	6.51	7.29	(0.25)	7.22 □
Eu	0.199	0.242	1.45	(1.05)	1.34	1.455	(0.064)	1.43 □
Tb	1.241	0.564	1.28	(1.47)	1.55	0.961	(0.120)	0.96 □
Yb	7.057	3.90	5.26	(1.12)	7.98	2.519	(0.165)	2.57 □
Lu	1.22	0.76	0.87	(0.16)	1.50	0.45	(0.04)	0.40 □
Hf	5.795	6.798	6.21	(0.82)		3.598	(0.159)	3.60 □
Ta	1.403	1.046	1.02	(0.12)		0.959	(0.115)	1.20 □
W	1.67	n.d.	—	—				
Pb	—	4.2	6.87	(1.42)				
Th	18.67	11.57	12.33	(1.67)		11.29	(0.54)	12.1 □
U	4.645	2.18	3.60	(0.99)		2.43	(0.83)	2.38 †

diagram can be constructed (Fig. 6) by which a realistic value for the actual volume change can be deduced. Gresens (1967) and Appleyard (1980) consider the distribution of points in a  $c/v$  diagram where the various component lines cross the zero change line for composition. Elements which are immobile during the alteration process should cluster together about the true  $F_v$  value. In Fig. 6 the elements Si, Ti, Al and K are grouped about the constant volume of  $F_v = 1.0$ , and if the assumption that these elements were basically immobile is correct, then the volume increase was clearly less than 10%. More data are needed before a quantitative value can be given.

#### Element Mobility in the Hjulsjö Alteration Zones

To a first approximation it is convenient to assume an isovolumetric process. The difference in weight of the chemical components in a unit volume between the schist and average of the metavolcanics have been calculated (Table 3). K<sub>2</sub>O is apparently conserved, but this value must be treated with caution considering the large standard deviation for the average K<sub>2</sub>O value (Table 2).

Al is apparently the least changed element, while depletion of Na, Ca and Fe is approximately balanced by the input of Mg and Si. Ti is also mobile, being depleted. As-

suming the Mg content of Proterozoic and modern seawater to be similar (though there are some suggestions it may have been higher, e.g. Guillon 1982), knowing the amount of excess Mg in the schist, and assuming total Mg depletion from the hydrothermal fluid; then the water/rock ratio can be calculated as  $\sim 100/1$ . High water/rock ratios of this magnitude are generally considered realistic (Bischoff and Seyfried 1978), favouring a low pH and fast reaction rates.

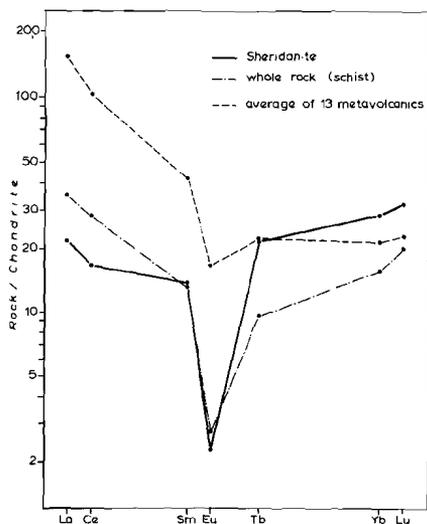


Fig. 5. Chondrite normalized plots (Evensen et al. (1978)  $\times 1.5$ ) for the chlorite, whole rock schist, and average of the least altered metavolcanics

Figures 7a, b show the relative mass enrichment and depletion of the Mg-schist as compared to the average of the chemically least altered metavolcanics in the Hjulsjö area. For the major oxides (Fig. 7a)  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MnO}$  and  $\text{FeO}$  are strongly depleted,  $\text{K}_2\text{O}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  remain more or less constant and  $\text{MgO}$  is strongly enriched in the altered rocks. Also shown in Fig. 7a for comparison is the depletion and enrichment of major oxides in Kuroko alteration zones (Iijima 1974). There not only  $\text{Na}_2\text{O}$  and  $\text{CaO}$  have been removed but also  $\text{K}_2\text{O}$  and  $\text{SiO}_2$  while  $\text{MgO}$  is more enriched than at Hjulsjö, and both  $\text{FeO}$  and  $\text{MnO}$  are enriched. The broadly similar Hjulsjö and Kuroko alteration zones are additionally both characterized by  $\text{MgO}$ -rich chlorites of almost identical composition (see Fig. 4).

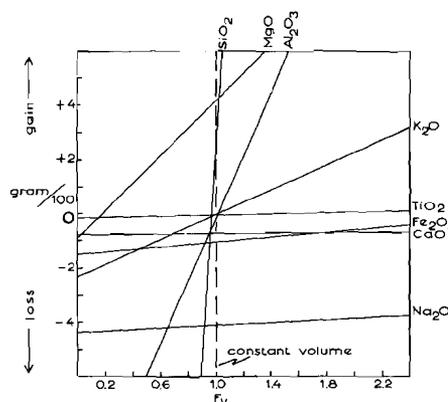


Fig. 6. Composition-volume diagram (Gresens 1967) for major elements; Hjulsjö schist relative to least altered metavolcanics.  $\text{P}_2\text{O}_5$  and  $\text{MnO}$  omitted for clarity, running sub-parallel to the zero gain line

Table 3. Chemical composition of altered schist and unaltered rock (average of meta-volcanics), and mass balance calculation, assuming isovolumetric change

	Altered rock		Unaltered rock		Difference	Difference as %
	wt%	g/unit vol	wt%	g/unit vol		
$\text{SiO}_2$	77.425	2,087.38	76.467	2,033.26	+ 54.12	+ 2.66
$\text{TiO}_2$	0.108	2.91	0.149	3.96	- 1.05	- 26.51
$\text{Al}_2\text{O}_3$	11.551	311.41	11.879	315.86	- 4.45	- 1.41
$\text{Fe}_2\text{O}_3^a$	0.462	12.46	1.517	40.34	- 27.88	-
$\text{MnO}$	0.0	0.0	0.006	0.16	- 0.16	- 100.00
$\text{MgO}$	4.618	124.5	0.561	14.92	+ 109.58	+ 734.62
$\text{CaO}$	0.041	1.11	0.752	20.00	- 18.89	- 99.47
$\text{Na}_2\text{O}$	0.234	6.31	4.363	116.01	- 109.70	- 94.56
$\text{K}_2\text{O}$	2.296	61.9	2.329	61.93	- 0.03	- 0.045
$\text{P}_2\text{O}_5$	0.015	0.4	0.024	0.64	- 0.24	36.63
$\text{H}_2\text{O}^b$	3.249	87.59	1.953	51.93	+ 35.66	+ 68.67
	100.00	2,696.00	100.00	2,659.00	+ 37.00	
Specific Gravity		2.696		2.659 ( $s=0.02$ )		

<sup>a</sup> Total iron content

<sup>b</sup>  $\text{H}_2\text{O}$  is assumed to be the difference between the sum of the oxides and 100%

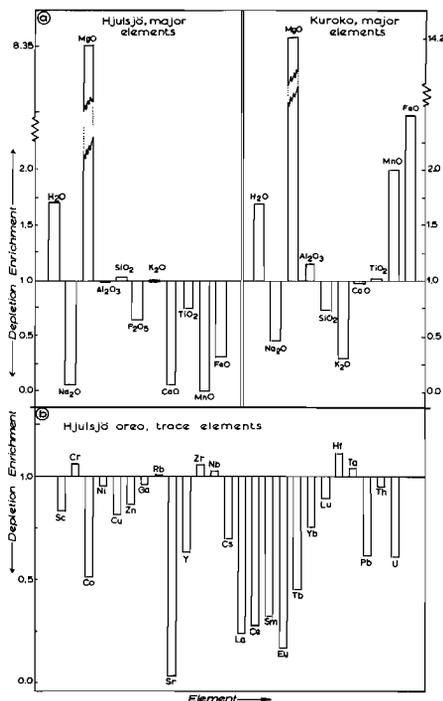


Fig. 7. Enrichment and depletion factors for the schist from the Hjulssjö alteration zone relative to the average of the least altered metavolcanics (equal volumes): a) major elements; with, for comparison, the enrichment and depletion found in altered rocks associated with the Kuroko ore deposits relative to their unaltered equivalents (data from Iijima 1974). b) trace elements

Most trace elements have been depleted (Fig. 7b). Rb and Sr mirror the behavior of K and Na respectively. Cs, known to be extremely mobile under hydrothermal conditions (Ellis and Mahon 1967, Arnórsson 1970, Surenda Pal. 1980), is not strongly depleted, probably being incorporated in newly forming phyllo-silicates (Ellis 1979). The low mobility of Ga, which substitutes for Al, is comparable in behaviour to Ga from the Reykjanes field (Arnórsson 1970), where Ti is also generally retained unless the grade of alteration is high, and where the mobility of Co, Zn, and Fe is seen to be enhanced by a low pH. In the Hjulssjö schistose zone Co, Zn and Fe have also been removed, suggesting a low pH, but the behaviour of Ni, apparently conserved, is somewhat anomalous. Pb and U have been removed in equal quantities. The large scale removal of trace elements, especially heavy metals is further evidence for a high water/rock ratio (Seyfried and Mottl 1982). The degree of mobility of the REEs has often been discussed (e.g. Graf 1977, Martin et al. 1978). Here they have all been removed from the rock in decreasing amounts with increasing atomic number, with the exception of Eu, which is more strongly depleted. The HREEs, retained in the chlorite, are the least depleted.

Finlow-Bates and Stumpfl (1981) considered only Zr and Ti to be truly immobile under hydrothermal alteration conditions, but at Hjulssjö while Zr, Hf and Ta were immobile, Ti and Y were removed from the rock. The high mobility of elements seen in the Hjulssjö alteration zones seems characteristic for extreme hydrothermal alteration, since many of the elements seen to be mobile at Hjulssjö are considered to be immobile under low grade metamorphic and alteration conditions (e.g. Winchester and Floyd 1976, Floyd and Winchester 1978, Pearce and Norry 1979).

#### Sub-Sea Floor Hydrothermal Alteration in the Hjulssjö Mg-Rich Schistose Zones

The evidence for sub-seafloor hydrothermal alteration in the Mg-rich schistose zones includes: (1) the progressive alteration of the original pyroclastic textures through hydrolysis of the feldspar and grain size increase in the matrix due to quartz recrystallization, (2) the discordant nature of the lensoid zones, aligned along old fault systems, (3) the similar radiometric ages obtained for the emplacement and the metamorphism of the meta-volcano-sedimentary sequence (Moorman et al. 1982, Oen et al. 1982), and (4) the enrichment in magnesium, contained in the sheridanite in the Mg-rich schistose zones.

From the petrography it is apparent that the feldspars underwent alteration to hydrous aluminosilicate phases, probably meta-halloysite, releasing Na and any Ca to the fluid, while K was retained to be eventually incorporated in muscovite. Magnesium then precipitated in the sites of old feldspar, suggesting some sort of Mg-Na exchange. The idea of converting kaolinite to a chloritic phase in order to remove ions from seawater is not new, but has been generally discounted as unrealistic under most marine conditions (see Drever 1974). However, under the extremes of hydrothermal alteration at Hjulssjö there is good microstructural evidence to support this process. Fe depletion proceeded independently of this. Favoured by a low pH (Arnórsson 1970) and high water/rock ratio, the removal of accessory Fe-oxide phases and the extraction of Fe from biotite to leave a phlogopitic mica, proceeded almost to completion. Above 100° C iron is removed as  $Fe^{2+}$  (Arnórsson 1970), and complexed with Cl (Burnham 1967).

The chlorite in the schistose zone grew first as small blades at the expense of the clay minerals (see Fig. 3c) and only in the core of the zone is the mineral developed as larger poikiloblasts. Microprobe analyses indicate a uniformity in major element composition for the chlorites, and no evidence has been found to suggest further element mobility during any later deformation or metamorphism. The abundance of accessory tourmaline has already been noted, and provides compelling evidence for boron metasomatism. The Broadlands hydrothermal fluid is known to contain unusually high boron concentrations, thought to be derived from underlying greywackes (Browne and Ellis 1970).

Geothermal systems which have been extensively studied include Wairakei and Broadlands, New Zealand (Steiner 1977, Weissberg et al. 1979) and Reykjanes Iceland (Tómasson and Kristmannsdóttir 1972). The system most comparable to Hjulssjö is that associated with the Kuroko mineralization, Japan, where modified seawater has interacted with felsic rocks, the latter gaining Mg and losing Na, K, and Ca to the fluid (Iijima 1974). Sulphates are commonly pre-

cipitated near to or around the Kuroko alteration zones (Sato 1974).

The exact nature of the chemical exchange between the felsic rocks and hydrothermal fluid, whether hydrogen metasomatism (Hemley and Jones 1964), or simple diffusion controlled cation exchange, is not yet fully understood, but can be constrained by a number of factors. Seawater derived hydrothermal fluids interacting with basaltic rocks are depleted in Mg and Na, and enriched in Ca and K relative to seawater (Arnórsson 1978), while Cl remains constant,  $\text{SO}_4$  is reduced to almost zero, and  $\text{HCO}_3$  increases dramatically. Which Na–K–Ca–Mg aluminosilicate forms depends on the relative activities of the metal ions, high aqueous Mg, as in seawater, introducing chlorite instead of Na–K phases (Hemley and Jones 1964), and the presence of Mg in feldspar-water systems leading to the rapid hydrolysis of the solid phase (Ellis and Mahon 1967). The water-rock interactions are strongly temperature dependent: low temperature interaction up to 200° C involves large scale addition of K to the rock (Bloch and Bischoff 1979, Munhá et al. 1980), fixed specifically in clays (Perry and Hower 1970), while at higher temperatures Mg and in some cases Na may be added to the rock. Mg-hydroxy-sulphates are precipitated directly from seawater above 280° C (Bischoff and Seyfried 1978) which appears to set a lower temperature limit for Mg-enrichment. (Arnórsson et al. (1978) record a temperature of 350° C at 200 m depth from Reykjanes.)

#### Experimental Data: Implications for Alteration in the Hjulsjö Zones

Data on the felsic rock-seawater system is scarce (i.e. Dickson 1977, Sakai et al. 1978) the most comprehensive data coming from Hajash and Chandler (1981) who reacted seawater with rocks of felsic to mafic compositions under different water/rock ratios (5/l, 50/l) and temperatures (200–500° C). In the rhyolite-seawater experiments there was a massive gain of Mg by the rock coupled to a loss of K, Fe, Mn and Si to the fluid. No explanation was offered for the behaviour of Na, which in most cases was gained by the rock, but in a few cases (i.e. experiments at 300° C, low water/rock ratios) was lost to the fluid, though the depletion was not equivalent to the loss of Na by the rock at Hjulsjö. The contrary behaviour of Na, added to the solid in the experiments of Hajash and Chandler (1981) is in conflict with the data from natural systems such as Hjulsjö and Kuroko. Altered *basic* rocks in some geothermal systems (i.e. Reykjanes) do gain Na, and Holland (1978) estimates that 10% of available Na is extracted from seawater in this way, still considerable, noting the relative abundances of Mg and Na in seawater. The zonation of *natural* systems, both laterally and vertically indicates a distinct sequential order for reaction and precipitation, effects that are not apparent in experimental closed systems where fluid and rock tend to equilibrate with each other, though whether equilibration is ever obtained in most types of water-rock experiments is doubtful (Wolery and Sleep 1983). In a natural system where the hydrothermal fluid moves through the rock via diffusion and infiltration (Bloch and Hofmann 1978) the rock will tend to equilibrate with a fluid of more or less constant bulk composition, as ions brought to the solid/liquid interface are removed by the fluid (Helgeson 1974).

Unlike Kuroko, anhydrite is lacking in the Hjulsjö area, but carbonate deposits associated with iron ores are abundant in the middle Leptite group, adjacent to the alteration zones, and if they are genetically related to the hydrothermal system which produced the alteration, as seems likely, then the calcium must have been leached out of the volcano-sedimentary sequence. Carbonate precipitation requires a low  $\text{PCO}_2$ , but transport in solution is enhanced by a high  $\text{PCO}_2$  in the geothermal fluid (White 1957, Arnórsson 1978). A high  $\text{PCO}_2$  in the Hjulsjö hydrothermal fluid, additionally evidenced by the mobility of Ti and Y during the leaching process (Hynes 1980), would lower the pH (Mottl and Holland 1978) and affect the activity of Na (Paces 1972), such that Na would be extracted more than K (Ellis 1971, Lagache 1976) while not significantly affecting the behaviour of Mg (Ellis 1971).

Kotov et al. (1977) examined the dissolution of feldspars in water to which dolomite had been added. In some cases where the dolomite/feldspar ratio was high, Na was completely lost to the fluid, the Na-minerals being replaced at temperatures in excess of 350° C by Mg-minerals. While Na was extremely mobile, K was generally retained in phyllosilicates. The results of Kotov et al. (1977) are directly applicable to the hydrothermal alteration system represented by the Hjulsjö schistose zones with respect to Na and K behaviour, except that at Hjulsjö the Mg is seawater derived. The calculations in Table 3 suggest that the mass of Na lost to the fluids is balanced by Mg gain. A correlation between leachable Na and Ca cations in basalt and Mg in seawater has been suggested by Seyfried and Mottl (1982), who note a critical boundary between rock dominated and seawater dominated conditions is passed at the point where the amounts of these elements are equivalent. The exchange of seawater magnesium for calcium in the rock has been commonly observed in natural hydrothermal systems (e.g. Ellis 1971, Mottl and Holland 1978, Rose and Burt 1979, Moris and Bendor 1982), but is of little relevance in felsic rock-seawater interactions (Paces 1972, Hajash and Chandler 1981), if only because of the low initial Ca of the rock. Mg-gain by the rock is limited by availability of feldspar for interaction: once alteration has occurred and a maximum Mg-input achieved, a balance will exist for this element between solid and liquid phase. The fluid composition is initially strongly modified by the rapid and preferential Mg depletion, but after the alteration, assuming the fluid ascending through any one point is of constant composition, any further exchange between solid and liquid will depend on factors other than chemistry. Assuming the removal and addition of other elements occurs simultaneously with the Mg addition, a state of quasi-equilibrium must exist. High water/rock ratios are clearly compatible with the solid phase changing bulk composition rather than the hydrothermal fluid. The chlorite which developed during the alteration process from an Mg-rich clay, or crystallized directly from the hydrothermal fluid may be expected to have retained some trace element characteristics of that fluid.

The chlorite in the alteration zones is enriched in elements such as Cr, Zn, Sb, Ta, Th, U, and HREE, and the formation of much chlorite in the schist prevents large scale loss of these elements to the fluid. Zr is not preferentially retained by the chlorite, but is still conserved in the rock, being retained in other minerals.

### Difference in Light and Heavy REE Behaviour

Alteration of the felsic pyroclastics produced not merely an overall REE depletion but a striking HREE enrichment, as a result of HREE incorporation in the chlorite. Alteration of a rhyolitic ash to montmorillonite produced no great change in REE pattern (Zielinski 1982), though Mg and Ca were added, and Na and K removed from the rock. Weathering of granites generally produces sediments whose sum of REEs is lower, but whose pattern is similar to that of the parent (Basu et al. 1982). The hydrothermal chlorite of Alderton et al. (1980) is HREE enriched, but has an LREE pattern parallel to, though with lower abundances than, the unaltered granite. At Hjulsjö while there is an HREE enrichment the LREEs are also depleted, but do not parallel the unaltered rock, having too low La and Ce values.

### The Hydrothermal Fluid at Hjulsjö: Comparisons with Modern Seawater

Using the constancy of ionic ratios in Paleozoic fluid inclusions in halite (Holser 1963), and the order of crystallization and constancy of mineralogy of evaporites (Holland 1972), Holser (1979) argues for the uniformity of seawater composition with time, in any case since the earliest Proterozoic evaporites. If this is correct, then the seawater participating in the hydrothermal fluid interacting with the Proterozoic pyroclastic rocks in the Hjulsjö area should be similar in composition to modern seawater.

The average of the REE values for seawater given by Elderfield and Greaves (1982), neglecting the values for the top 100 m and bottom boundary layer, has been calculated. This average for a North Atlantic profile differs from previous measurements (e.g. Elderfield and Greaves 1981, Hogdahl et al. 1968) in having slightly higher Ce, Sm, and Tb, and slightly lower La, Eu, and Yb values. Lu is taken from Bowen (1979), but may be too high.

The seawater normalized plot of the chlorite and "whole rock" schist is given in Fig. 8. The chlorite has an irregular pattern due in part to the Ce anomaly in seawater, but the HREE are strikingly regular, with seawater  $\times 10^6$  normalized values of  $\sim 0.8$ . The seawater normalized whole rock pattern does not display this HREE regularity indicating that other phases, such as tourmaline and zircon may be influencing the pattern. The irregular LREE pattern of the chlorite is partly inherited from the unaltered rock, though is additionally La and Ce depleted. No experimental data are available for the partitioning of REE between chlorite and seawater, though given the preference of chlorite for HREE it seems reasonable to assume that the partition coefficients are high for HREE, the depletion of La and Ce instead of all LREE in equal amounts indicates that for these elements they could be significantly lower. The similarity in Lu/Tb ratios for the chlorite (0.98) and seawater (0.97) is striking, and if the assumption that the chlorite equilibrated with the hydrothermal fluid is correct, and making some speculative assumptions about the partition coefficients, then the similarities in HREE abundances between the chlorite and modern seawater lead to the very tentative conclusion that the fluid in the Hjulsjö hydrothermal system, predominantly Proterozoic seawater, contained HREE in abundances similar to modern seawater.

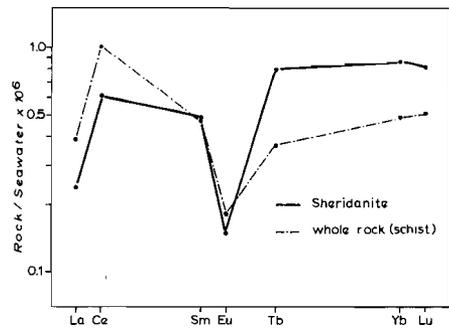


Fig. 8. Seawater  $\times 10^6$  normalized plot for the chlorite and whole rock schist showing the similarity in HREE distribution coefficients for the chlorite relative to seawater

### Conclusions

Field, petrographic and chemical evidence indicate that the discordant schistose zones NE of Hjulsjö are the result of Proterozoic hydrothermal interaction between seawater and felsic pyroclastic rocks. Mass balance calculations show that the gain of Mg by the rock can be approximately balanced by a loss of Na, Ca, Fe and Mn to the fluid, with K apparently conserved. The strong Na depletion is in conflict with experimental data, but probably results from a high  $PCO_2$  in the hydrothermal fluid. The alteration process is not fully understood, but appears to be two-stage in some cases, with alkali feldspar altering first to a kaolinite- or illite-group clay mineral, conserving K and losing Na, and with sericite forming along the relict cleavage, followed by a second stage in which Mg-chlorite develops from the clay, as Mg is added from the hydrothermal fluid, the sericite remaining in its original position, delineating the old feldspar cleavage.

The chlorite thus developed is very similar to the chlorite from the Kuroko alteration zones (see Shirozu et al. 1975). By at least partially equilibrating with the hydrothermal fluid, the chlorite can be expected to have retained some chemical characteristics of that fluid. The similarity of HREE abundances of the chlorite and modern seawater is striking. The preference for HREEs by chlorites has been noted above, and making certain assumptions about the partitioning of HREEs between the hydrothermal fluid and the chlorite, the inference is that Proterozoic seawater contained HREE in abundances similar to modern seawater.

The sum of the REEs for the whole rock is much less than that in the average for least altered metavolcanics, indicating that under the conditions of hydrothermal alteration with high water/rock ratios the REEs are highly mobile.

Magnesium enrichment, commonly known in Scandinavian literature as magnesium metasomatism, has long been recognized in the Svecofokarelian of Bergslagen, where it forms part of a characteristic ore-quartzite-Mg-rock association (Frietsch 1975). Originally the Mg-metasomatism was attributed to solutions derived from synorogenic granitic magmas (Geijer 1917), though later the metasomatic solutions were thought to have originated from within the country rock, driven through the rock in the front zones

of the granites (see Magnusson 1965). This view has been challenged by Koark (1962) who considered the magnesium, associated with syngenetic-exhalative ores in Falun, Sweden, to have been supplied from thermal springs. A parallel has been drawn by Schermerhorn (1978) between the Scandinavian ores and the massive sulphide deposits of Spain and S. Portugal, which are syngenetic submarine deposits resulting from the interaction of felsic volcanism and seawater, with associated Mg-enrichment.

The rifting model for Central Bergslagen, as proposed by Oen et al. (1982) invokes widespread sub-seafloor metamorphism and hydrothermal alteration to account for the formation and metamorphism of Fe-, Mn-, and sulphide deposits found in the Bergslagen Supracrustal Series. Mg-rich zones such as those at Hjulsjö are spatially, and probably genetically, related to some iron-ore-limestone deposits, and it is the opinion of the authors that most Mg-enrichment in Bergslagen, whether associated or not with Fe-ores is a result of seawater-felsic rock interaction in sub-seafloor hydrothermal systems.

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## Chapter 5

# High element mobility in 1.9–1.86 Ga hydrothermal alteration zones, Bergslagen, central Sweden: relationships with exhalative Fe-ore mineralizations

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### ABSTRACT

De Groot, P.A. and Baker, J.H., 1992. High element mobility in 1.9–1.86 Ga hydrothermal alteration zones, Bergslagen, central Sweden: relationships with exhalative Fe-ore mineralizations. *Precambrian Res.*, 54: 109–130.

The 1.9–1.86 Ga ensialic belt of western Bergslagen, Sweden, comprises a > 12 km thick felsic volcano-sedimentary sequence intruded by syn-volcanic granitic plutons and mafic dykes and sheets, developed in a rifted continental setting. Regional, low-temperature alteration of the supracrustal sequence produced greenschist to low amphibolite facies mineral assemblages. Localized, cross-cutting zones of intense alteration are developed in felsic volcanics which have been affected by the regional alteration, producing drastic changes in both mineralogy and chemistry. These zones are found close to the Hjulsjö granite–granophyre intrusive complex, most probably the heat source for the hydrothermal system, and related to the exhalative Sirsjöberg–Ösjöberg Fe-oxide deposits.

The Hjulsjö zones are subdivided into inner and outer zones, based on differences in mineralogy and chemistry resulting from the variable intensity of alteration. While the degree to which most elements are leached increases from the outer into the inner zones, Mg increases with alteration intensity, and Si and Al stay unchanged, although they were mobilized during alteration. Initially K, Rb, Fe and Mn increase in the outer zones, but are depleted in the inner zones. Rare earth elements (REE) are depleted, with the light REE being more depleted than the heavy REE. A pronounced negative Eu anomaly is generally present. The hydrothermal fluid was enriched in ore-forming metals during alteration and leaching. REE patterns of exhalative minerals indicate that the Fe-oxide deposits were derived from these hydrothermal fluids.

### Introduction

Two major types of alteration have been described in the 1.9–1.86 Ga Proterozoic ensialic belt of western Bergslagen, central Sweden (Sundius, 1923; Oen et al., 1982; Baker and De Groot, 1983):

(1) a widespread regional, low-temperature hydrothermal alteration process which altered the supracrustal rocks of the belt, and

(2) local, intense zones of alteration which strongly affected both supracrustal rocks and synvolcanic granites.

The alteration zones of the Hjulsjö area form the remnants of a hydrothermal conduit sys-

tem exposed at the present erosion level. Retrograde processes related to the waning stages of the alteration system have often overprinted the main, higher-temperature alteration assemblages. The form, mineralogy, and geochemistry of these zones, together with element mobility, and a comparison of the highly altered zones with the surrounding weakly, regionally altered supracrustals, are presented.

Exhalative Fe-(Mn-)oxide deposits consisting of small, restricted lenses or strata, and epigenetic replacement deposits (Oen, 1987) are common in Bergslagen. The exhalative deposits are thought to result from ascending, hydrothermal, metal-enriched fluids debouching

onto, or immediately below the ancient sea floor (Oen, 1987; Baker, 1989; Baker et al., in prep).

The relationships between mineralogy, chemical mobility and mineralization in the Hjulsjö hydrothermal alteration system are also discussed.

### Geological synopsis

The ensialic belt of western Bergslagen consists of a supracrustal sequence of felsic metavolcanics at least 10 km thick, overlain by metasediments more than 2 km thick, and is considered to have formed in a rifted continental setting (Oen et al., 1982; De Groot et al., 1988; Baker et al., 1988). Horizons of stratabound carbonate rock, iron oxides, and cherts are intercalated in the metavolcanics. A conglomerate layer occurs in the upper parts of the metasediments. Granite- and granophyredomes, and continental tholeiitic (Hellingwerf and Oen, 1986) dykes and sheets intrude the metavolcanics. Some small extrusive metabasaltic flows occur in the upper parts of the supracrustal sequence. Two major generations of granitic intrusions have been distinguished (e.g. Oen and Verschure, 1985). A distinct bimodal magmatic composition characterizes the Bergslagen region.

The supracrustal units have been tilted into a (sub)vertical position. A regionally developed foliation ( $S_n$ ) generally strikes parallel to, or at a low angle ( $< 10^\circ$ ) to the bedding. Two different phases of folding ( $F_n$  and  $F_{n+1}$ ), with steeply dipping, but widely diverging fold axes are reported by Carlon and Bleeker (1988) for the eastern parts of the Bergslagen region. Subvertical to vertical lineations are formed in the foliation plane ( $S_n$  or  $S_{n+1}$ ) by elongated minerals, rock fragments and lapilli. A later kink foliation ( $S_{n+2}$ ) is locally developed.

The structural development of the region has been described in terms of an aborted intracontinental rift (Oen et al., 1982; Oen, 1987),

and extended to include gravity subsidence and diapirism by De Groot et al. (1988).

### Alteration in the felsic supracrustals

The supracrustal rocks are regionally altered to greenschist assemblages in the central parts of the rifts, increasing to amphibolite assemblages towards the borders.

Early investigators (Sundius, 1923; Magnusson, 1925; Geijer and Magnusson, 1944) showed that potassic enrichment coupled to weak sodic leaching occurred in the higher stratigraphic units, while sodic enrichment coupled to potassic leaching occurred in the lower stratigraphic units of the Bergslagen supracrustal sequence.

The regional alteration is suggested to have developed in a sub-sea floor environment (Schermerhorn, 1978; Oen et al., 1982; Baker and De Groot, 1983; Lagerblad and Gorbatshev, 1985; Trägårdh, 1988), on the basis of (1) high Mg-content of altered rocks compared to less altered rocks (Baker and De Groot, 1983; Trägårdh, 1988), (2) the marine isotopic composition of stratabound carbonates (De Groot and Sheppard, 1988), and (3) hydrogen isotope values of silicates in the Hjulsjö alteration zones (De Groot, unpubl. data).

Following Holland (1978, 1984), we assume that the seawater composition has not changed drastically from Archean times to the present.

Although evidence exists for the major involvement of meteoric derived fluids in skarn mineralization processes in Bergslagen (De Groot, 1991), these are considered to be late stage hydrothermal processes active during the development of the Bergslagen ensialic belt. A change in fluid composition is supported by the geological evidence of the tectonic uplift and erosion of a submarine volcanic pile to form late-stage sediments (De Groot et al., 1988).

Zones of intense alteration are developed on a scale up to several kilometers long and are

superimposed on the regional alteration (e.g. Trägårdh, 1988). The cross cutting Hjulsjö zones (Fig. 1) have a more or less concentric structure (Fig. 2), related to the intensity of alteration. In some cases these zones are narrow and elongate. Some zones contain tectonically formed disc or cigar-like bodies of less altered rock up to several decimeters, embedded in a foliated mica-rich matrix.

Thermometry on chlorites from the altera-

tion zones using the method of Cathelineau and Nieva (1985a) yields temperatures between 300° and 350°C. Temperature estimates for the phlogopite–Mg-chlorite equilibrium boundary in the Hjulsjö system based on thermodynamic calculations (De Groot, 1990) yield temperatures of about 300°C. Petrographic observations show that phlogopite formed before Mg-chlorite, giving a lower temperature limit for chlorite formation in the al-

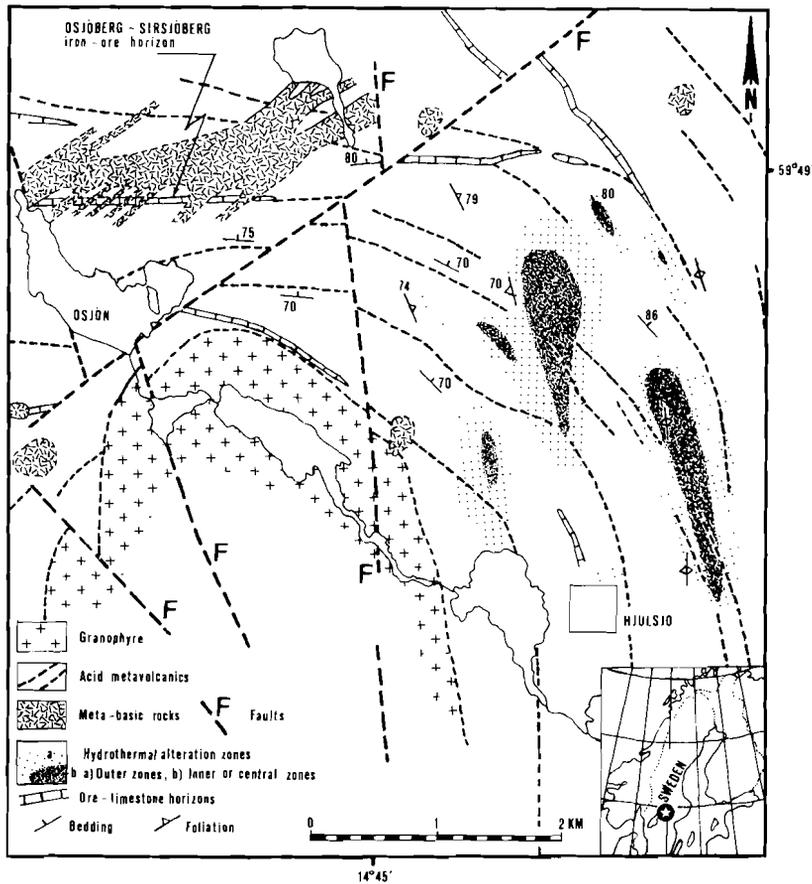


Fig. 1. Geological map of the Hjulsjö region (after Baker and de Groot, 1983) showing the position of the hydrothermal alteration zones.

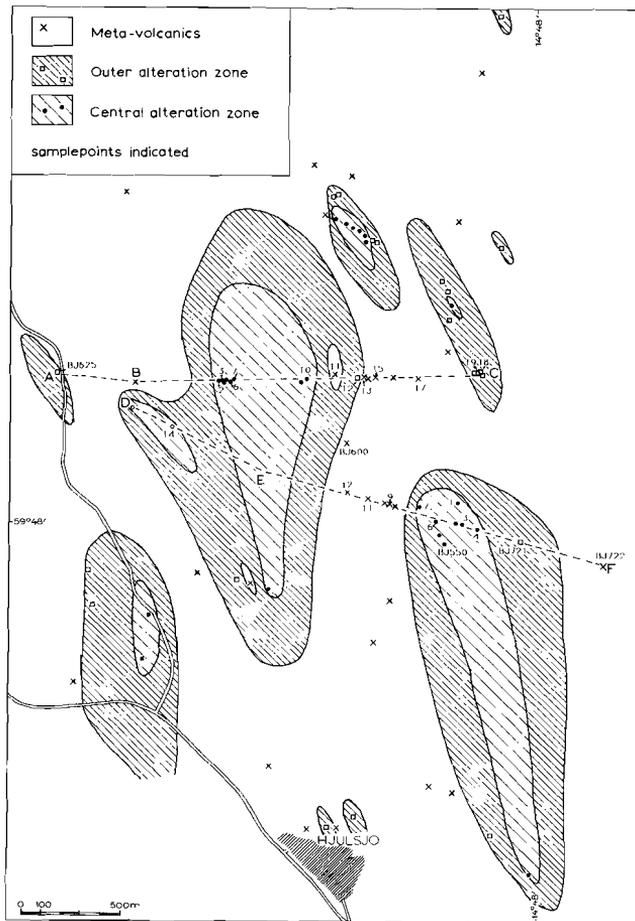


Fig. 2. Schematic representation of the Hjulsjö hydrothermal alteration zones. Dotted lines refer to profiles in Figs. 6 and 7.

teration system. An upper temperature limit for alteration can be determined by the reaction (Mg-rich)chlorite + quartz = talc + cordierite + H<sub>2</sub>O, by which chlorite alters at 520°C and 1 kbar (Massonne, 1989) or at just above 500°C at a pressure of 0.5 kbar (extrapolated, from Massonne, 1989).

The temperature range of 350°–500°C deduced above, is in good agreement with the temperature limits for Fe, Mn, Zn, and Cu mobilisation as determined experimentally by

Seewald and Seyfried (1990). While their conclusions are based on basalt–seawater interaction under specific experimental conditions, there is a close similarity between the conditions most favourable for metal transport and these inferred for the Hjulsjö alteration zones.

#### Analytical procedures

More than 100 rock samples from the alteration zones and host volcanics were analysed

for major elements by standard XRF techniques (accuracy:  $> 10 \text{ wt}\% = \pm 3\%$  and  $< 10 \text{ wt}\% = \pm 5\%$  ( $2\sigma$ )). Ni, Cu, Zn, Ga, Rb, Sr, Y, and Pb were analysed by XRF (ViéLeSage et al., 1979) (accuracy: generally better than  $\pm 5\text{--}15\%$  ( $2\sigma$ ) and increasing drastically near detection limits), and Sc, Cr, Co, Sb, Cs, Zr, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, and U on some of the samples were analysed by INAA ( $\pm 10\%$ ,  $2\sigma$ ) at the Interfaculty Reactor Institute (IRI), Delft (De Bruin, 1983).

Note that estimations of trace element mobility in hydrothermal systems are limited by element concentration and analytical precision.

### Hjulsjö alteration zones

The Hjulsjö alteration zones (Fig. 1) are located in felsic metavolcanics of the Lower Lepelite Group described by Oen et al. (1982) close to the granophyre of the Hjulsjö granophyre-granite complex (Baker, 1985). They comprise oval-shaped concentric zones cross-cutting the metavolcanics. The regional bedding bends around the granophyre-granite complex in a concentric form (Baker, 1985), probably modified by diapiric processes (Baker, 1985; De Groot et al., 1988). North of the intrusive complex and the alteration zones lies the Ösjöberg-Sirsjöberg magnetite and carbonate horizon, possibly representing exhalites derived from fluids circulating in the Hjulsjö system (Fig. 1).

The alteration zones can be sub-divided into outer (OZ) and inner or central (IZ) sub-zones (Fig. 2), based on specific mineral associations and relative mineral volumes (Table 1). The border between the metavolcanics and the OZ is defined arbitrarily by the relative abundance of alteration minerals, which increases gradually passing into the alteration zones. The border between the OZ and the IZ is defined by the disappearance of feldspars and appearance of phlogopite in the IZ. Mg-rich chlorite is only seen within the OZ and IZ of

the Hjulsjö system, and is not found in the metavolcanics surrounding the zones. However, this mineral cannot be used to delineate the metavolcanic-OZ boundary because it only appears sporadically in the OZ.

The Hjulsjö zones are comparable in terms of mineralogy to alteration zones such as the Amulet Upper A deposit (Hall, 1982) and the Millenbach Mine (Riverin and Hodgson, 1980), Noranda, Canada, and Broken Hill, Australia (Plimer, 1988; Beeson, 1990), as well as modern zones, or active hydrothermal systems such as Yellowstone (Sturchio et al., 1986) and Roosevelt hot springs thermal area (Christensen et al., 1983) in North America, Wairakei (Ellis and Mahon, 1977), Waiotapu (Hedenquist and Browne, 1989) and Broadlands (Browne and Ellis, 1970), North Island, New Zealand, and the Green Tuff Zone-Kuroko belt (Ohmoto and Skinner, 1983), Japan.

### Order of appearance of minerals in the alteration zones

Petrographic studies (Plate I) revealed that plagioclase alters to K-feldspar or albite, while alkali feldspar starts to alter into sericite along cleavage planes and into fine-grained dark material (possibly clay minerals or iron-(hydr)oxide particles) seen as clouding in feldspar. Baker and De Groot (1983) reported that the volumes between sericite in the pseudomorphed feldspars were altered directly from clay minerals to Mg-chlorite (sheridanite).

Biotite is altered mostly to chlorite and epidote. Sericite or coarser-grained muscovite are formed more abundantly at higher grades of alteration. Muscovite alters to phlogopite, or, less commonly, directly to Mg-chlorite. Phlogopite is mostly altered to Mg-chlorite. Mg-chlorite occurs either as elongated grains, often intergrown with sericite and phlogopite following the foliation (Plate IC, D), or as larger blasts along, or cross-cutting the foliation (Plate IB). Some of these blasts are kinked or

TABLE I

Distribution of minerals in the Hjulsjø alteration zones

	META VOLCANICS	OUTER ZONE	INNER ZONE
Quartz	—	—	—
K-feldspar	—	—	—
Plagioclase	—	—	—
Albite	—	—	—
Olig-And.	—	—	—
Biotite	—	—	—
Phlogopite	—	—	—
Fe-rich Chlorite	—	—	—
Mg-rich Chlorite	—	—	—
Muscovite (Sericite)	—	—	—
Epidote	—	—	—
Calcite	—	—	—
Sphene	—	—	—
Zircon	—	—	—
Tourmaline	—	—	—
Apatite	—	—	—
Fluorite	—	—	—
Magnetite	—	—	—
Rutile	—	—	—

broken by a later foliation. Quartz, present in all stages of alteration, increases in volume with increasing grade of alteration.

#### First stage, regional alteration processes

Post depositional submarine alteration of the volcanics (Oen et al., 1982; De Groot et al., 1988) affected a primary mineralogy of quartz, plagioclase (oligoclase-sanidine), K-feldspar (orthoclase, microcline), minor biotite, and accessories. Several complex reactions characterized the initial interaction between rock and a seawater type fluid, causing alteration of the feldspars:

- the anorthite and albite component of plagioclase may change to K-feldspar at temperatures below 100–150°C (e.g. Hajash and Chandler, 1981) according to the reaction equations [1] and [2] of Table 2, and to albite (Munhá et al., 1980; Hajash and Chandler, 1981) above this temperature [3]. The Si consumed by these reactions could be delivered by sericitization, and clay replacement of the feldspars, according to equations [4], [6] and [7] respectively (see below).

– plagioclase becomes “clouded” and alters to sericite along crystal cleavages (Plate Ia; see also Baker and De Groot, 1983), by hydrolysis reactions (Hemley and Jones, 1964) expressed in equations [4] and [5]. Clay formation follows, according to an equation of type [6], or by the formation of Na, K and/or

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#### PLATE I

(A) Oligoclase phenocryst in a fine-grained matrix altered to thin sericite grains, growing along the feldspar cleavage plains (see arrows). (B) Mg-chlorite (*Chl*) blast in a strongly foliated fabric of lens-shaped and recrystallized quartz (*Q*) grains and intergrown Mg-chlorite and muscovite (*Mu+Chl*). Most intensely altered parts of the inner alteration zones. (C, p. 116) Metavolcanite which is completely altered into a quartz-mica mineral paragenesis showing a weak foliation. Polarized light. *q*=quartz, *m*=muscovite, *p*=phlogopite, *s*=Mg-chlorite (sheridanite). (D, p. 116) Same photograph as (c), crossed nicols. Scale is indicated by the double arrow on the lower left side of the photographs, and stands for 0.5 mm on (a) and (b), and for 2 mm on (c) and (d).

## PLATE 1

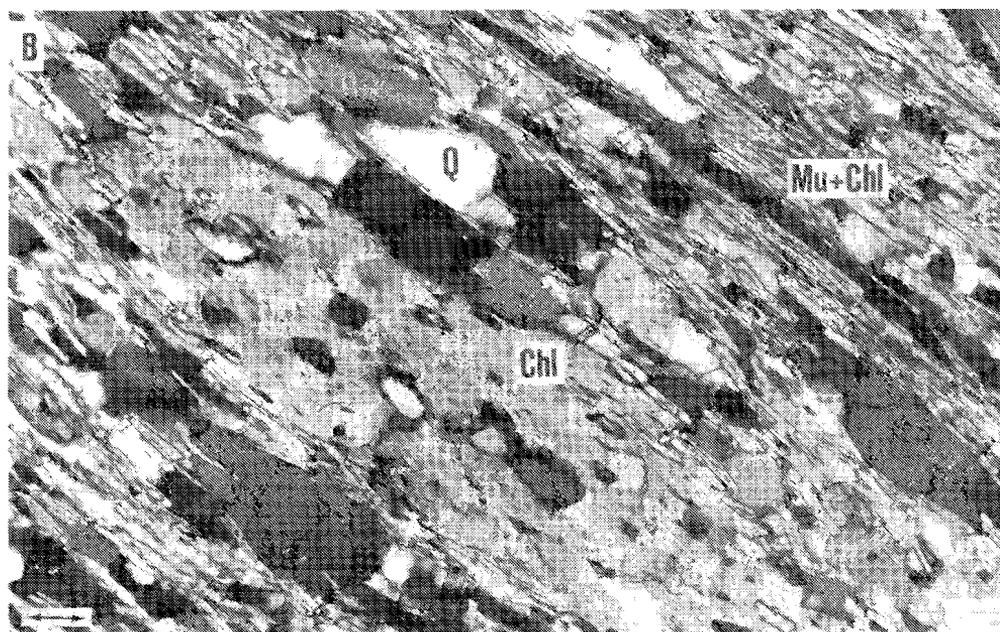
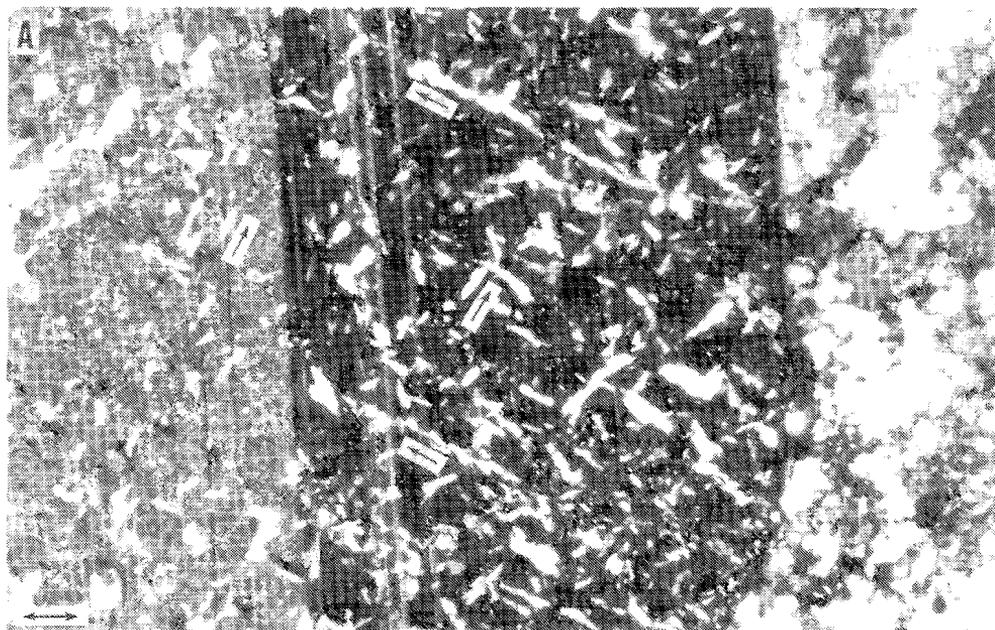


PLATE I

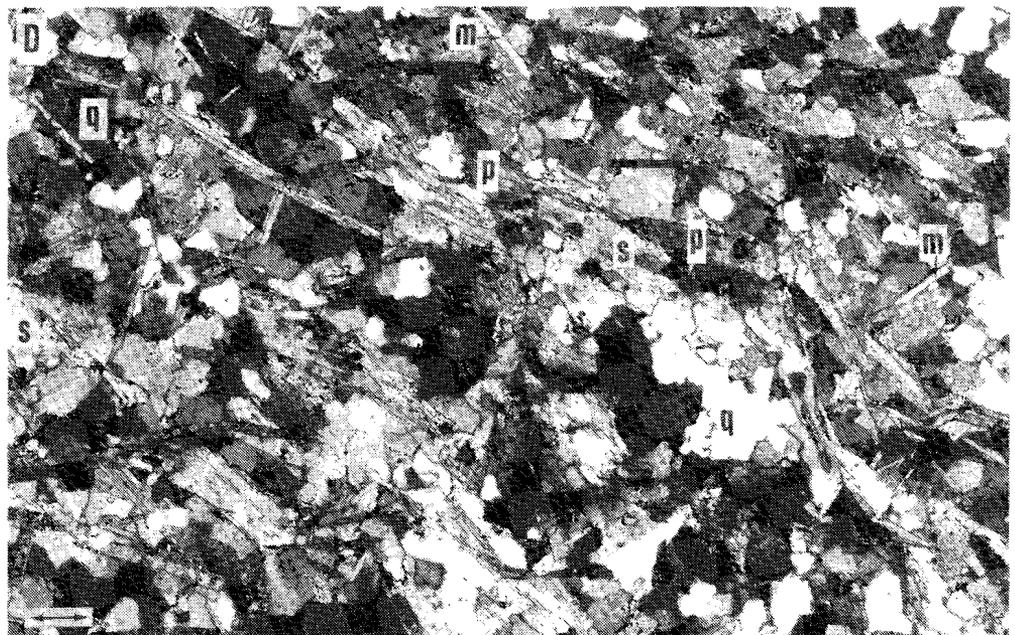
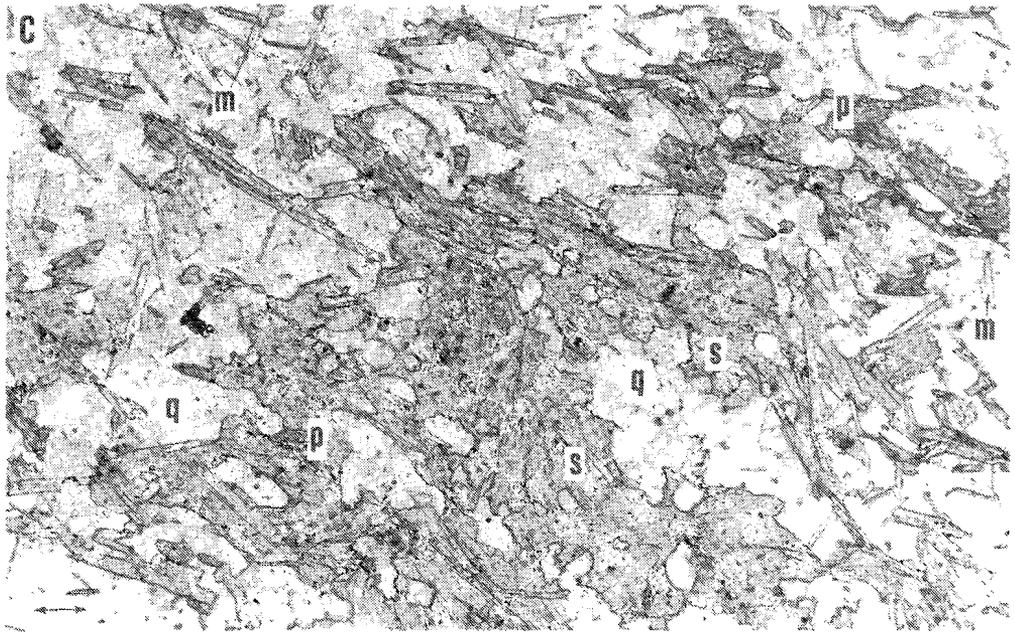


TABLE 2

Mineral reactions for the Hjulsjö hydrothermal alteration zones.

[1] <sup>a</sup>	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{K}^+ + 4\text{SiO}_2 = 2\text{KAlSi}_3\text{O}_8 + \text{Ca}^{2+}$
[2] <sup>a</sup>	$\text{NaAlSi}_3\text{O}_8 + \text{K}^+ = \text{KAlSi}_3\text{O}_8 + \text{Na}^+$
[3] <sup>b</sup>	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{Na}^+ + 4\text{SiO}_2 = 2\text{NaAlSi}_3\text{O}_8 + \text{Ca}^{2+}$
[4] <sup>c</sup>	$0.75\text{Na}_2\text{CaAl}_4\text{Si}_8\text{O}_{24} + 2\text{H}^+ + \text{K}^+ = \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 1.5\text{Na}^+ + 0.75\text{Ca}^{2+} + 3\text{SiO}_2$
[5] <sup>c</sup>	$\text{Na}_2\text{CaAl}_4\text{Si}_8\text{O}_{24} + 4\text{H}^+ + 2\text{X}^{\text{M}^+} = 2\text{M}_x\text{Al}_2\text{Si}_x\text{O}_{10}(\text{OH})_2 + 2\text{Na}^+ + \text{Ca}^{2+}$
[6] <sup>c</sup>	$\text{Na}_2\text{CaAl}_4\text{Si}_8\text{O}_{24} + 4\text{H}^+ + 2\text{H}_2\text{O} = 2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2 + 2\text{Na}^+ + \text{Ca}^{2+}$
[7] <sup>d</sup>	$1.5\text{KAlSi}_3\text{O}_8 + \text{H}^+ = 0.5\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + \text{K}^+ + 3\text{SiO}_2$
[8] <sup>e</sup>	$2\text{K}(\text{Mg, Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 4\text{H}^+ = \text{Al}(\text{Mg, Fe})_5\text{AlSi}_3\text{O}_{10}(\text{OH})_8 + (\text{Mg, Fe})_2^{2+} + 2\text{K}^+ + 3\text{SiO}_2$
[9] <sup>e</sup>	$\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 9\text{Mg}^{2+} + 2\text{K}^+ + 6\text{SiO}_2 + 12\text{H}_2\text{O} = 3\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 2\text{OH}^-$
[10] <sup>e</sup>	$\text{NaAlSi}_3\text{O}_8 + \text{K}^+ + 3\text{Mg}^{2+} + 4\text{H}_2\text{O} = \text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + \text{Na}^+ + 6\text{H}^+$
[11] <sup>e</sup>	$2\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 4\text{H}^+ = \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 2\text{K}^+ + \text{Mg}^{2+} + 3\text{SiO}_2$
[12] <sup>e</sup>	$3\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 10\text{Mg}^{2+} + 6\text{H}_2\text{O} = 2\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 5\text{Al}^{3+} + 3\text{K}^+ + 2\text{H}^+ + 3\text{SiO}_2$
[13] <sup>e</sup>	$2.33\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 0.33\text{Mg}^{2+} + 2.68\text{SiO}_2 = 2\text{Mg}_{0.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 0.66\text{H}^+ + 2.33\text{H}_2\text{O}$
[14] <sup>e</sup>	$2\text{Mg}_{0.167}\text{Al}_{2.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2 + 11.316\text{Mg}^{2+} + 18.64\text{H}_2\text{O} = 2.33\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 22.632\text{H}^+ + 0.35\text{SiO}_2$
[15] <sup>e</sup>	$2\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{Mg}^{2+} + 8\text{H}_2\text{O} = \text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 2\text{Al}(\text{OH})_3 + \text{SiO}_2 + 10\text{H}^+$
[16] <sup>e</sup>	$1.5\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{K}^+ = \text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2 + 1.5\text{H}_2\text{O} + \text{H}^+$

<sup>a</sup>From Glazner (1988).<sup>b</sup>From Munhá et al. (1980) and Hajash and Chandler (1981).<sup>c</sup>From Hemley and Jones (1964).<sup>d</sup>From Exley (1976).<sup>e</sup>From Jasiński (1988).

Mg bearing hydrosilicates (e.g. Honnorez, 1981) filling the volumes outlined by the sericite. Exley (1976) suggested that sericite (muscovite  $\pm$  montmorillonite) is an intermediate product of kaolinite, supported by the phase diagrams of Hemley and Jones (1964) and Jasiński (1988). Clay minerals are found in Bergslagen as rare relicts in altered feldspars (Baker and De Groot, 1983).

– K-feldspar alters less easily, and is converted mainly to sericite (Exley, 1976) illustrated by equation [7].

Plagioclase and alkali feldspar alter to kaolinite, while K-feldspar alters to sericite, at a later stage of the same alteration process. These types of alteration are equivalent to the *argillic (-sericitic) assemblages and potassic silicate assemblages* of Meyer and Hemley (1967) and Hemley and Jones (1964).

Magmatic biotite is altered mostly to chlorite, at low temperatures [8] (Hemley and Jones, 1964). Epidote, rutile, sphene, sericite, and magnetite or hematite are also formed

from biotite as minor alteration phases.

Summarizing the mineralogical and chemical changes of the WAM relative to the least-altered metavolcanics (Fig. 3; see *Chemistry of the zones* for explanation of figure), K is enriched in the rock, Na is moderately leached by alteration of plagioclase to K-feldspar, and Ca although leached from the plagioclase, is retained in the rock (2J13 and 2J21, Fig. 3). At more elevated temperatures (> 150°C) albite is expected to form with Na uptake and Ca (or K) depletion of the rock. Albite formation and high Na content is common in WAM in Bergslagen (Sundius, 1923; Van der Velden et al., 1982). Feldspar starts to alter to sericite and clay minerals, increasing the K concentration of the rock and elevating the pH (consumption of  $\text{H}^+$  during reaction) of the fluid.

The pH of the fluid is buffered by the formation of Mg-hydroxide or -hydroxisilicates, which promotes feldspar alteration. Fe and Mn are enriched in this stage (Fig. 3), most probably in the form of small oxide or hydroxide

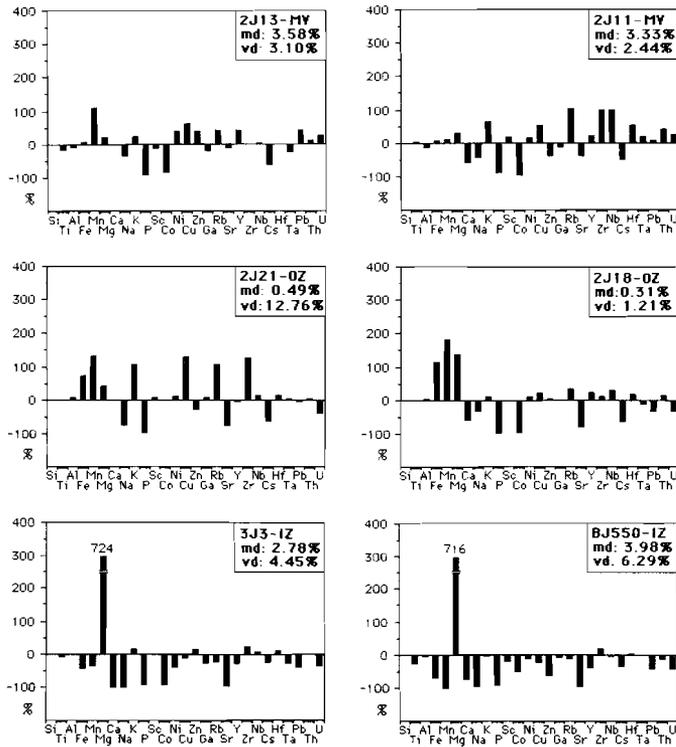


Fig. 3. Depletion–enrichment diagrams for elements analysed in the altered rocks of the Hjulsjö region. The diagrams are calculated by the mass–volume balance isocon-method (Grant, 1986) referring to the mean element concentrations of a group of 12 least-altered volcanics of the Bergslagen region (see text). *MV*=metavolcanics (equivalent to WAM in text), *OZ*=outer zone, *IZ*=inner or central zone, *md*=mass decrease, *vd*=volume decrease.

particles, or incorporated into clay or mica structures. Surprisingly Si, although mobile during the alteration reactions, is not changed in concentration during this stage. Aluminum, as is often the case in hydrothermal systems, is immobile.

### Second stage, localized alteration processes

Petrographic investigation shows the following sequence in the formation of new mineral phases: sericite/muscovite–phlogopite–Mg-chlorite. Thermodynamic calculations (De Groot, 1990) (Fig. 4) indicate that this se-

quence results mainly from increasing temperature.

Reactions of sericite followed by albite to phlogopite and phlogopite to Mg-chlorite are given by equations [9], [10] and [11] (Jasiński, 1988).

The phlogopite field is restricted to temperatures  $<100^{\circ}\text{C}$  in a prograde system (De Groot, 1990), while phlogopite is rare or mainly altered to Mg-chlorite. In some cases, when phlogopite is not available, a direct alteration of sericite to Mg-chlorite could occur, following reaction [12] (modified from Meyer and Hemley, 1967).

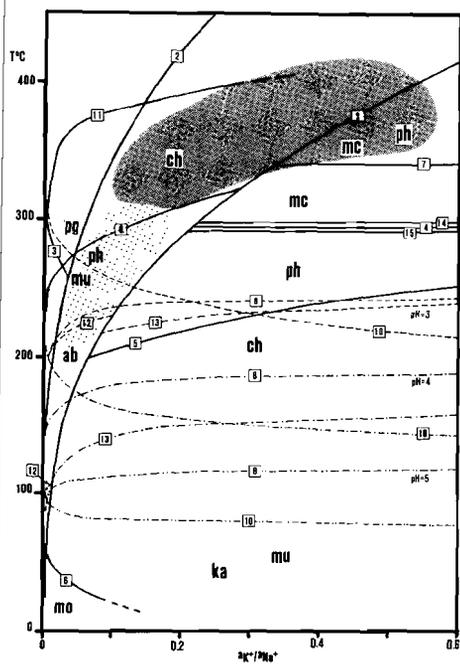


Fig. 4.  $a_{K^+}/a_{Na^+}$  versus temperature for a two feldspar (albite and microcline)-muscovite-paragonite-phlogopite-montmorillonite-kaolinite-Mg-chlorite-fluid phase system (after De Groot, 1990). Thermodynamic data are from Jasiński (1988) and references therein. Activity coefficients are calculated following the method described by Truesdell (1984). Silica is saturated in the system. Solid curves: fluid-mineral equilibrium curves at seawater conditions. Dashed curves: same conditions and pH fixed at 3. Dash-dot curves: same conditions, pH=4. Double dash-dot curves: same conditions, pH=5. Curves: 1 = microcline-albite, 2 = muscovite-paragonite, 3 = paragonite-albite, 4 = K-montmorillonite-microcline, 5 = K-montmorillonite-muscovite, 6 = K-montmorillonite-kaolinite, 7 = kaolinite-muscovite, 8 = muscovite-Mg-chlorite, 9 = phlogopite-Mg-chlorite, 10 = muscovite-phlogopite, 11 = kaolinite-muscovite, 12 = albite-phlogopite, 13 = Mg-chlorite-microcline, 14 = muscovite-microcline, 15 = microcline-kaolinite (first mineral phase at low temperature or high  $a_{K^+}/a_{Na^+}$  side of curve). *ab* = albite; *ch* = Mg-chlorite; *ka* = kaolinite; *mc* = microcline; *mo* = K-montmorillonite; *mu* = muscovite; *pg* = paragonite; *ph* = phlogopite. Stippled area on diagram approximately represents outer zone, and grey area inner zone mineralogy.

Clay minerals of the kaolinite group are directly altered to Mg-chlorite (Baker and De Groot, 1983), or could firstly alter to a montmorillonite clay and subsequently to Mg-chlorite where thermodynamic equilibrium prevails (see also Jasiński, 1988). These reactions are of the type [13] and [14], or [15] (Jasiński, 1988) representing direct alteration of kaolinite to Mg-chlorite.

Some of the clay minerals, probably at lower temperatures, could alter to sericite instead of Mg-chlorite [16] (Jasiński, 1988).

The mineral paragenesis of the most altered parts of the IZ in the Hjulsjö system includes quartz-sericite/muscovite-phlogopite-Mg-chlorite (Plate IB-D), and is considered to form in a prograde alteration system (De Groot, 1990). Quartz could be progressively formed during reactions [4], [6], [7], [8], [11] and [12]. Some silica is consumed by plagioclase altering to alkali feldspars, possibly by the formation of Mg-bearing sepiolite at low temperatures, or through reactions of the type given by equations [9] and [13].

Sericite is formed abundantly at the expense of feldspar in an early stage of alteration [4], [7] and could also be formed from clay minerals [16]. Some of the sericite/muscovite is converted into phlogopite, or less commonly directly to Mg-chlorite at higher temperatures approaching the peak of the alteration process (about 300–350°C) [9], [12].

Phlogopite (Plate IC, D) replaces sericite above 200°C [9] and possibly albite above 225°C [10] (Fig. 4) during interaction with the fluid phase, but is altered into Mg-chlorite [11] (Plate IB) above about 300°C (Fig. 4), thus accounting for its rare appearance in the Hjulsjö zones.

During the waning stages of the alteration process a relatively rapid cooling of the system produces retrograde reactions.

Although competing mineral reactions give different directions of element mobility, the final quartz-muscovite-Mg-chlorite paragenesis is in accordance with continuous leaching

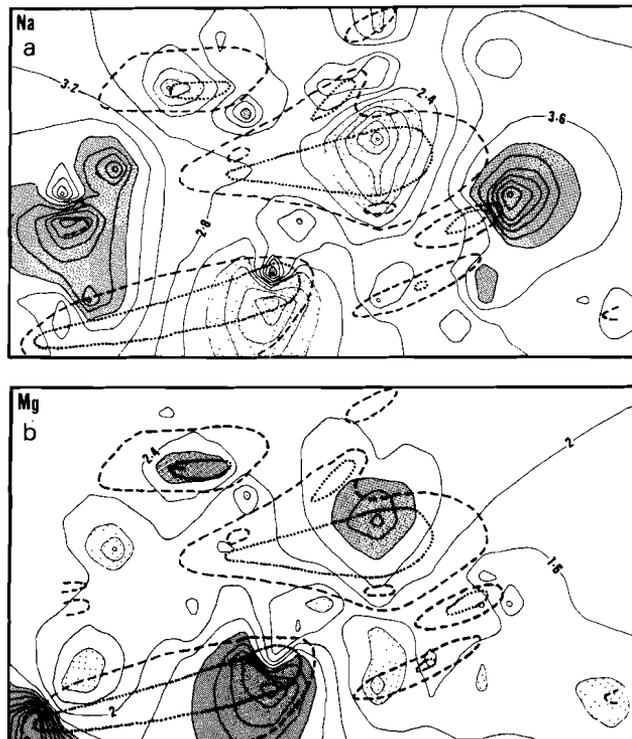
of Na, moderate leaching of K, and increasing enrichment of Mg in the rock compared to the first alteration phase. Fe and Mn are leached drastically by dissolution of the oxide-hydroxide particles. Si and Al, as in the first stage, remain more or less unchanged (see Fig. 3).

#### Chemistry of the zones

The chemistry of the metavolcanics changes from the IZ and OZ into the surrounding volcanics with specific element increases and decreases. Changes are shown in Fig. 3 in the form of enrichment/depletion diagrams constructed using the mass-volume balance *isocron method* of Grant (1986). Only major elements were used in determining mass-volume

changes in altered rocks and these changes are used to indicate trace element variations. The mean of 12 samples of metavolcanics (Table 3) considered to be least altered (Baker and De Groot, 1983) are used as a pre-alteration reference composition. Two representative samples of the weakly altered metavolcanics (WAM), the outer zone (OZ) and the inner zone (IZ) were used in the mass-volume balance calculation (Table 3).

The results presented in Fig. 3 enable both the *trend* and *degree* of element enrichment and depletion to be estimated. Na, P, Co, Sr and Cs are depleted with respect to least-altered compositions in the WAM, OZ and IZ. Ca is clearly depleted in the IZ, but is unchanged or depleted through the WAM and OZ. Fe and Mn



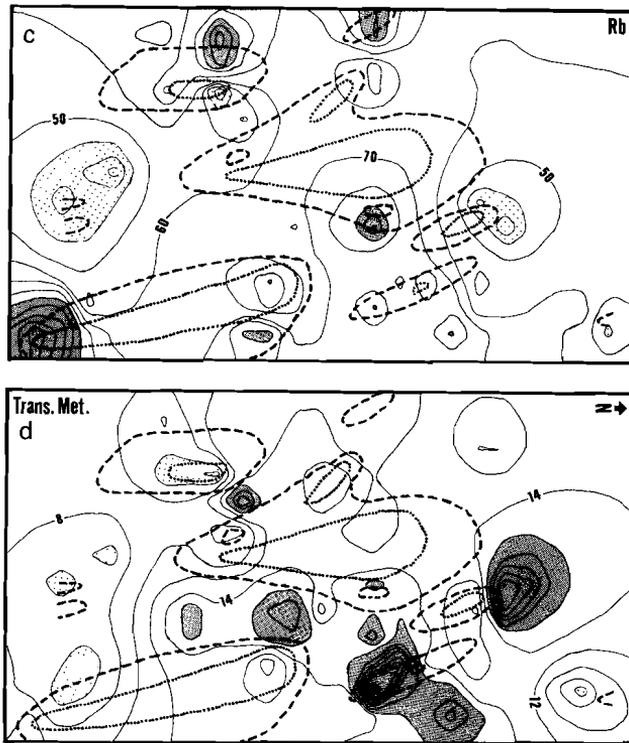


Fig. 5. Contoured concentrations for Na, Mg, Rb, and the transition elements (Ni, Co, Cr, Ti). The outlines of the alteration zones are shown as heavy broken (OZ) and dotted lines (IZ). Relatively enriched areas are indicated by densely dotted areas:  $> 4.0\%$  for  $\text{Na}_2\text{O}$ ;  $> 2.8\%$  for  $\text{MgO}$ ;  $> 90$  ppm for Rb;  $> 16$  ppm for transition elements, while depleted areas are shown by dotted areas:  $< 1.6\%$  for  $\text{Na}_2\text{O}$ ;  $< 1.2\%$  for  $\text{MgO}$ ;  $< 40$  ppm for Rb;  $< 6$  ppm for transition elements. Numbers on contours are percentages for  $\text{Na}_2\text{O}$  and  $\text{MgO}$  or ppm for Rb and transition elements.

are slightly enriched in the WAM, become strongly enriched in the OZ and strongly depleted in the IZ. Ni, Cu, Rb, Y and Th are enriched in both the WAM and OZ, but depleted in the IZ. K also follows this behaviour, but without clear enrichment or depletion in the IZ. Pb and U are enriched in the WAM, but depleted in both the IZ and OZ. Mg is enriched through the entire system and is accompanied by increases, becoming smaller towards the IZ, in Zr, Hf and Nb. Si is the only element which fails to show any enrichment or depletion. However, it should be noted that Fig. 3 shows

loss and gain as a percentage of the original concentration, and changes in Si of  $< 5\%$ , though not visible in Fig. 3, may be significant. Al shows only very slight enrichment or depletion in the zones. Ti shows a minor depletion in IZ. The elements Sc, Zn, Ga and Ta do not show any clear behaviour.

Elements which show a depletion in excess of 50% in the IZ are Ca, Na, Fe, Mn, P, Co and Sr. Depletion in the OZ is substantially less, though still high for P and Sr. However, enrichments of Fe, Mn and Mg in the OZ are in excess of 100%.

TABLE 3

Analytic values of least-altered volcanics and samples used in mass–volume balance (Fig. 3)

	12 meta- volcanics <sup>a</sup>	Std. dev. (n=12)	2J13	2J11	2J21	2J18	3J3	BJ550
SiO <sub>2</sub>	76.54	1.67	78.85	78.91	77.30	76.08	77.18	77.43
TiO <sub>2</sub>	0.15	0.03	0.13	0.17	0.15	0.14	0.14	0.11
Al <sub>2</sub> O <sub>3</sub>	11.89	0.51	11.06	10.21	12.72	12.20	12.17	11.55
Fe <sub>2</sub> O <sub>3</sub> *	1.52	0.51	1.69	1.80	2.63	3.23	0.90	0.46
MnO	0.01	0.01	0.01	0.01	0.01	0.02	0.00	d.l.
MgO	0.56	0.35	0.70	0.78	0.80	1.31	4.66	4.62
CaO	0.75	0.44	0.77	0.36	0.75	0.33	d.l.	0.04
Na <sub>2</sub> O	4.37	1.93	2.88	2.67	1.25	3.00	d.l.	0.23
K <sub>2</sub> O	2.33	1.45	2.90	4.11	4.90	2.62	2.70	2.30
P <sub>2</sub> O <sub>5</sub>	0.24	0.01	0.02	0.01	0.02	0.01	0.02	0.02
Total			99.02	99.03	100.54	98.94	97.77	96.75
Sc	5.05	1.09	4.72	6.29	5.40	5.09	5.17	4.16
Co	10.39	2.83	1.60	0.58	10.27	0.59	0.75	5.26
Ni	3.76	0.79	5.43	4.50	4.18	4.20	2.40	3.54
Cu	6.29	1.09	14.00	9.98	14.50	7.66	5.74	5.00
Zn	12.72	3.52	18.21	8.04	9.16	13.01	15.03	5.04
Ga	15.58	1.33	13.20	14.00	16.70	15.40	11.70	14.80
Rb	49.65	28.82	72.58	105.00	102.80	67.65	40.16	44.97
Sr	62.03	33.04	55.80	39.00	18.20	15.20	2.30	1.94
Y	51.35	11.06	76.30	64.50	49.90	62.70	38.20	32.10
Zr	198.75	24.71	210.00	407.50	453.00	220.40	252.00	246.30
Nb	10.99	1.09	12.00	22.50	12.80	14.50	12.00	11.20
Cs	1.05 <sup>b</sup>	0.83	0.40	0.56	0.40	0.39	0.81	0.71
Hf	6.21	0.82	6.51	9.87	7.21	7.47	7.00	6.80
Ta	1.02	0.12	0.82	1.27	1.07	0.91	0.75	1.05
Pb	6.87	1.42	10.00	7.69	6.69	4.69	4.49	4.20
Th	12.33	1.67	14.18	18.32	12.84	14.41	12.70	11.57
U	3.60 <sup>c</sup>	0.99	4.71	4.70	2.18	2.57	2.43	2.19

<sup>a</sup>Values represent the mean of the least-altered metavolcanics.<sup>b</sup>Mean on 4 samples.<sup>c</sup>Mean on 11 samples.\*Fe<sub>2</sub>O<sub>3</sub> represents Fe-total.

Std. dev. = standard deviation.

From this we can conclude that with increasing intensity of alteration most elements become depleted in the IZ relative to the least altered metavolcanics, a few elements remain unchanged, and only Mg is strongly enriched.

The spatial distribution of some elements in the Hjulsjö region are shown in Fig. 5a–d. Figure 5a shows the somewhat irregular depletion of Na in the OZ and IZ. Figure 5b on the contrary shows the higher concentrations of Mg as alteration increases. The behavior of Rb (and K) is shown in Fig. 5c, with higher values in the metavolcanics and decreasing concentra-

tions in the OZ and IZ respectively. Finally, the depletion of some transition elements (Ni, Co, Cr, Ti) with increasing alteration is shown in Fig. 5d.

Figures 6 and 7 show chondrite-normalized rare earth element (REE) (Table 4a, b) plots along two sections through the alteration zones and surrounding metavolcanics. There is a clear depletion of REEs in the altered rocks relative to magmatic compositions (Fig 8a), going towards the inner zones. The (light) LREEs are depleted most, as is shown by a change of the La<sub>n</sub>/Sm<sub>n</sub> ratio from  $\gg 1$  to  $\leq 1$ ,

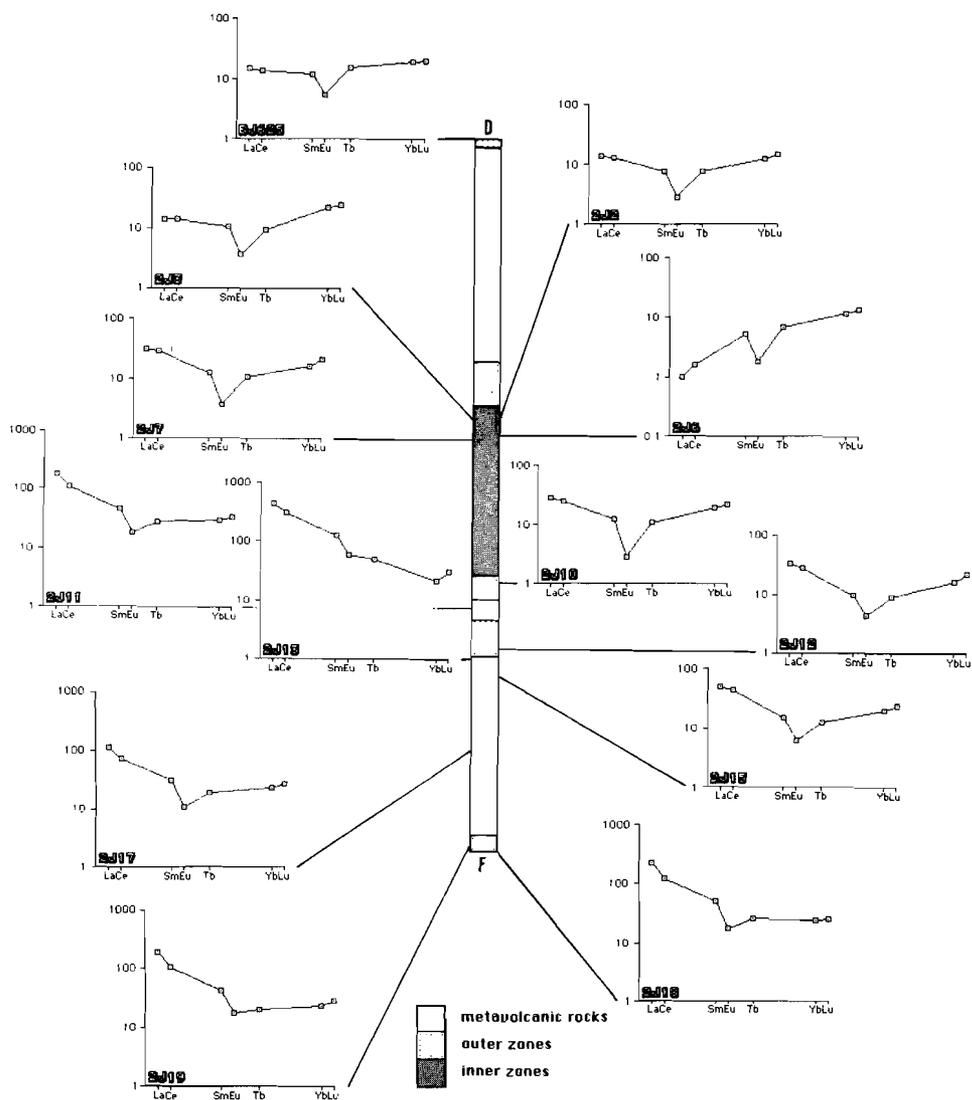


Fig. 6. Section 2J (A–B–C in Fig. 2). Chondrite-normalized (Evensen et al., 1978,  $\times 1.5$ ) REE plots for samples used to construct the section are shown. Sample positions on the section line, shown as a bar, are to scale (see Fig. 2). Metavolcanic rocks, outer and inner alteration zones are marked by clear, stippled and grey zones, respectively, in the section bar.

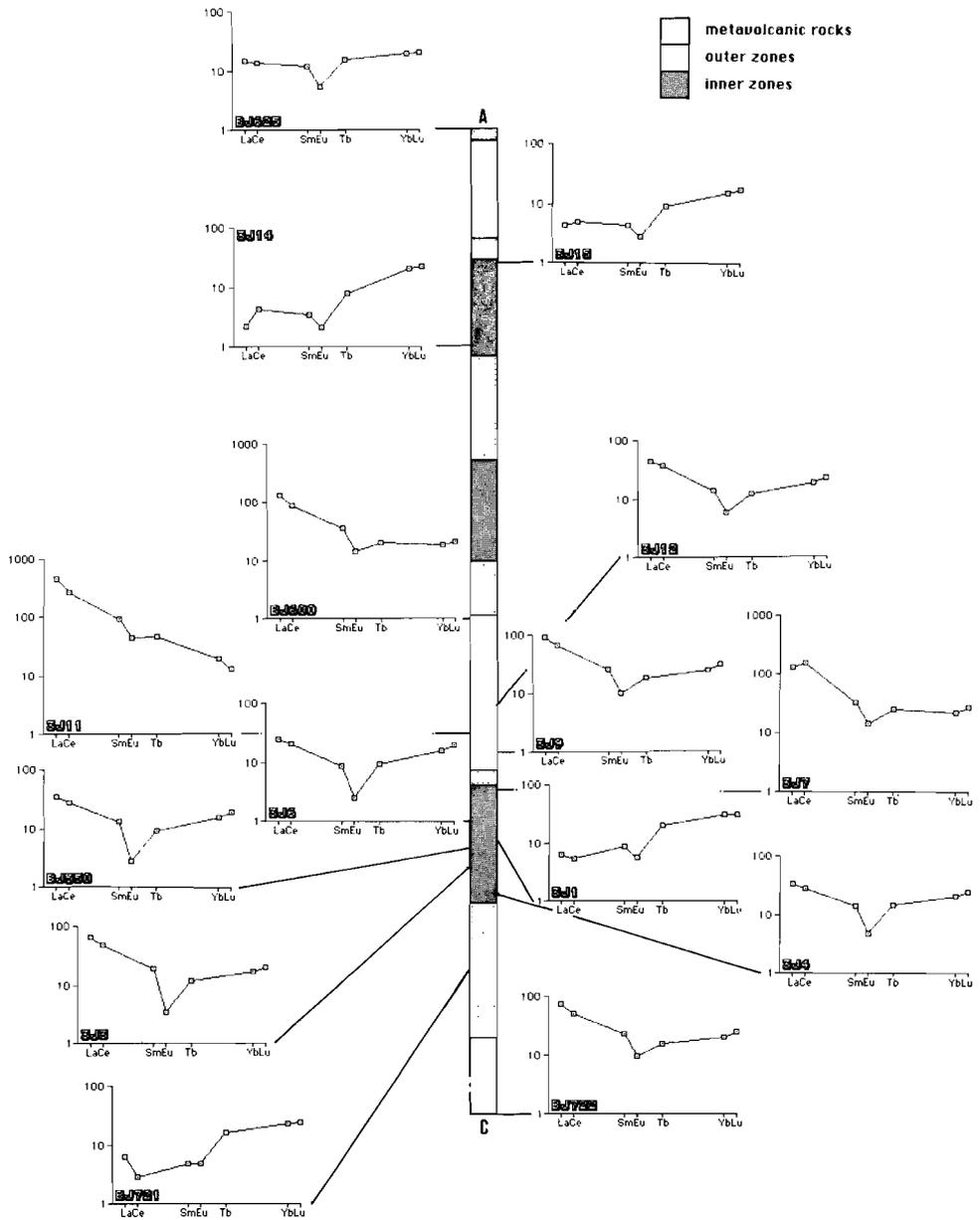


Fig. 7. Section 3J (D-E-F in Fig. 2). For explanation see Fig. 6.

TABLE 4

(a) Rare earth element values of samples shown in Fig. 5.

	BJ624	2J2	2J3	2J6	2J7	2J10	2J11	2J12	2J13	2J15	2J17	2J19	2J18
La	5.35	4.93	5.14	0.37	11.18	10.54	64.80	12.13	158.80	18.62	41.21	67.51	82.62
Ce	12.68	12.06	13.41	1.54	26.94	23.61	107.90	25.60	290.70	41.44	69.69	99.70	117.90
Sm	2.68	1.76	2.48	1.19	2.99	2.82	10.62	2.32	28.90	3.37	7.25	9.72	11.37
Eu	0.46	0.24	0.32	0.16	0.32	0.32	1.56	0.37	5.19	0.52	0.93	1.54	1.55
Tb	0.89	0.44	0.55	0.39	0.64	0.64	1.62	0.52	2.97	0.74	1.10	1.16	1.48
Yb	4.77	3.10	5.65	2.88	4.22	4.22	7.68	4.21	5.47	5.00	5.65	5.60	5.78
Lu	0.77	0.56	0.94	0.51	0.82	0.82	1.36	0.85	1.18	0.89	1.01	1.10	0.96

(b) Rare earth element values of samples shown in Fig. 6

	BJ625	3J15	3J14	BJ600	3J12	3J11	3J9	3J7	3J6	3J1	BJ550	3J3	3J4	BJ721	BJ722
La	5.35	1.55	0.82	48.23	16.00	163.00	33.73	48.18	9.08	2.32	13.17	23.48	12.45	2.33	27.03
Ce	12.68	4.65	4.13	84.61	34.78	261.20	66.44	151.30	20.33	5.05	27.23	46.38	27.50	2.73	47.48
Sm	2.68	0.98	0.80	7.99	3.30	21.80	5.92	7.35	2.02	2.01	3.11	4.37	3.21	1.11	5.29
Eu	0.46	0.24	0.19	1.21	0.50	3.84	0.86	1.23	0.22	0.48	0.24	0.30	0.40	0.42	0.83
Tb	0.89	0.53	0.46	1.13	0.72	2.70	1.07	1.44	0.55	1.17	0.56	0.67	0.84	0.92	0.87
Yb	4.77	3.78	5.07	4.52	4.65	4.84	6.07	5.29	3.98	7.59	3.40	4.07	5.06	5.69	4.87
Lu	0.77	0.68	0.85	0.81	0.86	0.48	1.16	1.02	0.75	1.20	0.76	0.77	0.96	0.90	0.96

while negative Eu anomaly becomes progressively greater. (Heavy) HREEs are apparently less mobile being only slightly depleted, with a change of the  $Tb_n/Lu_n$  ratio from  $> 1$  to  $\pm 1$ .

#### REE behaviour during alteration processes

The Hjulsjö region, hosting the conduit zones of a hydrothermal alteration system, comprises volcanic rocks of rhyolitic composition which show mildly fractionated REE patterns with a negative slope ( $La_n/Yb_n$  ratio  $> 1$ ) and a pronounced negative Eu anomaly (Baker, 1985) (Fig. 8a), characteristic for crustal derived rhyolitic to high silica rhyolitic volcanics or their intrusive equivalents (e.g. Tarney and Windley, 1977; Hildreth, 1978; Alderton et al., 1980) (Fig. 8b).

From figures 6 and 7 and a comparison with least-altered volcanics (Fig. 8a) it can be concluded that the REE were mobile during interaction of the hydrothermal fluid with the rocks of the alteration zone.

The fixation of trace elements in solid phases is controlled by distribution coefficients ( $K_d$

values) between the different solid and fluid phases existing in a specific system (e.g. Hanson, 1978; Möller and Morteani, 1983; Haskin, 1984; Nabelek, 1987), and is dependent on variables including the chemistry of the different phases,  $T$ ,  $P$ ,  $p_{H_2O}$ ,  $f_{O_2}$ ,  $pH$ ,  $I_{fluid\ phase}$ .

A distinction can be made between magmatic melt-mineral  $K_d$  values (e.g. Schnetzler and Philpotts, 1970; Haskin, 1979) or fluid-mineral  $K_d$  values, although these  $K_d$  values are often reported to be surprisingly similar (Cullers et al., 1970, 1973). However, since Cullers et al. (1970, 1973) used pure water as the fluid phase and Cathelineau and Nieva (1985b) reported immobility of REEs in pure water systems, the application of their results to hydrothermal fluids (generally brines) is limited.

The variation in REE contents in different parts of the Hjulsjö alteration zones presents strong evidence for hydrothermally controlled REE fractionation between minerals produced by the alteration of felsic volcanics and a fluid phase. The REE patterns of hydrothermally altered felsic volcanics indicate that the REE pattern in the hydrothermal fluid was domi-

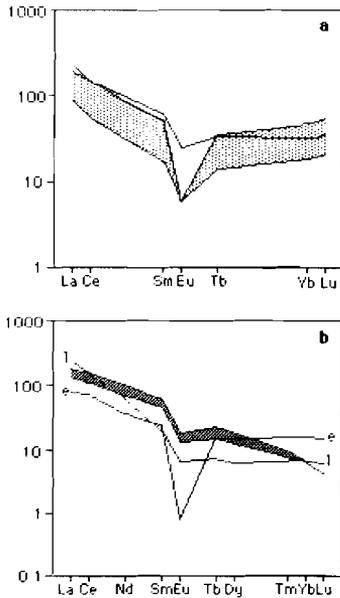
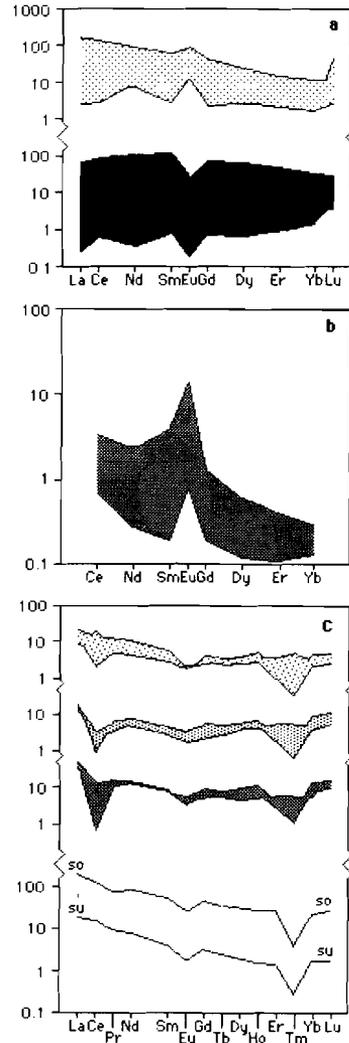


Fig. 8. Chondrite-normalized (Evensen et al., 1978) REE diagrams. (a) For the mean values of the group of 12 least-altered metavolcanics (line) and the granite-granophyre of the Hjulsjö complex (shaded area; Baker, 1985), and (b) for Cornwall granites (shaded area; Alderton et al., 1980) and early (line labelled *e*) and late (line labelled *l*) ignimbrites. Bishop Tuff (Hildreth, 1979).

Fig. 9. Chondrite-normalized (Evensen et al., 1978) REE diagrams. (a) For magnetites of exhalites in the western Bergslagen region showing positive (shaded area) and negative (black area) Eu anomalies (Baker et al., in prep.). (b) for East Pacific Rise (EPR) exhaling fluids (Michard et al., 1983; Michard and Albarède, 1986). (c) for seawater at 0–15 m depth (light shaded area), at 1250–1500 m depth (medium shaded area), and at 3250–4500 m depth (dark shaded area) (Goldberg et al., 1963; Elderfield and Greaves, 1982; De Baar et al., 1983, 1985), and for river water: Garonne/Dordogne river, suspension (line labelled *su*) and solution (line labelled *so*) (Martin et al., 1976).

nated by rock-leaching processes. The REE concentrations in the rock decrease by about one order of magnitude, which, depending on the water/rock ratio, would give absolute concentrations in the fluid several orders higher



than in seawater (Elderfield and Greaves, 1982; De Baar et al., 1985) (Fig. 9c) or meteoric (river) water derived fluids (e.g. Elderfield et al., 1990). The REE pattern in the fluids can be expected to give an inverse picture of the leached pattern of the rocks. REE patterns

comparable to such fluid patterns (Fig. 9a) have been measured in some magnetites of exhalative Fe-oxide horizons in western Bergslagen (Baker et al., in prep.). These are similar to REE patterns from exhaling fluids on the seafloor reported by Michard et al. (1983), Michard and Albarède (1986), and Michard (1989) (see Fig. 9b), as well as fossil exhalative mineralizations (e.g. Lottermoser, 1989; Barrett et al., 1990).

Scavenging of REEs by hydroxides, as in exhalative systems, is described by Ruhlin and Owen (1986) and Barrett and Jarvis (1988). Magnetite in the Sirsjöberg-Ösjöberg exhalites is considered to be formed and precipitated primarily as Fe-hydroxide, and is (re)crystallized to magnetite during diagenesis. REE patterns of chemical sediments around sea floor exhalation vents have been shown to result from dilution of vent fluids with seawater, giving a more seawater type pattern further away from the events (Marchig et al., 1987). The variation in magnetite REE pattern from western Bergslagen can be explained by a similar mixing process.

## Conclusions

The Hjulsjö alteration zones represent part of a hydrothermal system which probably was driven by the heat of the Hjulsjö granophyric intrusion (Baker and De Groot, 1983). In the alteration zones the high mobility of many elements drastically changed the chemistry and mineralogy of the host felsic volcanics. Although Si and Al are strongly mobilized during the alteration processes, they remain unchanged in total content throughout the zones. Mg, and to a lesser extent Zr, Hf and Nb, are enriched in the system. All other elements are depleted or show a more irregular, initially enriched but later depleted trend (e.g. Fe and Mn) approaching the most altered parts of the zones.

A relationship is considered to exist between

the Hjulsjö zones and the Sirsjöberg-Ösjöberg mineralized horizon.

Summarizing the information on the Hjulsjö region of Bergslagen, the main components of a complete hydrothermal system are represented:

(1) a sub-volcanic intrusion (Hjulsjö granophyre) acting as a heat source and driving force for a hydrothermal system,

(2) convection of a fluid through, and interacting with, the crust to form the Hjulsjö alteration zones,

(3) debouching fluids on the sea floor to form the Sirsjöberg-Ösjöberg deposits (Baker et al., in prep.).

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## Chapter 6

### A model for the formation of potassic and sodic alteration phases during hydrothermal processes: application of thermodynamic models to natural systems

P. A. DE GROOT

The potassic and sodic alteration trends documented in the felsic supracrustal rocks of the Bergslagen region, south-central Sweden, are discussed in terms of  $a_K/a_{Na^+}$  and temperature in a simple two feldspar-quartz-fluid system, and in a two feldspar-muscovite-paragonite-phlogopite-montmorillonite-kaolinite-Mg-chlorite-fluid system.

The 1.9–1.86 Ga region of western Bergslagen consists of a thick pile (> 10 km) of felsic volcanic rocks, overlain by a more than 2 km thick sedimentary sequence. The volcanic rocks are intercalated with lenses of marble, chert and iron oxides, and are intruded by granitic plutons, rhyolitic domes and tholeiitic dykes and sills. A few "spilitized" tholeiitic pillow lavas occur in the lower parts of the sedimentary sequence.

The stratigraphically higher parts of the volcanic pile are K-altered, while the lower parts are Na-altered (Sundius 1923). The supracrustal rocks suffered regional greenschist to lower amphibolite facies metamorphism and amphibolite facies metamorphism in contact zones around some of the plutons. The supracrustal rocks are generally tilted into a subvertical position. More extensive descriptions and references for further reading may be obtained in Baker & Hellingwerf (1988).

The felsic volcanic rocks of Bergslagen originally had an approximately rhyolitic composition (Oen et al. 1982, Van der Velden et al. 1982), comprising quartz, plagioclase (oligoclase to andesine), K-feldspar, minor biotite and accessory minerals. Since this plagioclase is unstable under the conditions of the alteration systems discussed here (altered into alkali feldspars or alteration products), it is omitted from the system. All the systems discussed here are considered to be silica saturated or oversaturated.

Fig. 1A shows a selection of albite-K-feldspar-fluid equilibrium curves in a  $a_K/a_{Na^+}$  versus temperature diagram. Curve 1 represents equilibrium between two feldspars and an alkali fluid (Einaudi 1987). Curve 2 is an equilibrium curve of two feldspars and an alkali fluid of a composition considered to represent crustal rock fluids (open square; Giggenbach 1984). Curve 3 (based on data from Jasiński 1988) is a two feldspar curve in equilibrium with seawater at 1

bar, curve 4 at 1 kbar and curve 5 at 5 kbar. Curves 4 and 5 (also based on Jasiński 1988) are included to show the influence of pressure on these equilibrium systems.

If an element such as Ca were added to the alkali systems (curves 1 and 2), then the equilibrium curves would shift towards the lower right-hand corner of the diagram (increasing ionic strength), as reported by Orville (1963). This same type of shift is demonstrated by the equilibrium curve for feldspars and seawater, the latter containing Ca and many more ions.

A proposed fluid evolution path (stippled line with arrows) for a seawater-type fluid seeping down into, and interacting with the felsic rock is displayed in Fig. 1A. The composition of seawater at 25 °C is shown as a solid square. This seawater fluid is slowly heated at deeper levels by intruding granitic diapirs functioning as heat sources. A nearly constant  $a_K/a_{Na^+}$  ratio is maintained and the path crosses the two feldspar-fluid equilibrium curve at about 100–150 °C. A path which crosses rather than follows the equilibrium curve is more probable since reaction of fluid and rock is too slow to maintain an equilibrium situation (see Giggenbach 1984 for a similar process) while the temperature increases steadily. At this point, *K-alteration* shifts into *Na-alteration*. During temperature increase, the exchange between fluid and rock becomes more intense and pushes the fluid path towards the feldspar-fluid equilibrium curve until equilibrium is reached. If the temperature continues to increase after equilibrium is attained, equilibrium will be maintained and *sodic phases* will be formed. The fluid composition is enriched in K and follows the equilibrium curve. If the temperature of the fluid drops after reaching the equilibrium curve or after following the curve to higher temperatures, *potassic phases* will be formed and Na will be released into the fluid. A possible deviation of the fluid from the equilibrium curve gives a similar trend in mineral phase formation as that following the equilibrium curve. A major restriction is that the water/rock ratio may not exceed 10–20. At greater values, a complete leaching of elements may occur (e.g. Mottl 1983).

Since the alteration system discussed here is

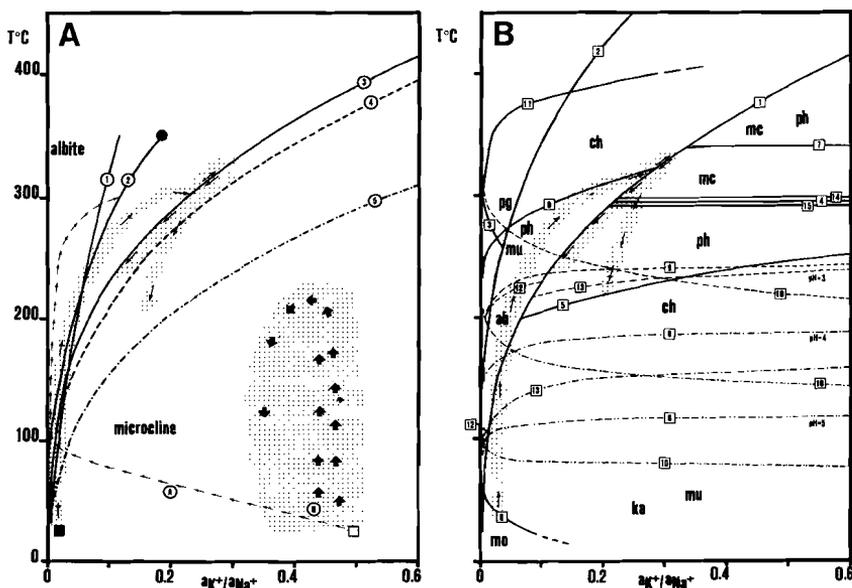


Fig. 1. ■ A.  $a_K/a_{Na}$  versus temperature for the system quartz-albite-K-feldspar-fluid phase. Equilibrium curves for two feldspars (albite and microcline) and a fluid phase are given. Curve 1 is based on data as presented by Einaudi (1987). Curve 2 is from Giggenbach (1984). Curves 3, 4 and 5 are based on thermodynamic data from Jasiński (1988). Open square: crustal rock fluids (Giggenbach 1984). Solid square: seawater composition (e.g. Bischoff & Seyfried 1978). Solid dot: deep fluid (Giggenbach 1984). Stippled path: seawater fluid path (see text for explanation). Path A (small arrows): flow path of descending groundwater (Giggenbach 1984). B: possible region and fluid flow path of wall-rock alteration in the Bodie Mining District, California (O'Neil et al. 1973). ■ B.  $a_K/a_{Na}$  versus temperature for a two feldspar (albite and microcline)-muscovite-paragonite-phlogopite-montmorillonite-kaolinite-Mg-chlorite-fluid phase system. The stippled path is the same fluid path as in Fig. 1A. Thermodynamic data are from Jasiński (1988) and references therein. Activity coefficients are calculated following the method described by Truesdell (1984). Solid curves: fluid-mineral equilibrium curves at seawater conditions. Dashed curves: same conditions and pH fixed at 3. Dash-dot curves: same conditions, pH = 4. Double dash-dot curves: same conditions, pH = 5. Curves: 1: microcline-albite, 2: muscovite-paragonite, 3: paragonite-albite, 4: K-montmorillonite-microcline, 5: K-montmorillonite-muscovite, 7: kaolinite-muscovite, 8: muscovite-Mg-chlorite, 9: phlogopite-Mg-chlorite, 10: muscovite-phlogopite, 11: kaolinite-phlogopite, 12: albite-phlogopite, 13: Mg-chlorite-microcline, 14: muscovite-microcline, 15: microcline-kaolinite (first mineral phase at low temperature or high  $a_K/a_{Na}$  side of curve). ab = albite; ch = Mg-chlorite; ka = kaolinite; mc = microcline; mo = K-montmorillonite; mu = muscovite; pg = paragonite; ph = phlogopite.

only partly represented by the simple two feldspar-quartz-fluid system, and because alteration phases will form as soon as fluid-rock interaction takes place, a diagram of  $a_K/a_{Na}$  versus temperature, including the stability fields of alteration phases found in the Hjulsjö system (see Baker & De Groot 1983), has been constructed (Fig. 1B). Equations of phase equilibrium are from Jasiński (1988). Activity coefficients are calculated by the *Debye-Hückel* equation as given by Truesdell (1984) using constants from Helgeson et al. (1981).

The same fluid path as proposed in Fig. 1A is used in Fig. 1B. At low temperature, the re-

sults are somewhat ambiguous, possibly because of kinetic rather than equilibrium control on the alteration reactions and low reactivity between the fluid and the rock. The transition of *K-alteration* to *Na-alteration* in the diagram is in accordance with the field evidence (the distribution of K- and Na-altered felsic volcanic rocks as mentioned above). Furthermore, the respective formation of albite, muscovite, phlogopite and Mg-chlorite is in accordance with the petrographically determined mineralogical order of formation (De Groot & Baker in prep.). The peak of alteration of the Hjulsjö system gives the mineral paragenesis: quartz-muscovite-Mg-

chlorite ( $\pm$ phlogopite), fixing the temperature of formation at about 300–350°C (Cathelineau & Nieva 1985). Some mineralization may occur in the downgrading parts of the system, and is possibly responsible for the biotite (phlogopite) schist zones often found near skarn alterations or exhalative venting systems. The Mg-chlorite and phlogopite described in this paper formed during the hydrothermal alteration process, contrasting with the common view that they formed during regional metamorphism. Arguments for hydrothermal formation are: (1) that these minerals are only formed in highly altered zones, (2) that the high element mobility in these altered zones suggests a very high water/rock ratio and a reasonably high temperature for the system, and (3) the perfect mineralogical similarity with hydrothermal alteration systems in general (Burnham 1962; Hemley & Jones 1964; Riverin & Hodgson 1980; Hall 1982; Mottl 1983). If these minerals were formed during metamorphism, an intensive low-temperature alteration with clay mineral formation should have occurred first. During metamorphism, recrystallization of the clay minerals into chlorite-phlogopite would cause dewatering, evidence for which is lacking. It rather may be said that, after formation, the quartz-muscovite-Mg-chlorite ( $\pm$ phlogopite) paragenesis recrystallized during greenschist facies metamorphism. The potassic alteration phases usually found in the wall rocks of skarn mineralizations in Bergslagen are explained as the high-level parts (ascending fluids, decreasing temperature) of the alteration systems, lying on the right-hand side or potassic part of the stability diagram of Fig. 1B.

Other hydrothermal alteration systems in felsic rocks, in some cases related to ore mineralization, can be explained using this type of diagram. Porphyry copper fluid paths have been explained by Einaudi (1987) while fluid paths for alkali (meteoric) ground waters have been proposed by Giggenbach (1984) (the latter shown in Fig. 1A as path A). Gold lodes of the Bodie district, California, were formed at 200–250°C by fluids of meteoric origin, showing potassically altered wall rocks of originally intermediate composition (O'Neil et al. 1973) (B in Fig. 1A).

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## Chapter 7

### 7.1 - INTRODUCTION TO THE THE USE OF STABLE ISOTOPES

#### a - methods

NOTATION AND STANDARDS:

The isotopic values in this study are given in the standard delta notation:

$$\delta (\text{‰}) = \{(R_{\text{sample}} - 1)/R_{\text{standard}}\} \cdot 10^3$$

Fractionations are given as:

$$\alpha_{A-B} = (R_A/R_{\text{standard}})/(R_B/R_{\text{standard}}) = (R_A/R_B)$$

where R =  $^{18}\text{O}/^{16}\text{O}$ ,  $^{13}\text{C}/^{12}\text{C}$ , or D/H and A and B are samples which are in isotopic equilibrium with each other.

$$\Delta (\delta X - \delta Y) = z (\text{‰})$$

gives the difference in isotopic values between phases X and Y in z per mille (‰).

Oxygen and hydrogen isotopic values are reported relative to V-SMOW (Vienna - Standard Mean Ocean Water) and carbon isotopic values relative to the PDB (PeeDee Belemnite) standard.

Standards which were used during the analytical work are:

NBS-19 [marble] with isotopic values:

$$\delta^{18}\text{O} = -2.20\text{‰} [\text{PDB}] \text{ or } 28.67\text{‰} [\text{V-SMOW}]; \delta^{13}\text{C} = 1.93.$$

V-SMOW [water] with:  $\delta^{18}\text{O} = 0\text{‰}$  and  $\delta\text{D} = 0\text{‰}$ ,

NBS-1A [water] with:  $\delta^{18}\text{O} = -24.41\text{‰}$  and  $\delta\text{D} = -182.7\text{‰}$ , and

SLAP [water] with:  $\delta^{18}\text{O} = -55.36\text{‰}$  and  $\delta\text{D} = -426.6\text{‰}$

NBS-28 [quartz] is assumed to have  $\delta^{18}\text{O} = 9.6\text{‰}$ . Uncorrected values obtained at Utrecht University on NBS-28 were:

$$\delta^{18}\text{O} = 9.42 \pm 0.1\text{‰} (n = 23).$$

Corrections are made on basis of this value.

NBS-30 [biotite] gave:  $\delta\text{D} = -66.1 \pm 0.4\text{‰} (n = 4)$

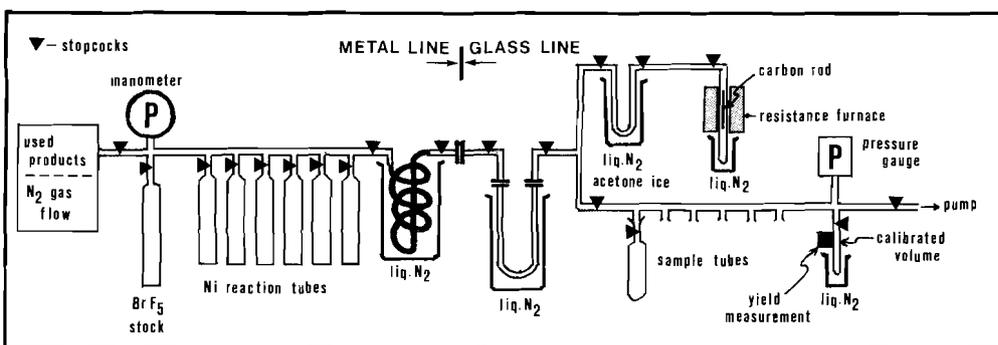
*Oxygen isotopes:* Silicate oxygen line (Fig. 1):

Basically oxygen isotope analysis on silicate minerals is carried out according to the procedure as described by Clayton and Mayeda (1963).

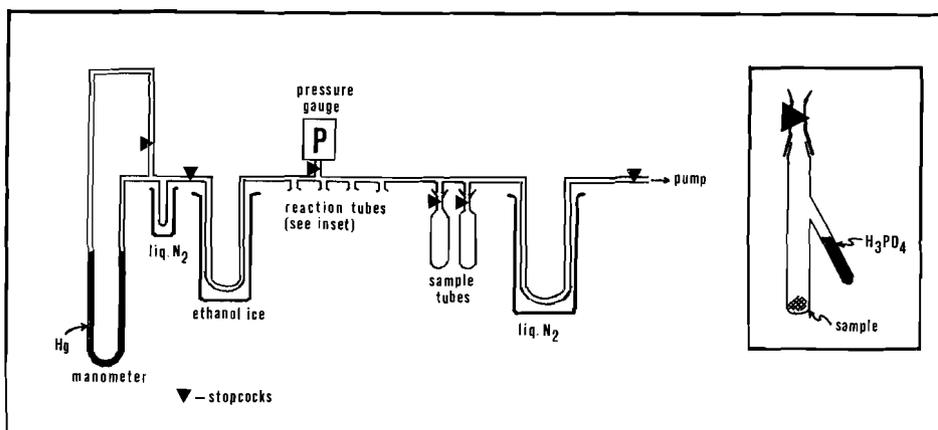
The extraction line used at Utrecht contains a metal part (stainless steel, monel and nickel) and a glass part, and is operated under high vacuum conditions (pressure below  $5 \cdot 10^{-6}$  mbar). Silicate minerals are reacted overnight with  $\text{BrF}_5$  in nickel tubes at  $500^\circ$  to  $700^\circ\text{C}$ , depending on the structure and composition of the mineral. Loading the reacting tubes with the samples is carried out under a dry  $\text{N}_2$  gas flow.  $\text{BrF}_5$  is added in approximately 5 times the stoichiometric amount of oxygen in the silicate. A

short prereaction with  $\text{BrF}_5$  at  $100^\circ\text{C}$  or lower (depending on the type of sample) is carried out to remove any adsorbed water from the sample or reaction tube walls, in case some water (humid air) was accidentally introduced during sample loading.

$\text{O}_2$  gas is extracted and passed over a hot carbon rod (doped with a platinum solution to catalyse the reaction), externally heated by a resistance furnace to  $670^\circ\text{C}$ , to form  $\text{CO}_2$  gas which is frozen into a sample tube and measured in a mass spectrometer (VG Sira-24 EM). Complete extraction of oxygen from the silicates is required to avoid isotopic fractionation. Yield measurement is carried out using a pressure transducer in a volume-calibrated glass finger.



**Figure 1.** Oxygen isotopic extraction line ("BrF<sub>5</sub>-line") for silicate samples.



**Figure 2.** Carbon and oxygen stable isotope analytic extraction line for carbonate materials.

*Oxygen and carbon isotopes:* Carbonate line (Fig. 2):

Carbonate minerals (calcite, dolomite) are reacted in special glass tubes under high vacuum with 100% phosphoric acid (see review by Bowen, 1988; pp. 589-610) to extract CO<sub>2</sub> gas from the minerals.

Reaction is carried out at 25°C for all calcites and dolomites. Samples containing only calcites were reacted for at least 10 hours and those containing only dolomites were reacted for at least 5 days. Mixtures with calcite as a major component are reacted for 3-4 hours to obtain the calcite-CO<sub>2</sub> and where dolomite is the major component calcite-CO<sub>2</sub> is obtained after 1-1½ hours of reaction and the dolomite-CO<sub>2</sub> after 5 days reacting of the rest of the sample.

The CO<sub>2</sub> gas is collected in sample tubes on a high vacuum line by freezing with liquid nitrogen, and is measured in a mass spectrometer (VG Micromass 602D double collector) to obtain carbon and oxygen isotopic values. All carbonate values are corrected for <sup>13</sup>C and <sup>17</sup>O variations after Craig (1957).

*Hydrogen isotopes:* Hydrogen line 1- CRPG (Centre de Recherches Pétrographiques et Géochimiques) (Fig. 3a):

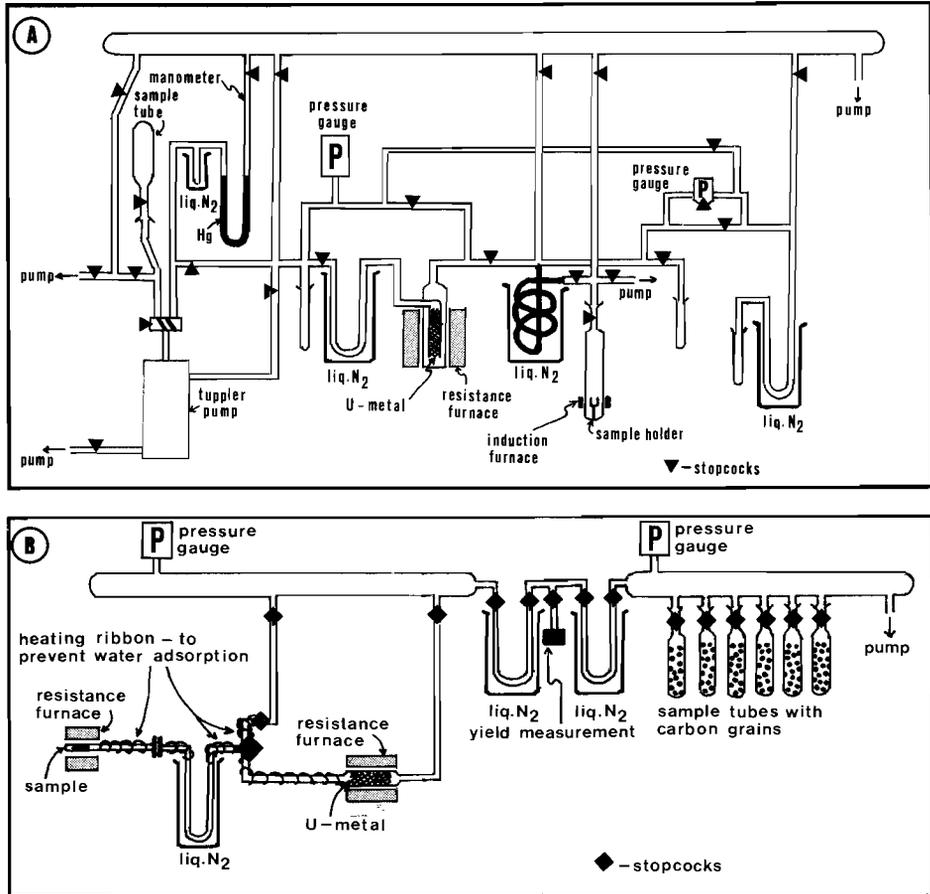
Hydrogen isotope analyses on silicate minerals followed a procedure modified from Bigeleisen et al. (1952).

- Minerals, wrapped in molybdenum foil and placed in platinum crucibles in special glass tubes (after evacuating degassing on a vacuum line under constant pumping at about 100°C for at least 3 hours, but in most cases more than a night) are heated to 1500°C by an induction furnace, liberating all crystal water, which is collected in a trap cooled with liquid nitrogen,
- Capillary glass tubes containing water are placed in glass containers. After evacuating they are broken and water is collected in a liquid nitrogen trap,
- Rock fragments with fluid inclusions are placed in a stainless steel or copper tube which is sealed on one side and closed by a stopcock at the other side. After evacuating and careful degassing, the tube containing rock fragments is crushed under a hydraulic press to liberate the inclusion fluids, and water is collected in a liquid nitrogen trap.

The water in the liquid nitrogen trap is passed through an uranium metal bearing furnace at 800°C to reduce the water to H<sub>2</sub> gas, which is collected in a sample tube by means of a Tupper-pump. Manometric yield measurements were carried out before collecting the gas in a sample tube. No heating to avoid H<sub>2</sub>O adsorption on the system walls was applied here.

The H<sub>2</sub> gas is measured in a mass spectrometer (VG Micromass 602D double collector) to obtain D/H ratios.

**Hydrogen line 2:** RUU (Rijksuniversiteit Utrecht) (Fig. 3b):  
 This extraction line differs in some parts from the one described above. Degassing to remove any adsorbed waters on the samples was carried out on the extraction line at a temperature between 90° - 100°C during a time varying between a night and 20 min. At least one of the duplicate runs was degassed for a long period (> 3 hours). No difference in results larger than the analytic precision was found between the short and long degassed runs.



**Figure 3.** Hydrogen isotope analytic lines. a) The hydrogen isotope line at the CRPG, Vandoeuvre-lès-Nancy, France; b) The hydrogen isotope line at the RUU, Utrecht, The Netherlands.

Heating of the samples occurs in quartz-glass tubes between 1300-1370°C by means of an external resistance furnace to liberate all the crystal water

from the silicates. The H<sub>2</sub>O, collected by freezing in a liquid-N<sub>2</sub> cooled trap and after separating from CO<sub>2</sub> by changing the liquid-N<sub>2</sub> for acetone-ice, was passed over hot U-metal (665°C) to convert it into H<sub>2</sub> gas. The H<sub>2</sub> gas is adsorbed on activated carbon grains in sample tubes by freezing with liquid-N<sub>2</sub>. The H<sub>2</sub> gas samples are measured on a mass spectrometer (VG 903 triple collector).

Those parts of the analytical system which are in contact with the H<sub>2</sub>O are heated to 90°-100°C by heating ribbons to avoid adsorption of H<sub>2</sub>O on the system walls. Yields were roughly measured in an uncalibrated volume.

### **b - fractionations**

Knowledge of water-mineral and mineral-mineral isotopic fractionations is essential for interpretation of the results. Fractionation factors were taken from the literature. They are obtained in different ways: experimentally, empirically and theoretically. Those fractionation data, which were determined by different methods and are comparable to each other, are considered the most reliable ones.

Using isotopic fractionations, it is of major importance to know if the interacting phases were in equilibrium with each other.

The mineral-water and mineral-mineral fractionation literature data are often inconsistent. In general, isotopic fractionations below 400°C become less accurate with decreasing temperature. In many cases extrapolation of fractionation values to higher or lower temperatures than the temperature range at which the fractionations were determined is necessary. The validity of this procedure may be disputable in some cases, and it should only be used with the greatest care.

No further discussion about these matters is given here. Instead, I refer to the detailed discussions and overviews by O'Neil (1986) and Kyser (1987). These works also show compilations of fractionation data in tables and diagrams.

## 7.2 - SAMPLE PREPARATION

Sample preparation for isotopic analysis started with the selection of samples as fresh as possible, except in the special case where the most altered samples were used as a control on the influence of weathering (De Groot and Kreulen, 1993/chapter 9). The samples were crushed to less than 0.7 mm in the case of separate mineral analysis, and to a fine powder in case of whole rock analysis. Minerals were separated by a Frantz magnetic separator, heavy liquid- and binocular-hand picking methods. Purity and quality of mineral separates was tested by XRD-analysis.

One sample (GP A1) from the Orotorp alteration zone mica schist was separated chemically (at the CRPG, Vandouevre-lès-Nancy, France). Quartz and muscovite are strongly intergrown in this sample. The colourless appearance and the fine grained texture of the minerals made it impossible to separate them in another way. The chemical method to clean the quartz from the muscovite is described by Kiely and Jackson (1964) and Syers et al. (1968). This method was tested for isotopic fractionations introduced by the cleaning method, and was found to give no fractionations bigger than the precision of the isotopic analytical technique. Additional information on preparation routines are given in chapters 8 and 9.

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## Chapter 8

### Carbonate rocks from W. Bergslagen, Central Sweden: isotopic (C, O, H) evidence for marine deposition and alteration by hydrothermal processes

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*Key words:* Carbonate rock, stable isotopes, Proterozoic, Bergslagen, Sweden

#### Abstract

Carbon and oxygen isotope ratios for calcite and dolomite from stratabound carbonates, carbonate veins and clots in W-(Mo-) and Zn-Pb sulphide skarns, and for a calcite from a Mn-skarn from the Bergslagen region, central Sweden, are presented. Stratabound carbonate carbon isotopes ( $\delta^{13}\text{C} \sim 0\text{‰}$ ) imply a marine milieu of deposition.

The  $\delta^{18}\text{O}$  values of stratabound carbonates can be divided into two groups: one associated with stratiform iron-oxide deposits (RSC) and the other unrelated (NRSC). Stratabound dolomites of the NRSC are depleted in  $^{18}\text{O}$  compared to the 'most Proterozoic dolomite' field. NRSC calcites have a range of  $\delta^{18}\text{O}$  values (+12 to +19‰) similar to the lower half of the 'most Proterozoic calcites' field. Whether the RSC  $\delta^{18}\text{O}$  values (+6 to +11‰) are primary values or values formed by exchange of the RSC with a hydrothermal fluid during the skarn alteration of associated stratiform iron-oxide deposits, is not clear. Calcites and dolomites, from skarn altered iron-oxide deposits, W-(Mo-)skarns, and a sulphide skarn, as late phase veins and clots, have distinguishable  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, placing the respective skarns into separate fields. They have, in general, low  $\delta^{13}\text{C}$  (-2 to -8‰) and low  $\delta^{18}\text{O}$  (+6 to +12‰) values, except for the calcite veins in the sulphide skarn. The  $^{18}\text{O}$ -depletion of the carbonates most probably occurred during exchange with sea water at temperatures of  $300 \pm 50^\circ\text{C}$ , or meteoric waters if the temperatures were lower. The types of  $\delta^{18}\text{O}$  values and their range are comparable to well documented sea water hydrothermal systems of younger age from ocean floor ophiolites and many relatively low altitude meteoric-hydrothermal systems.

The low carbon and oxygen isotope values of the carbonate veins and clots in W-(Mo-) and Fe-skarns are typical for such skarns. They indicate the influx of  $\text{CO}_2$ -bearing hydrothermal fluids where the  $\text{CO}_2$  is either of magmatic origin or derived from sedimentary carbonate formations after major loss of  $\text{CO}_2$  through decarbonation reactions.

Slate hosted calcite from a Ca-Mn-skarn, is isotopically similar to both the skarn associated carbonates and a concretionary carbonate. Diagenetic modifications of organic matter-bearing sediments, exchange of a sedimentary carbonate with hydrothermal fluids, or, more probable, a combination of these two events, were responsible for the isotopic composition of the calcite in this skarn.

## Introduction

This paper presents some initial results of an ongoing stable isotope (C, O, H) study on carbonate minerals and fluid inclusions from the 1.8–1.9 Ga ensialic belt of Bergslagen, Central Sweden (Fig. 1). Different types of carbonate-bearing samples were chosen to determine whether the sediments were deposited in a marine or fresh water milieu, and what type of fluids circulated through this sedimentary crust and caused the formation of associated mineralizations.

### Regional geology

The ensialic belt of Bergslagen (Oen et al. 1982; Vivallo & Rickard 1984; Oen 1987) consists of a supracrustal sequence (dated 1.9–1.8 Ga by U-Pb; Welin et al. 1980; Åberg et al. 1983) comprising a thick pile (>10 km) of felsic volcanics (historically named Hälleflinta and Leptites: Sundius 1923; Magnusson 1925, 1970), overlain by a sedimentary packet of black and grey slates (dated 1.86 Ga by Sm-Nd: Miller et al. 1986), which are at least 2 km thick. The felsic volcanics are intruded by granite domes and continental tholeiitic (Hellingwerf & Oen 1986) dykes and sills, while a few meta-basaltic flows (spilites) occur in the black slates, at the base of the slate pile. Although basalts form a relatively small volume compared to the felsic rocks, this is an excellent example of bimodal, coeval magmatism (Van der Velden et al. 1982; Vivallo & Rickard 1984).

Oen et al. (1982) and Oen (1987) related the development of the belt, the deposition of the supracrustals, and the plutonism and volcanism with a continental rift process, resulting finally in an aborted rift. They divided the Bergslagen Supracrustal Sequence into a Lower Leptite Group, a Middle Leptite Group, and an Upper Leptite-Hälleflinta and Slate Group.

The supracrustals in the belt are generally tilted into a (sub-)vertical position by granitic diapirism and by gravity tectonism as described by De Groot et al. (1988). The supracrustals are weakly metamorphosed (greenschist facies) in the central part of the belt. They grade into amphibolite facies on the east and west sides of the belt, touching the

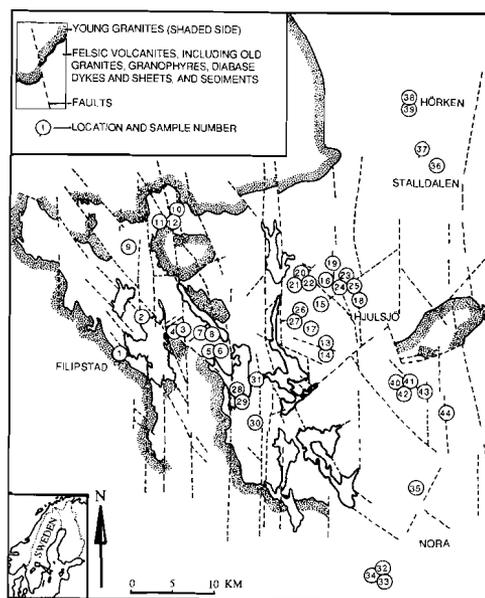


Fig. 1. Simplified map of W. Bergslagen after Oen et al. (1982) and Baker (1985a; p. 91, Fig. 1) showing sample locations and sample numbers (see Table 1).

1.64–1.78 Ga granitoids (Oen & Verschure 1985) which encircle the belt (Fig. 1).

Discussions about a regional and local scale alteration in the W. Bergslagen area by e.g. Baker & De Groot (1983), Lagerblad & Gorbatshev (1985), and Baker (1985a, b), are mostly based on the chemistry and mineralogy of the altered and unaltered wall-rocks and their associated mineralizations. They indicate sources for fluids involved in the skarn-forming processes, but the arguments are not conclusive. Many of the W-(Mo)-skarns, from which carbonate isotopic analyses are reported in this paper (Table 1), are described by Hellingwerf & Baker (1985). A detailed description of the Gruvåsen area is given by Hellingwerf (1984). Carbonate, or carbonate bearing rocks are present throughout the entire supracrustal sequence, but are mostly concentrated in the Middle Leptite Group and in the lower part of the Upper Leptite-Hälleflinta and Slate Group of Oen et al. (1982). A

Table 1. Mineralogy and carbon, oxygen, isotope data for stratabound, and vein carbonates and hydrogen isotope values of fluid inclusions in vein calcite.

NO	SAMPLE	DESCRIPTION	COMPOSITION§		CALCITE		DOLOMITE		δD
			(in%)		δ <sup>13</sup> C	δ <sup>18</sup> O	δ <sup>13</sup> C	δ <sup>18</sup> O	
			ct	dol					
Parsberg area:									
1	s* GG1	Gåsgruvan	finegr. marble: cont. silic./>100m#	85		0.14	12.53		
2	s HW Gt	Getön	adjac. mag +Pb,Zn,Ag sulf. min./>50m	67		-0.09	18.62		
Gruvåsen area:									
3	s HW B15-64	Gruvåsen	adjac. Cu,Zn,Fe sulf. min.+ chert b./700m	20	75	-0.22	15.60	0.10	15.60
4	s HW B15-184	Gruvåsen	adjac. Cu,Zn,Fe sulf. min.+ chert b./700m	28	65	-0.42	13.07	0.01	13.86
5	s 77HW85	Limbergsåsen	finegr. marble: cont. silic./700m	22	45	0.40	18.45	1.01	19.62
6	s 77HW86	Limbergsåsen	finegr. marble: cont. volc. fragm./700m	40	17	0.35	18.62		
7	s 77HW139	Bovik	finegr. marble: cont. mica/700m	32	63	-0.44	16.67	0.20	16.84
8	s 77HW140	Bovik	finegr. marble: cont. silic./700m	15	60	-0.03	14.49	0.40	15.30
Långban area:									
9	s LB1	Långban	adjac. Mn-skarn: pure dol	2	98			1.71	16.32
10	s Da78	Gåsborn	finegr. marble/<10m	*54		-0.15	14.42		
11	s Da81	Gåsborn	finegr. marble/<10m	*96		0.10	15.16		
12	sf DaA2	Gåsborn	finegr. marble/<10m	*95		-3.09	7.91		
Hjulsjö area:									
13	vw BJ Sk1	Skropen	ct clots in amph sch qz skarn	*100		-5.70	7.55		
14	s BJ Sk2	Skropen	adjac. amph sch qz skarn/7-8m	98		0.30	14.89		
15	sf B.11.18L	Killingberget	adjac. Fe-ox. dep.+bt-sköjl/7-8m	*67		0.35	8.33		
16	s B.1152	Hjulsjö	finegr. marble/low m	*65		-2.82	6.51		
17	s B.1366	Hjulsjö	marble-chert layer into sk. alt. grst./1m	*100		0.56	13.17		
18	s BJ461C	Hjulsjö	finegr. marble: cont. gt+mag/2-3m	*44		-2.83	6.51		
19	sf MM269B3	Bredösjö	finegr. marble	*94		0.33	8.32		
20	sf Cab1B	Sirsjöberg	finegr. marble adjac. Fe-sk. horiz./120m	98		-2.87	17.59		
21	sf Si2	Sirsjöberg	finegr. marble adjac. Fe-sk. horiz./120m	95		0.01	6.83		
22	vf Si3	Sirsjöberg	skarnified Fe-oxide horiz./120m	35		-2.01	8.80		
23	vf Öb2	Ösjöberg	vein-ct in Fe-skarn/>100m	*40		-2.24	7.77		
24	vf Öb3	Ösjöberg	ct clots in Fe-skarn/>100m	*100		-3.47	6.86		
25	sf Öb5	Ösjöberg	finegr. marble: cont silic./>100m	70		0.39	7.05		
26	s Si1	Stolpberget	marble adjac. Fe-skarn/±5-10m	98		0.49	16.65		
27	s Si2	Stolpberget	finegr. marble: cont. amph bt/±5-10m	*94		-1.91	7.60		
Grythyttan area:									
28	s HW BN1	Bjurskogsån	finegr. marble/>100m	60	28	-0.17	16.34		
29	s HW BN2	Bjurskogsån	finegr. marble/>100m	65	18	0.89	16.28		
30	s AR1	Djupvikén	finely laminated dol-chert= strom./±10m	6	70			-0.19	13.04
31	(v) 77Md302/18	Grythyttan	ct in exhal.-sed. Mn-skarn/<1-2m	17		-7.80	10.17		
Erntorp area:									
32	s HW NV576	Erntorp	breccia below Zn,Pb sulf. min./100m	18	45	-1.78	17.12	-1.25	17.67
33	vs ERN S1	Erntorp	vein-ct in Zn(Pb) sulf. cont. schist	*50		-0.79	20.15		
34	s ERN M1	Erntorp	finegr. marble: cont. chert b./>100m	70	9	0.43	19.25		
Striberg area:									
35	vw HW HC2	Hultagruvor	ct clots in Fe-W-skarn	78		-4.87	6.15		-63
Stålldalen-Hörken area:									
36	s B9	Båtens	marble adjac. sch gt skarn/60m	27		-3.14	9.64		
37	vw W71	Stålldalen	ct clots in amph gt sch skarn	*100		-8.09	6.48		-62
38	sf Fr E19	Hörken	finegr. marble adjac. Fe-skarn	85		0.21	10.73		
39	sf Fr E20	Hörken	finegr. marble adjac. Fe-skarn	85		-0.31	8.29		
Grängen area:									
40	vw Db1	Dunderbo	coarse dol dot in chl bt amph sch Fe-sk.	*100				-4.65	8.11
41	vw Db2	Dunderbo	dol clots in chl bt amph sch Fe-skarn	*4	75			-3.53	9.28
42	s Db-S	Dunderbo	marble: cont. silic.		55			-3.85	8.92
43	vw Ah	Annehill	interst. ct in px amph gt qz sch skarn	10		-3.63	8.27		
Jämböls area:									
44	vw Sp1	Sparrbergsgruvan	dol/ct clots in gt vesuv amph bt sch sk.	*17	70	-3.51	11.37	-3.51	10.17

Delta (δ) values in per mil (‰). Abbreviations : adjac. = adjacent to; alt. = altered; amph = amphibole; bt = biotite; chert b. = chert bands; chl = chlorite; cont. = contains; ct = calcite; dep. = deposit; dol = dolomite; exhal. = exhalative; Fe-ox. = Fe-oxide; finegr. = fine grained; gt = garnet; grst. = greenstone; horiz. = horizon; interst. = interstitial; mag = magnetite; px = pyroxene; qz = quartz; sch = schaeelite; sed. = sedimentary; silic. = silicate minerals; sk = skarn; strom. = stromatolite; sulf. min. = sulfide minerals; vesuv = vesuvite; volc. fragm. = volcanic (rhyolite) fragments.

\* s = stratabound carbonate (NRSC); sf = stratabound carbonate associated with stratiform Fe-oxide deposits (RSC); vw = carbonate clots in W-(Mo)-skarn; vf = calcite clots or veins in skarn altered Fe-oxide deposits; vs = calcite veins in a (Zn-Pb) sulphide skarn; (v) = carbonate as granules, aggregates and veins in a Mn-skarn.

§ Proportion of carbonates in whole rock sample.

\* Proportion of calcite in separates or partially separated minerals.

# Thickness of carbonate layer.

major division can be made between: (1) stratabound carbonates, and (2) carbonates formed as veins or clots during skarn<sup>1</sup> mineralization.

Within this division the following groups can be distinguished:

- (1) a – Major and minor carbonate horizons which are not associated with mineralizations. The major horizons are formed by massive lenses of relatively pure, fine grained (grains  $\leq 2$  mm) carbonates more than 50 m thick; they are generally composed of calcite at lower stratigraphic levels and of calcite or calcite–dolomite mixtures at higher stratigraphic levels, and seldom show lamination or alternation with chert laminae or bands. The minor horizons of the same type of massive carbonate are 10 m or less thick; they are generally composed of calcite and, more often than the thick layers, show lamination and alternation with chert laminae or bands.
- b – Major and minor carbonate horizons are associated with stratiform iron-oxide deposits; they further show the same characteristics as the carbonate horizons described under a.
- (2) a – Clots of carbonate (calcite and dolomite) formed in W-(Mo-)skarns.
- b – Calcite formed as veins or clots during skarn alteration of stratiform iron-oxide deposits.
- c – Calcite veins associated with Zn-Pb-sulphide skarn mineralization
- d – Small calcite bodies (several mm thick and up to 1 cm long) formed in layered Ca-Mn-skarns occurring in the slates of the Upper Leptite-Hälleflinta and Slate Group of Oen et al. (1982).

The stratabound carbonates, the calcites from the

<sup>1</sup>Skarn in this paper is defined as a carbonate containing rock or layer, wall rock included, which is altered by hydrothermal processes into a calc-silicate rock. In Bergslagen skarns are not normally directly associated with an intrusive granitic body.

slates, and most of the skarn-related carbonates are recrystallized due to diagenesis and/or regional metamorphism. The stratabound carbonates are more or less intensely folded, which is best seen in the laminated carbonates. The carbonate grains often show undulatory extinction in thin section. Sample locations are given in Fig. 1, and sample descriptions are given in Table 1.

### Analytical procedure

Rocks containing calcite, and mixtures of calcite and dolomite (Table 1) were crushed to a grain size below  $63 \mu\text{m}$  for BJ118L, BJ152, BJ461C, MM269B3, Da78, Da81, and DaA2, and below  $120 \mu\text{m}$  for the other samples. For samples HW HG2, BJ Sk1, W71, Öb2, Öb3, St2, Db1 and Db2 calcite was separated from the silicates in the rock and handled separately. The mineralogical composition of the carbonates was measured by standard X-ray techniques. The carbonates were reacted with  $>100\%$   $\text{H}_3\text{PO}_4$  at  $25^\circ\text{C}$  using the method of McCrea (1950) and the  $\text{CO}_2$ -yields were measured manometrically. Calcites were reacted for at least 10 hours while dolomites were reacted for at least 5 days. Mixtures in which calcite was the major component were reacted for 3–4 hours to obtain the calcite- $\text{CO}_2$ . Where dolomite was the major component, the samples were first reacted for 1–1½ hour to obtain the calcite- $\text{CO}_2$  (calcite content of total carbonate in rock at least 20%) and then for at least 5 days to obtain the dolomite- $\text{CO}_2$  (Epstein et al. 1964). The  $\text{CO}_2$  from samples containing sulphides (Öb2, ERN S1, and Ah) were purified using  $\text{Ag}_3\text{PO}_4$  (Smith & Croxford 1975). For 70% of the samples, duplicate extractions gave differences in  $\delta^{13}\text{C}$  of less than  $\pm 0.2\%$  and for  $\delta^{18}\text{O}$  of less than  $\pm 0.12\%$ .

Calcite samples W71 and HW HG2 were crushed under vacuum to collect  $\text{H}_2\text{O}$  from fluid inclusions. The samples were weighed and evacuated in cleaned stainless-steel tubes, and then heated for 3 days at  $100^\circ\text{C}$  to remove all the absorbed water from the surface and pores of the minerals. After crushing, the  $\text{H}_2\text{O}$  from the fluid was purified using a combination of a liquid nitrogen and an acetone-

dry ice trap. The pure water was passed through an uranium furnace heated to 800°C and reduced to H<sub>2</sub> gas after the method described by Friedman (1953) and Godfrey (1962), and yields were measured manometrically. No duplicate extractions could be made because of the small amount of calcite available (<18 g). Isotopic ratios for carbon and oxygen were measured on CO<sub>2</sub> gas, and for hydrogen on H<sub>2</sub> gas with a VG – Micromass 602D double collector mass spectrometer. The values are reported here in the usual delta notation ( $\delta$ ) in per mil (‰) with  $\delta^{13}\text{C}$  against PDB and  $\delta^{18}\text{O}$  and  $\delta\text{D}$  against the SMOW standard. All carbonate values are corrected for  $^{13}\text{C}$  and  $^{17}\text{O}$  variations after Craig (1957).

## Results

Carbon and oxygen isotope values of the analysed carbonates from Bergslagen are listed in Table 1 and are plotted as  $\delta^{13}\text{C}$  against  $\delta^{18}\text{O}$  values in Fig. 2. This figure includes calcite and dolomite reference fields for Early to Middle Proterozoic (1.6–2.5 Ga) marine carbonates based on the compilation of data given by Veizer & Hoefs (1976). For  $\delta^{13}\text{C}$ , the overwhelming majority of their data fall between +2 and –3‰ and these boundaries can be considered to be relatively well defined. In contrast the  $\delta^{18}\text{O}$  boundaries are less well defined probably because the data base includes marine carbonates that have undergone varying degrees of diagenetic exchange. Most Proterozoic dolomites, however, display a very restricted range of  $\delta^{18}\text{O}$  values (+25 to +21‰) in contrast to the wide range of values for calcite and lack of peak in the histogram (see Fig. 4 in Veizer & Hoefs 1976). Without entering into the problem of dolomitization and noting that, in general, calcite undergoes oxygen isotope exchange more readily than dolomite (Northrop & Clayton 1966), the more restricted field for Proterozoic dolomites is considered to more closely represent the field of ‘unaltered’ Proterozoic marine carbonates. Most of the stratabound carbonates, related (RSC; stars in Fig. 2) or not related (NRSC; circles in Fig. 2) to stratiform iron oxide deposits, have  $\delta^{13}\text{C}$  values around zero, and all plot within

the proposed range of Proterozoic marine carbonate values. The  $\delta^{18}\text{O}$  values, however, show a large continuous range, with NRSC  $\delta^{18}\text{O}$  values between +12 and +20‰ for both calcites and dolomites – a range lower than that of most Proterozoic dolomites and similar to the lower half of the ‘most Proterozoic calcites’ field (Fig. 2). The RSC  $\delta^{18}\text{O}$  values of +6.5 to +11‰ are clearly depleted in  $^{18}\text{O}$  compared with the former, NRSC group of carbonates. In the NRSC there does not appear to be a relationship between the  $\delta^{18}\text{O}$  value of the calcite or dolomite and the nature or proportion of silicate minerals directly associated with the stratabound carbonates, or the nature of the immediately surrounding felsic volcanics.

A finely laminated carbonate-chert (AR1) is thought to be a stromatolite, partly silicified during a later alteration (Boekschoten et al. 1988). Carbon isotopic values are consistent with Proterozoic marine values and oxygen isotopic values are  $^{18}\text{O}$  depleted in a similar way to the above described carbonates. One calcite (Cab 1B) connected with a stratiform iron-oxide deposit altered into skarn gives a relatively low  $\delta^{13}\text{C}$  value of –2.87‰ which is comparable with  $\delta^{13}\text{C}$  values of calcites formed in the skarn phase, but it has a normal  $\delta^{18}\text{O}$  value for NRSC.

Calcite clots and veins (stars in solid circles in Fig. 2), formed during skarn alteration of the stratiform iron-oxide deposits, have lower  $\delta^{13}\text{C}$  values ( $-3.5 < \delta^{13}\text{C} < -2\text{‰}$ ) than the RSC, and are similar in  $\delta^{18}\text{O}$  values to most of the RSC calcites. Minor ( $\leq 10$  m thick) carbonate horizons of NRSC (3 samples) and RSC (1 sample) show the same  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values as calcites in these skarns. Carbonates in W-(Mo-)skarns (squares in Fig. 2) have both low  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values compared with the marine Proterozoic field. Their  $\delta^{18}\text{O}$  values are similar to the  $\delta^{18}\text{O}$  values of the RSC-type carbonates. Such  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values are comparable to vein-type carbonates in skarns from contact aureoles associated with granitic intrusions (see Valley 1986: p. 455, Fig. 6). They define a separate field from that defined for Fe-skarn calcite isotope values. The  $\delta\text{D}$  values for fluid inclusion H<sub>2</sub>O from two of the W-(Mo-)skarn calcites are very similar at –60‰. These values are plotted in Fig. 3 against

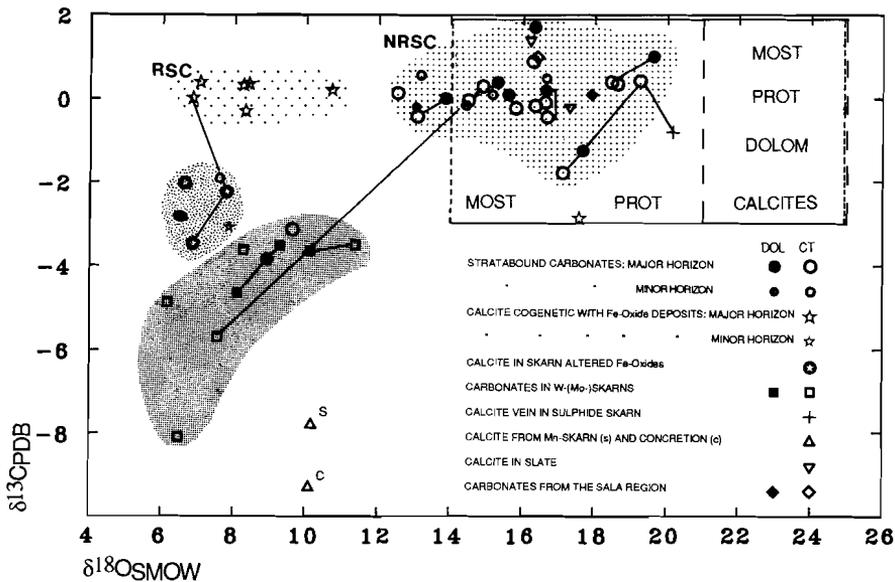


Fig. 2. Values of  $\delta^{18}\text{O}_{\text{SMOW}}$  against  $\delta^{13}\text{C}_{\text{PDB}}$  of calcites (open symbols) and dolomites (solid symbols) from stratabound carbonates (circles and stars), and carbonates in skarn altered Fe-oxide deposits (stars in solid circles), W-(Mo)-skarns (squares), and a sulphide skarn (cross). Also given are calcite from a Mn-skarn (triangle marked with s), calcite from the mass of a septarian concretion (Ehlin & Koark 1980) (triangle marked with c), and disseminated calcites from two slate samples containing the concretion (Ehlin & Koark 1980) (inverted triangles). Two carbonate samples from the Sala region (Schidrowski et al. 1975) (diamonds) are included for comparison. Connected samples are linked by tie-lines. *Square-pattern stippled* and *diamond-pattern stippled* areas define fields of stratabound carbonates (NRSC, see text) and stratabound carbonates related to stratiform iron-oxide deposits (RSC) respectively. The *irregular stippled* field defines carbonate veins and clots in skarn altered iron-oxide deposits, and the *densely stippled* field carbonate clots in W-(Mo)-skarns.

the vein calcite and the calculated  $\delta^{18}\text{O}$  of water in equilibrium with the host calcite for 200°C, 250°C, 300°C, and 400°C. This temperature range was measured on fluid inclusions ( $T_{\text{homogenisation}}$ ) in the calcite, although most of the values obtained were close to 250°C; for this reason the calculated water composition at 250°C is marked with a small box on Fig. 3. The temperatures are not very precise and the salinity of the fluids could not be determined because of the small size of the inclusions (<10  $\mu\text{m}$ ); halite-cubes were observed in some inclusions and imply the existence of a highly saline fluid (>15% equiv. NaCl) in some of them. All the inclusions have a regular rectangular shape. They are, however, probably secondary because they are situated in trails touching the crystal-boundaries.

The calcites did not necessarily reequilibrate isotopically with such secondary fluids. Therefore, the calculated  $\delta^{18}\text{O}$   $\text{H}_2\text{O}$  value in equilibrium with calcite is probably not identical to that of the secondary inclusions measured for  $\delta\text{D}$ . For this reason, vertical arrows are given on Fig. 3 to emphasize that the  $\delta\text{D}$  value of the fluid associated with the *crystallization* of the calcite is not known. The single vein calcite (ERN S1) in a Zn-Pb sulphide skarn, formed in a fault zone, is totally different compared to the other skarn carbonates. The veins are only 2 to 3 mm thick and are associated with major sphalerite and galena (Hellingwerf pers. comm. 1987). Its mineral paragenesis and geological setting is different from the W-(Mo-) and Fe-skarn carbonates.

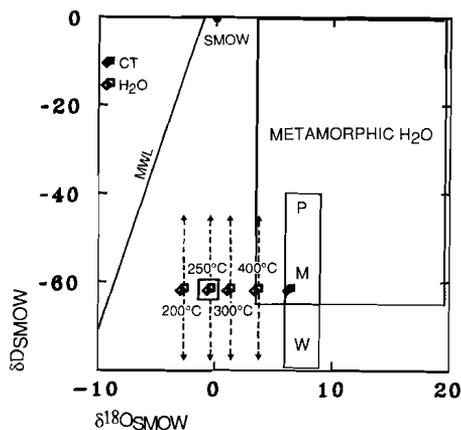


Fig. 3. Skarn calcite  $\delta^{18}\text{O}_{\text{SMOW}}$  plotted against  $\delta\text{D}_{\text{SMOW}}$  from  $\text{H}_2\text{O}$  of secondary fluid inclusions in the skarn calcite (solid symbols). Calculated values of  $\text{H}_2\text{O}$  in equilibrium with calcite containing given  $\delta\text{D}$  values, at 200°C, 250°C, 300°C, and 400°C are plotted as open symbols. The vertical broken lines are drawn to stress the fact that the fluid of the secondary inclusions most probably did not equilibrate with the calcite (see text). The box around the 250°C value points to the most probable temperature of the (secondary) fluid phase. Fields for metamorphic  $\text{H}_2\text{O}$  and primary magmatic  $\text{H}_2\text{O}$  (PMW) (from Sheppard, 1986; p. 171; Fig. 4), the meteoric water line (MWL), and the standard mean ocean water (SMOW) point are shown for reference.

Slate (quartzitic siltstone) from the Grythyttan region contains Ca-Mn carbonates as disseminated granules, interstitial aggregates, and fracture filling veinlets (Oen et al. 1986). Calcite from such a slate sample (77Md302/18) from the Grythyttan region has  $\delta^{13}\text{C}$  of  $-7.8\text{‰}$  and  $\delta^{18}\text{O}$  of  $+10.2\text{‰}$ . These values are very similar to those of the massive part of a septarian concretion in the Grythyttan slate quarry, 500 m north of our sample location ( $\delta^{13}\text{C}$  of  $-9.3\text{‰}$  and  $\delta^{18}\text{O}$  of  $+10.1\text{‰}$ ; Ehlin & Koark 1980). Two calcite-bearing slate samples surrounding the concretion, reported by Ehlin & Koark (1980), give  $\delta^{13}\text{C}$  values of  $+1.4\text{‰}$  and  $-0.2\text{‰}$  and  $\delta^{18}\text{O}$  values of  $+16.2\text{‰}$  and  $+17.3\text{‰}$  respectively, which are comparable with the isotopic values of the stratabound carbonates of Bergslagen.

## Discussion

### Stratabound carbonates

All of the  $\delta^{13}\text{C}$  values of the stratabound carbonates (NRSC and RSC, Table 1, Fig. 2) fall within the proposed range of marine carbonate values for the early to middle Proterozoic period. It is probable, for the following reasons, that most of these carbonates have essentially retained their primary pre-diagenetic and pre-metamorphic  $\delta^{13}\text{C}$  values. Most of the carbonates, whether dolomite or calcite, have the same  $^{13}\text{C}/^{12}\text{C}$  ratio ( $\sim 0 \pm 0.5\text{‰}$ ) on a regional scale, despite the wide range of  $\delta^{18}\text{O}$  values. Many of the samples come from massive carbonate dominated units with no petrographic evidence for decarbonation. During diagenesis and low to middle grade metamorphism carbon isotope ratios are often not significantly modified (Keith & Weber 1964; Sheppard & Schwarz 1970). These ratios are therefore characteristic of their marine origin. By analogy, then, the felsic volcanics in Bergslagen were deposited under sea water. Although this interpretation has been proposed previously (e.g. Oen et al. 1982; Van der Velden et al. 1982; Baker & De Groot 1983; Vivallo 1985) it was based on less definite evidence than the carbon isotope data. The  $\delta^{18}\text{O}$  values of the NRSC calcites and dolomites are up to  $8\text{‰}$  depleted in  $^{18}\text{O}$  compared to the 'most Proterozoic dolomites' field, which is considered to be the most probable field of marine Proterozoic carbonate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. The majority of the calcite  $\delta^{18}\text{O}$  values, however, are consistent with the range found for 'most Proterozoic calcites'. Calcites and dolomites from the Svecofennian of central Sweden commonly show  $\delta^{18}\text{O}$  values of between  $+14$  to  $+18\text{‰}$ . Such values are also reported for two carbonate samples from the Sala region, about 100 km east of Stålldalen, by Schidlowski et al. (1975) (diamonds in Fig. 2) and for some samples of the Bergslagen region by Billström et al. (1986). The results of Billström et al. (1986) are, however, not integrated with our results because no information was given on whether a carbonate sample was stratabound or skarn-related.

Thus *all* NRSC type calcites and dolomites from central Sweden are systematically  $^{18}\text{O}$ -depleted rel-

ative to the 'most Proterozoic dolomite' field. This suggests that *all* of the  $\delta^{18}\text{O}$  values of the carbonates either were modified during diagenetic, hydrothermal and/or metamorphic processes or have closely retained their primary sedimentary values. This latter interpretation implies that either the temperature of formation of these carbonates was about 15 to 60°C higher than that for 'most Proterozoic dolomites' assuming isotopically similar waters, or the associated waters were depleted in  $^{18}\text{O}$ , if the temperatures were similar. Isotopic homogenisation on a scale greater than a few metres during regional metamorphism does not appear to have been an important process because nearby samples can have  $\delta^{18}\text{O}$  differences of 1‰ or more. Thus the  $\delta^{18}\text{O}$  variations of the calcites could in part be due to local scale exchange with the associated silicates during the regional metamorphism or be inherited from the pre-regional metamorphic alteration processes. The latter may be the dominant process because of the relatively restricted range of  $\delta^{18}\text{O}$  values of the dolomites and some of the carbonate units are essentially pure (>95%) calcite or dolomite.

The RSC calcites are directly associated with iron-oxide deposits. If the RSC were deposited on a sea floor then the isotope values should be comparable with the NRSC values or the 'most Proterozoic dolomite' field. The far lower  $\delta^{18}\text{O}$  values of RSC calcites (+7 to +11‰) compared to the NRSC, implies that either these calcites exchanged with more  $^{18}\text{O}$ -depleted fluids at approximately the same temperature of formation as the NRSC or, if the  $^{18}\text{O}/^{16}\text{O}$  ratios of the fluids were relatively comparable, the temperatures of formation of the RSC calcites must have been  $\geq 30^\circ\text{C}$  higher than those of NRSC, or  $100^\circ$  to  $250^\circ\text{C}$  higher than 'most Proterozoic dolomites'. Alternatively the range of  $\delta^{18}\text{O}$  values reflects both variations in temperature and fluid composition. Waters in equilibrium with the most  $^{18}\text{O}$ -depleted calcites ( $\sim +6\text{‰}$ ) have  $\delta^{18}\text{O} \sim 0 \pm 2\text{‰}$  for  $T \sim 300 \pm 50^\circ\text{C}$ , a value similar to that proposed for Proterozoic sea water (e.g. Muehlenbachs 1986; Sheppard 1986). Lower temperatures require more  $^{18}\text{O}$ -depleted waters; such waters could be of meteoric origin. These fluids could be similar to those involved in forming the

clot and vein carbonates in the skarn alteration of the stratiform iron oxide deposits.

The C- and O-isotope compositions of RSC calcites are different for either one or both isotopic ratios in carbonates from BIF-type deposits (Becker & Clayton 1972). Also the carbonates associated with BIF-type deposits are usually Fe-Mg rich (siderite, ankerite, dolomite) and not calcitic like the RSC.

This sea water or meteoric hydrothermal alteration process operated on a regional scale and could also have been responsible for the large scale alteration of the associated volcanics. Such systems often produce alteration assemblages or minerals with quite variable  $\delta^{18}\text{O}$  values because of variations in water/rock ratio, permeability, etc., as well as temperature. In fact the types of  $\delta^{18}\text{O}$  values of the carbonates (NRSC and RSC) and their range are comparable to those observed in well documented sea water hydrothermal systems of younger age – ocean floor, ophiolites (e.g. Muehlenbachs 1986 and references therein) and many meteoric hydrothermal systems where  $\sim -60 < \delta\text{D} < 0\text{‰}$  (e.g. Clayton et al. 1968). This interpretation implies that the isotopic composition of the different rock units were often not significantly modified by subsequent processes and therefore the later regional metamorphic event was not associated with large scale fluid transport processes.

#### *Carbonates from W-(Mo-)skarns*

This group of samples has low  $\delta^{13}\text{C}$  values (between  $-3$  and  $-8\text{‰}$ ) and low  $\delta^{18}\text{O}$  values (between  $+6$  and  $+11\text{‰}$ ). Although these carbonates are associated with skarn mineralizations they cannot have formed during in situ decarbonation because they occur as clots, a late mineralized phase in the skarns. A hydrothermal fluid must therefore have been involved. The nature and source of this fluid has not yet been clearly documented because the regional metamorphism may have modified the fluid inclusion evidence. All the fluid inclusions which have been observed are secondary and are therefore probably post-skarn formation. Also, no hydrous minerals are found in these clots.

In skarns the  $\text{CO}_2/\text{H}_2\text{O}$  ratio is usually quite small ( $X_{\text{CO}_2} < 0.1$ ; e.g. Taylor & O'Neil 1977) and

therefore the oxygen isotope composition of the calcite or dolomite is controlled by the  $\delta^{18}\text{O}$  value of the aqueous fluid and the temperature of precipitation. As discussed above, the  $\text{H}_2\text{O}$  part of the fluid phase could be either of sea water or meteoric origin. The  $^{13}\text{C}$ -depleted carbonates with  $\delta^{13}\text{C} \sim -3$  to  $-8\text{‰}$  imply that the  $\delta^{13}\text{C}$  value of the  $\text{CO}_2$  in the fluid was about  $-2$  to  $-7\text{‰}$  at temperatures above  $200^\circ\text{C}$  (Bottinga 1968). The more  $^{13}\text{C}$ -depleted values of this range could be of magmatic origin, could come from decarbonation reactions or could come from the hydrolysis of organic carbon.

Magmatic carbon with  $\delta^{13}\text{C} \sim -5 \pm 3\text{‰}$  has often been proposed as the dominant source of vein carbonate carbon in skarn deposits (e.g. Taylor & O'Neil 1977; Einaudi et al. 1981). Identical  $^{13}\text{C}$ -depleted values could also be generated during decarbonation of carbonates initially with sedimentary type  $\delta^{13}\text{C}$  values. For example, using a Rayleigh type fractionation model, 60% to essentially 100% decarbonation would be necessary to produce the wide range of  $\delta^{13}\text{C}$  values. This process requires that decarbonation occurred in one place and was followed by precipitation of vein carbonate in another place from the residual  $\text{CO}_2$  in the hydrothermal fluid. It also implies that the volumetric importance of the carbonates decreases rapidly with decreasing  $\delta^{13}\text{C}$  values. Similarly, the observed  $\delta^{13}\text{C}$  values could be reflecting the hydrolysis of organic carbon, which is strongly  $^{13}\text{C}$ -depleted. The necessary organic matter would have to be associated with either the stratabound carbonates, which are found within the volcanic sequence, or the overlying shales. Although the present data cannot distinguish among these three possibilities, they all require the transfer of a  $\text{CO}_2$ -bearing fluid to form the carbonate clots.

Two of the stratabound (NRSC) samples have isotopic values in the same range as the W-(Mo-) skarn carbonates. A possible explanation is that because of their short distance from a skarn they were altered by the same fluid as that forming the skarn.

#### *Calcite in skarn altered iron oxide deposits*

Most of the stratiform iron-oxide deposits in W. Bergslagen are altered into a skarn during later hydrothermal events. Mobilization of elements and mineral phases occurred during the skarn forming processes, as well as late formation of calcite veins or clots in the skarn. The  $\delta^{13}\text{C}$  ( $-2$  to  $-4\text{‰}$ ) and  $\delta^{18}\text{O}$  ( $+6$  to  $+8\text{‰}$ ) ranges are small (perhaps because only three samples were analysed). They define a distinct field (irregular stippled area in Fig. 2) from the W-(Mo-)skarn carbonate field (densely stippled area in Fig. 2). Keeping in mind the smaller range of isotopic values and the less negative  $\delta^{13}\text{C}$  values for the former, similar explanations as for the W-(Mo-) skarn carbonates can be given.

Minor ( $<10\text{m}$  thick) calcite horizons of the NRSC (3 samples) and RSC (1 sample) have similar isotope values as the 'Fe-skarns' discussed here. These NRSC horizons are situated close to 'Fe-skarn' or are expected to be close. They are, because of their limited thickness, altered isotopically (and eventually chemically) by the same fluids as involved with the skarn. Sample St2 of the NRSC contains clots of silicate minerals (amphibole, mica). It is situated in the border zone of an Fe-skarn at Stolpberget, which is unambiguously not stratiform. This skarn most likely formed along or in a (meta-) diabase dyke, striking N340E – a general strike direction for major joint systems and diabase dykes in this part of Bergslagen – and cuts the Stolpberget stratabound minor carbonate horizon with a distinctly different isotopic signature. Alteration processes and the isotopic compositions of this fluid associated with this skarn seem to be similar to those for the skarn alteration of the stratiform iron-oxide deposits.

#### *Calcite veins in a sulphide skarn*

A small vein containing calcite and Zn-Pb-sulphides in a fault zone near Erntorp (Ern S1) is isotopically close to the NRSC values. Two stratabound carbonate samples, one (HW NV576), a fragment in a breccia from below the major zone of stratiform Zn-Pb-sulphide mineralisation, and the other (ERN M1) from a massive marble bed containing chert horizons up to several dm thick (Hel-

lingwerf et al. 1988, see Table 1 and Fig. 2), have NRSC type values. The genesis of this mineralization is not yet fully understood.

#### *Calcites from slate*

The carbon and oxygen isotope compositions of calcite from the Ca-Mn-skarn vein carbonates (SVC) in the Grythyttan slate are similar to both the values of calcite and dolomite from the skarns and a calcite from a concretion in the slates (Fig. 2). The latter has been interpreted by Ehlin & Koark (1980) to be precipitated during the diagenesis of organic matter-bearing sediments.

Oen et al. (1986) have presented evidence for microbial fossils in a Ca-Mn skarn and suggested that the sediment was composed of laminae of mats of organic material interlayered with cherts. During the diagenesis of such a sediment  $^{13}\text{C}$ -depleted carbonates could have been precipitated. The  $\delta^{13}\text{C}$  values of the SVC could thus have been inherited from the diagenetically modified sediment.

Alternatively the isotopic compositions of the SVC were produced during the reaction of hydrothermal fluids on the sediment and their origin could be similar to that of the skarn associated carbonates. This interpretation implies that pre-existing sedimentary carbonates were isotopically modified by the hydrothermal fluids, as part of the carbonate is not in veins but is disseminated in the slate. The observed isotopic compositions may well be reflecting a combination of the sedimentary and diagenetic processes and a hydrothermal event.

#### **Conclusions**

Different groups of carbonates can be distinguished in the W. Bergslagen region. The stratabound carbonates were deposited in a marine environment as based on their carbon isotopic compositions. They can be divided into two groups with different  $\delta^{18}\text{O}$  values. One group (RSC; +6 – +11‰) is associated with iron-oxides whilst the other (NRSC; +12 – +20‰) is not. This difference could be an useful tool in exploration to trace the proximity of stratiform iron-oxide deposits (eventually altered into skarn). The moderate (NRSC)

to low (RSC)  $\delta^{18}\text{O}$  values of these carbonates probably record a sea water or meteoric hydrothermal process with the RSC carbonates forming at a higher temperature (possibly 30 to 200°C) than the NRSC carbonates, assuming similar fluids.

Carbon dioxide of magmatic and/or decarbonation origin was introduced during deposition of calcite and dolomite veins and clots in the skarns. Different types of skarns show different ranges for both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, and thus define different fields without any overlap. Discrimination between such skarn types can therefore be made based on the isotopic composition of carbonates.

Further studies to obtain more detailed information about the insufficiently understood hydrothermal processes and oxygen isotopic depletion in the vein, clot, and RSC carbonates and skarns are in progress.

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## Chapter 9

### **HYDROGEN AND OXYGEN ISOTOPE STUDIES OF Fe ± Mn AND W - Mo SKARNS, BERGSLAGEN, CENTRAL SWEDEN; EARLY PROTEROZOIC SEA WATER AND HYDROGEN ISOTOPE EXCHANGE UNDER SURFACE CONDITIONS.**

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#### **Abstract**

The 1.90 - 1.86 Ga ensialic belt of western Bergslagen comprises a more than 12 km thick sequence of felsic volcanic rocks and sediments predominantly derived from volcanics. The sequence contains Fe - Mn and W - Mo skarns, and stratiform (BIF - type) Fe - Mn oxide deposits. Sulfide bearing skarns occur as a minor component in the sequence. The skarns are derived from the interaction of a fluid with carbonate layers and diabase dykes and sills.

Hydrogen and oxygen isotope analyses of skarn minerals show a wide range of  $\delta D$  values together with a narrow range of  $\delta^{18}O$  values. The isotopic compositions of fluids in equilibrium with the skarn minerals were calculated for a temperature range of 200 - 500°C. High- $\delta D$  fluids are 10 - 20‰ lower than present day sea water. The fluids represent either Early Proterozoic sea water or Early Proterozoic low latitude meteoric water. In both cases the  $\delta D$  value of the 1.9 - 1.8 Ga sea water deviated by less than 20‰ from its present value.

Low  $\delta D$  values observed in the skarn minerals are tentatively explained as a  $\delta D$ -shift caused by exchange of high- $\delta D$  minerals with low- $\delta D$  modern meteoric water at surface conditions. Fresh and strongly weathered samples were analysed to prove this theory. A clear negative shift of  $\delta D$  is found in weathered samples compared with the fresh ones. The water contents in phlogopites and amphiboles do not unambiguously follow this trend. Additional study on low temperature isotope exchange is needed.

## Introduction

The Bergslagen region is known for its Fe, Mn, Cu, Ag, W, Pb, Zn ore deposits that were of historical economic importance to the area. The ores can be divided in volcanogenic exhalative deposits (BIF type iron  $\pm$  manganese oxide deposits, VMS type massive sulphides, or mixed oxide and sulphide deposits) and skarn mineralizations. Most of the stratiform exhalative ore deposits were buried under felsic volcanics, metamorphosed, mobilized and chemically changed by hydrothermal processes, and these later processes superimposed new skarn mineralizations on the originally exhalative deposits. Granitic diapir intrusions induced hydrothermal fluid circulation whereas tectonic activity created the channels for fluid transport.

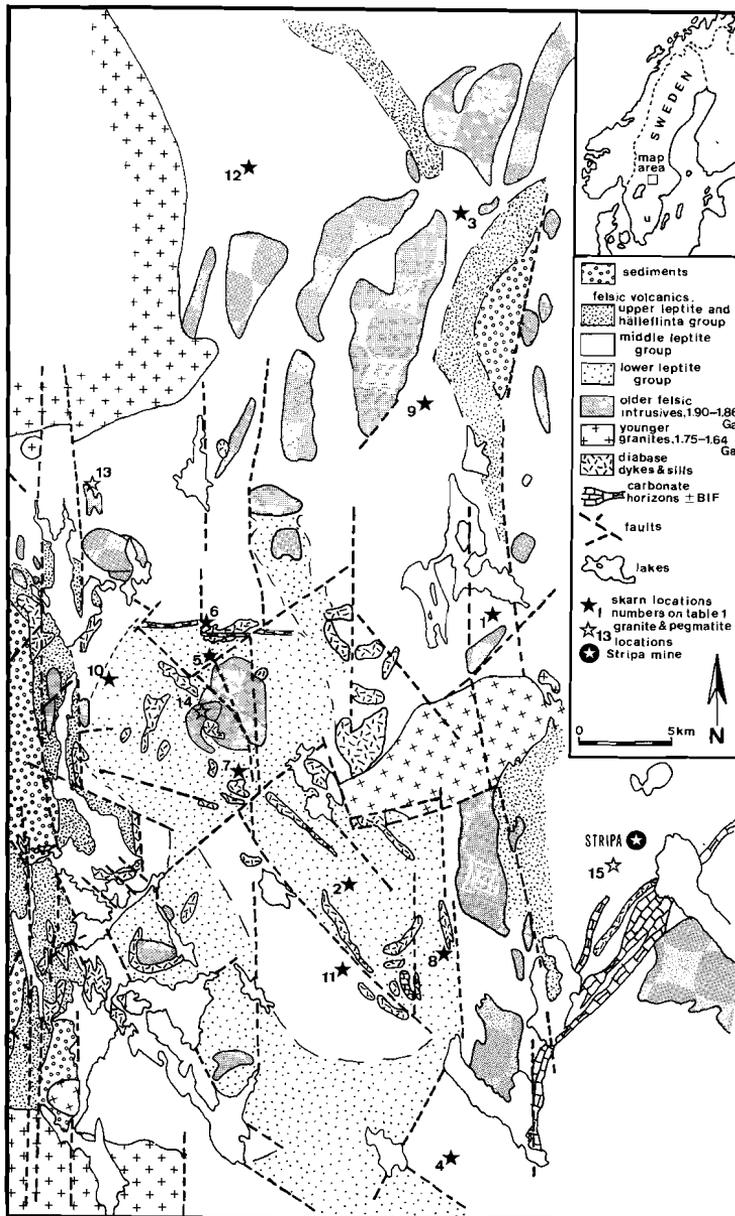
The aim of this study was to obtain information on the hydrothermal processes and their relationship with the ore mineralizations. A marine setting is indicated by marine carbonates (carbon isotopes: De Groot and Sheppard, 1988) and Mg-enrichment of the felsic volcanics in the hydrothermal systems (Baker and De Groot, 1983). The marine setting of the Bergslagen basins hosting the ore mineralizations gave a marine isotopic imprint to the hydrothermal fluids. The very humid present-day climate raises the question of possible isotopic interaction of meteoric water with rocks now exposed at the surface.

## Geological setting

The 1.90 - 1.86 Ga western Bergslagen ensialic belt is situated in the central part of Sweden, west of Stockholm (Fig. 1). It comprises a sequence of felsic volcanics of more than 10 km thickness, which is covered by a sedimentary sequence of at least 2 km thick, composed of shale or slate and conglomerates derived from the felsic volcanics (Sundius, 1923; Oen et al., 1982; Van der Velden et al., 1982; Baker, 1985a; Lundström, 1987, 1988; Baker et al., 1988). Lenses of carbonates, cherts, and iron  $\pm$  manganese deposits occur intercalated in the volcanic sequence. Continental tholeiitic dykes and sills (Hellingwerf and Oen, 1986) and rare spilitized basalts represent the mafic component, whereas granitic or granophyric intrusions together with felsic volcanics represent the felsic component of a bimodal magmatism (Van der Velden et al., 1982; Vivallo and Rickard, 1984; Lagerblad and Gorbatshev, 1985).

The stand of the supracrustal sequence is sub-vertical. Foliation is generally (sub-)parallel to the bedding of the supracrustals. A steeply dipping lineation occurs in the foliation plane. Carlon and Bleeker (1988) recognized at least two generations of folding in the Håkansboda region, about 5 km ENE of the Stripa mine. De Groot et al. (1988) related folding to the intrusion of granite diapirs.

The volcanics and the sediments were altered progressively to greenschist and then lower amphibolite facies mineral parageneses. Highly altered zones (up to several km wide) mark the conduits of hydrothermal circulation systems (e.g. Hjulsjö zones; Baker and De Groot, 1983; De Groot and Baker, 1992). Fluid inclusion studies by Damman (1989) indicate vein



**Figure 1.** Geological map of the West Bergslagen region, central Sweden (After Oen et al., 1982, and Baker and Drucker, 1988). Locations of skarns are marked on the map by solid stars; locations of granites and a pegmatite by open stars. For numbers of locations see table 2.

pressures of approximately 4 kbar, rapidly dropping to 2 - 1 kbar pressure ( $\approx$  assumed lithostatic pressure) during the hydrothermal alteration stage. Escape of hydrothermal fluids to the sea floor caused exhalative mineral deposits, while fluid circulation deeper in the crust caused reaction with carbonate horizons and mafic rocks resulting in skarn formation. Exhalative deposits buried in supracrustal rocks were in part remobilized and skarn altered by circulating fluids.

The skarns of the Bergslagen region can be divided in two major groups:

i) Fe  $\pm$  Mn skarns, and ii) W - Mo skarns. Intermediate types also exist. The skarns contain variable volumes of sulphides (base metal, Fe), distributed irregularly over the ore province.

Detailed descriptions of the skarns analysed for stable isotopes in this study can be found in Geijer and Magnusson (1944), Magnusson (1970), Hübner (1971), Grip (1978), Ohlsson (1979), Baker (1985c), Hellingwerf and Baker (1985), Oen (1987), Baker and Hellingwerf (1988a,b), Cheilietz (1988).

### **Geographic position of the Bergslagen region at 1.90-1.86 Ga and implications for isotopic meteoric water composition**

Paleomagnetic work (Poorter, 1981; Pesonen and Neuvonen, 1981; Pesonen et al., 1989; Mertanen et al., 1989) indicates that at 1.90 - 1.86 Ga ago the position of Bergslagen was between 30°N and the equator. This has implications for the isotopic composition of meteoric water from the Bergslagen region at that time. Meteoric water must have been relatively close to sea water (Dansgaard, 1964; Sheppard, 1986), with  $\delta D$  between -10 and -40‰ and  $\delta^{18}O$  between 2.5 and 6.3‰ lower than the sea water isotopic composition of that time. The coastal position of Bergslagen and the absence of mountains (e.g. De Groot et al., 1988) precludes isotopic shifts of the meteoric water from these values.

The proposed ancient isotopic composition of meteoric water differs markedly from the present composition of meteoric water in the Stripa region ( $\delta^{18}O = -11.5‰$  (Moser et al., 1989), and  $\delta D = -82‰$ , calculated after Craig (1961)).

### **Analytical methods**

Oxygen isotope analyses on silicate minerals were carried out following the method of Clayton and Mayeda (1963), using  $BrF_5$  as a reagent. A carbon-rod, doped with a platinum solution and heated externally with a resistance furnace to 670°C, converts  $O_2$  to  $CO_2$ . The  $CO_2$  has collected and measured on a VG Sira 24 mass spectrometer.

Most samples (75%) were analysed in duplicate or triplicate, giving a reproducibility better than  $\pm 0.2‰$ . A  $\delta^{18}O$  value of  $9.42 \pm 0.07‰$  ( $n = 23$ ) was obtained for the NBS-28 quartz standard over the period of measuring.

Analyses are corrected to the NBS-28 having a  $\delta^{18}O$  value of 9.60‰.

**Table 1.** List of mineral - water oxygen and hydrogen isotopic fractionations.

mineral	combined factors	references	$10^3 \ln \alpha$	temperature
<b>OXYGEN:</b>				
amphibole	quartz - hornblende	Bottinga and Javoy (1975)	$3.15(10^6/T^2)-0.3$	500-800
	quartz - water	Bottinga and Javoy (1973)	$4.1(10^6/T^2)-3.7$	500-800
	hornblende - water		$0.95(10^6/T^2)-3.4$	500-800
phlogopite (biotite)		Bottinga and Javoy (1973,1975)	$0.4(10^6/T^2)-3.1$	500-800
muscovite		Bottinga and Javoy (1973)	$1.90(10^6/T^2)-3.1$	500-800
chlorite		Wenner and Taylor (1971)	$1.56(10^6/T^2)-4.7$	50-500
serpentine		Wenner and Taylor (1971)	$1.56(10^6/T^2)-4.7$	50-500
talc		Noack et al. (1986)	$3.3(10^6/T^2)-4.8$	25- 95
epidote	quartz - zoisite	Matthews et al. (1983)	$1.56(10^6/T^2)$	400-700
	quartz - water	Matsuhisa et al. (1979)	$3.34(10^6/T^2)-3.34$	250-500
	zoisite - water		$1.78(10^6/T^2)-3.34$	--
<b>HYDROGEN:</b>				
amphibole		Graham et al. (1984)	-22.0	350-650
phlogopite (biotite)		Suzuoki and Epstein (1976)	$-21.3(10^6/T^2)-2.8$	> 400
		Hoefs (1987)	see Fig. 8, p. 29	≤ 400
muscovite		Hoefs (1987)	see Fig. 8, p. 29	250-800
chlorite		Graham et al. (1987)	$-3.7(10^6/T^2)-24$	500-700
serpentine		Taylor (1974)		25-400
talc	no fractionations published; see fractionations of phlogopite			
epidote	epidote - water	Graham et al. (1980)	$29.2(10^6/T^2)-139$	< 300
		Graham et al. (1980)	-36.0	300-650
	epidote - seawater	Graham and Sheppard (1980)	see Fig. 1, p. 240	350-550

Hydrogen isotope analyses on silicate minerals were carried out following a procedure modified from Bigeleisen et al. (1952).

Samples were degassed at 100°C to remove any adsorbed waters. At least one of each duplicate sample was degassed for longer than 3 hours, while the other was mostly degassed for only a short period. No differences larger than the normal analytical precision were found between the short and long degassed samples.

Water was extracted from the silicates using an external resistance furnace operating at 1300° to 1370°C. The liberated H<sub>2</sub>O was reacted with hot U-metal (665°C) to produce H<sub>2</sub> gas, which was collected on activated charcoal at liquid-N<sub>2</sub> temperature, and measured on a VG 903 triple collector mass spectrometer. Yields were measured manometrically before collecting H<sub>2</sub> in a sample tube. Parts of the extraction line which are in contact with H<sub>2</sub>O are heated to 90°-100°C to avoid adsorption.

A  $\delta D$  value of  $-66.1 \pm 0.4\%$  (n = 4) was obtained for the NBS-30 biotite standard over the period of measuring.

Some of the samples were analysed (by PdG) for H-isotopes at the CRPG, Vandoeuvre-lès-Nancy, France, where a slightly different analytical method was used. Samples, placed in molybdenum foil and platinum crucibles in evacuated glass tubes, were heated by an induction furnace to 1500°C. Instead of freezing on activated charcoal a Tupler pump was used to collect the H<sub>2</sub> gas. No heating to avoid H<sub>2</sub>O adsorption on the walls was applied here. The H<sub>2</sub> gas samples were measured on a VG - Micromass 602D double collector mass spectrometer.

Mineral separates were obtained by using a Frantz magnetic separator followed by hand picking. The mineral separates are 98% pure or better, except for Öb2 (quartz), Öb3 (albite), and St5 (talc,  $\pm$ pyrophyllite) samples, which contained higher percentages of impurities. Samples Sp1, Sp2 and Sp3 were treated with dilute hydrochloric acid to remove calcite.

All  $\delta^{18}O$  and  $\delta D$  values are related to the Vienna-SMOW standard and given in the standard per mil (‰) notation.

## Fractionation equations

### *I - Oxygen*

Mineral - water oxygen isotopic fractionations used in this study are summarized in table 1.

### *II - Hydrogen*

The amphibole - water fractionations of Graham et al. (1984) are used, taking into account the differences in tremolite, hornblende and arfvedsonite fractionations. Biotite or phlogopite - water fractionation factors are poorly known at low temperatures. The Suzuoki and Epstein (1976) curves are used above 400°C, and the curves by Hoefs (1987) below 400°C. Phlogopite (s.s.) shows a smaller fractionation than biotite, and is more comparable with muscovite (Suzuoki and Epstein, 1976). The Mg-contents

**Table - 2.** Hydrogen and oxygen isotopic values of minerals from skarns, the Dunderbo alteration zone and felsic intrusives from the western Bergslagen region.

No. sample: notes:	mineral:	$\delta D$	range[n]	$\delta^{18}O$	range[n]	
1 <i>Adamsgård</i> Adg 1	[W-skarn]					
	Mg-Hornbl	-89.2		5.02		
	Epidote	-29.2	0.9[2]	4.84	0.19[2]	
	Quartz			9.43	0.15[2]	
2 <i>Dunderbo</i>	[W-Fe-skarn]					
	Db 3	Tremolite	-83.7	1.1[2]	5.69	0.09[2]
	Db 4	Phlogopite	-44.7	1.8[3]	3.74	0.09[2]
	Db 5*	Phlogopite	-66.8	2.0[30]	2.84	0.01[2]
	Db 91-1A/OM	Edenite	-93.5		5.00	[BLOCK]
		Phlogopite	-69.5		3.00	[BLOCK]
	Db 91-1A	Edenite	-97.5	0.0[2]	4.90	0.08[2] [BLOCK]
		Phlogopite	-70.2		2.80	0.01[2] [BLOCK]
	Db 91-1B	Phlogopite	-71.9		3.00	0.14[2] [BLOCK]
	Db 91-1C	Edenite	-85.8	0.4[2]	5.05	[BLOCK]
	Db 91-1D	Na-Tremol	-89.5	0.8[2]	4.87	0.01[2] [BLOCK]
	Db 91-1E	Mg-Arfved	-91.8		4.89	[BLOCK]
	Db 91-1F	Edenite	-93.7		4.96	0.07[2] [BLOCK]
	3 <i>Hörken</i> Rr 19	[Fe-skarn]				
Hedenberg				4.71	0.03[2]	
4 <i>Hultagruvor</i> HW HG2	[W-Fe-skarn]					
	Heden/Aug			3.77	0.09[3]	
5 <i>Killingberget</i>	[Fe-skarn]					
	BJ 118	Edenite	-84.9	1.4[3]	3.80	0.01[2]
	BJ 118KB	Edenite	-98.0		4.74	0.02[2]
		Phlogopite	-76.1	0.6[3]	2.95	0.06[2]
6 <i>Sirsjöberg - Ösjöberg</i>	[Fe-skarn]					
	Sir 7	Quartz			7.59	0.05[2]
	Sir 8	Piemontite	-12.8	0.9[4]	2.86	0.00[2]
	Öb 2	Clinocllore	-87.9	0.8[3]	1.48	0.07[2]
		Quartz(dirty)			8.23	0.29[2]
	Öb 3	Mg-Hornbl	-90.1	0.3[2]	4.98	0.10[2]
		Albite(dirty)			6.15	
	Öb 4	Clinocllore	-80.0	0.4[2]	3.25	0.03[2]
	Öb 6	Quartz(light)			7.75	0.01[2]
		Quartz(dark)			7.40	0.05[2]

table - 2 (continued)

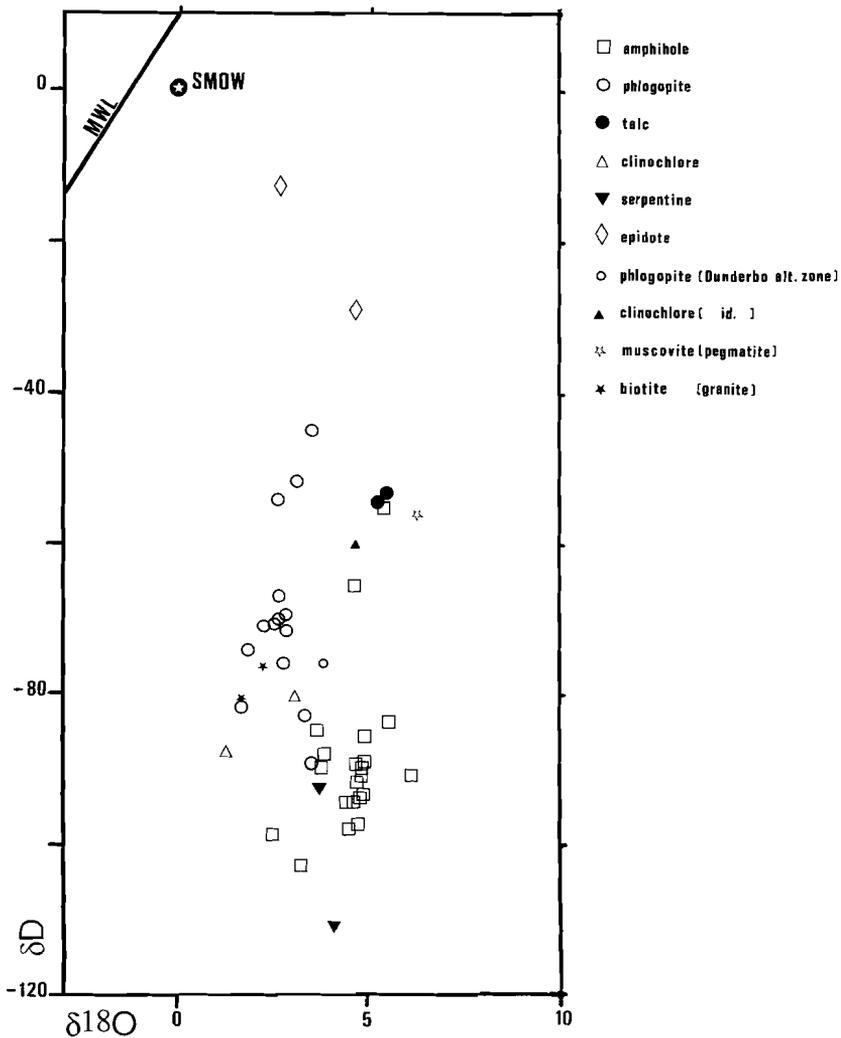
No.	sample: notes:	mineral:	$\delta D$	range[n]	$\delta^{18}O$	range[n]	
7	<i>Skropen</i>	[W-skarn]					
	Sk BJ1	Albite			7.91	0.07[2]	
	Sk BJ3	Albite			8.02	0.02[2]	
	Sk P1	Fe-Pargas			3.98	0.07[2]	
		Quartz			8.89	0.04[2]	
	Sk P2	Quartz			8.85	0.05[2]	
		Hedenberg			4.52	0.00[2]	
	Sk P3	Quartz			8.80	0.01[2]	
	Sk P4	Quartz			8.92	0.07[2]	
	Sk P7	Diopside			4.83	0.04[2]	
8	<i>Sparrbergsgruvan</i>	[W-Fe-skarn]					
	Sp 1	Chrysotile	-92.5	1.1[2]	3.88	0.23[3]	
	Sp 2	Pargasite	-90.2	0.9[3]	3.91	0.09[2]	
	Sp 3	Lizardite	-110.5	2.0[2]	4.24	0.12[2]	
	Sp BJ1	Quartz			10.51	0.01[2]	
	Sp 91-1A/I	Eden/Parg	-91.0		6.28	0.18[2]	[ALT]
	Sp 91-1A/II	Phlogopite	-83.0		3.51		[ALT]
	Sp 91-4	Phlogopite	-88.4		3.73	0.04[2]	[ALT]
9	<i>Ställdalen</i>	[W-skarn]					
	W 71	Fe-Pargas	-98.9	0.9[2]	2.62	0.07[2]	
		Quartz			7.70	0.09[4]	
	W P1	Mg-Hornbl	-103.1	0.4[3]	3.37	0.01[2]	
	W P5	Albite			7.92	0.03[2]	
	W P7	Hedenberg			3.55	0.10[2]	
10	<i>Stolpberget (Sikfors)</i>	[Fe-skarn]					
	St 3	Edenite	-55.2	1.6[4]	5.58	0.07[2]	
	St 4	Phlogopite	-54.1	1.7[3]	2.84	0.05[2]	
	St 5	Talc(Pyro)	-54.4	0.9[3]	5.42	0.03[2]	
	St 6	Phlogopite	-51.6	1.1[4]	3.28	0.02[2]	
	St 91-1A	Phlogopite	-70.7		2.71		[ALT]
	St 91-2	Na-Tremol	-65.5		4.83		[ALT]
		Talc	-53.2	0.2[2]	5.60		[ALT]
11	<i>Timansberg</i>	[Fe-skarn]					
	Tb 91-1	Phlogopite	-71.1		2.43		[ALT]
	Tb 91-2	Mg-Arfved	-88.3		4.04	0.01[2]	[ALT]
		Phlogopite	-81.8		1.86	0.07[2]	[ALT]

table - 2 (continued)

No. sample: notes:	mineral:	$\delta D$	range[n]	$\delta^{18}O$	range[n]
<i>Dunderbo alteration zone</i>					
12 <i>Yxsjöberg</i>	<i>[W-skarn]</i>				
Yx AM1	Edenite	-91.0	0.9[4]	4.97	
Yx AM2	Hedenberg			4.11	
	Quartz			9.11	0.03[2]
Yx HW1	Mg-Hornbl	-94.5		4.64	
Yx HW2	Phlogopite	-74.1		2.03	
	Quartz			7.93	0.06[2]
Yx HW3	Mg-Hornbl	-94.5		4.58	0.09[2]
<i>Dunderbo alteration zone</i>					
GP 1L2	Phlogopite	-76.1		3.99	
GP 1L3	Clinochlore	-60.0	1.9[2]	4.86	
<i>Granites</i>					
13 <i>Västra Gråshöjden Granite</i>					
VG 4	Quartz			8.13	0.10[2]
	Microcline			6.88	0.10[2]
	Biotite	-76.7		2.45	
GP WG2	Quartz			8.81	
14 <i>Hjulsjö Granite</i>					
BJ 51	Quartz			8.92	
BJ 392	Quartz			8.79	
	Biotite	-80.9		1.82	0.07[2]
<i>Pegmatite</i>					
15 <i>Reboda Pegmatite</i>					
Rb Pegm	Muscovite	-56.3		6.44	0.19[2]

The  $\delta D$  and  $\delta^{18}O$  are given in per mil relative to the SMOW standard. Range defines the deviation from the reported value if more than one measurement was made. The number of measurements is given in brackets. \*: Sample Db 5 was used as laboratory standard for hydrogen isotopic analysis, and is therefore measured many times. BLOCK refers to samples of the single block from the Dunderbo skarn, which was studied for possible hydrogen exchange of modern meteoric water with the rock. ALT refers to samples which are collected as weathered as possible, contrary to the other samples which were collected as fresh as possible. The numbers in the first column refer to locations as given on figure 1.

Mg-Hornbl = Mg-Hornblende; Na-Tremol = Na-Tremolite; Mg-Arfved = Mg-Arfvedsonite; Heden/Aug = Hedenbergite/Augite; Fe-Pargas = Fe-Pargasite; Hedenberg = Hedenbergite; Eden/Parg = Edenite/Pargasite; Talc(Pyro) = Talc(Pyrophyllite).

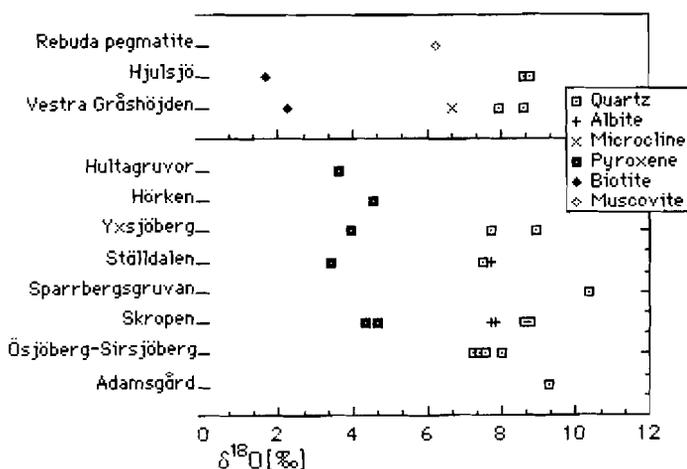


**Figure 2.** A  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  diagram showing the isotopic compositions of minerals from skarns of the western Bergslagen region. Isotopic values of samples from the alteration zone surrounding the Dunderbo skarn, from two granites and from a pegmatite are also included. SMOW = Standard Mean Ocean Water; MWL = Meteoric Water Line (Craig, 1961). The delta values are in per mil (‰) relative to the SMOW standard.

of the phlogopites were not analysed; therefore biotite fractionation factors are used, noting that the phlogopite fractionations may be 5 to 10‰ smaller. See table 1 for a summary of the mineral - water hydrogen isotopic fractionations.

### Rock sampling

Since most of the mining activity in the region stopped a long time ago, it is impossible to obtain fresh, *in situ* samples. Nearly all the mining pits and shafts are flooded and the only way to collect samples is by searching the dumps. All samples were taken from old mine dumps, except for samples from the Yxsjöberg mine and samples from the Ställdalen site (outcrop). Care was taken to select samples as fresh as possible, with the exception of those samples which were taken to study the effect of present weathering (see results and discussion).



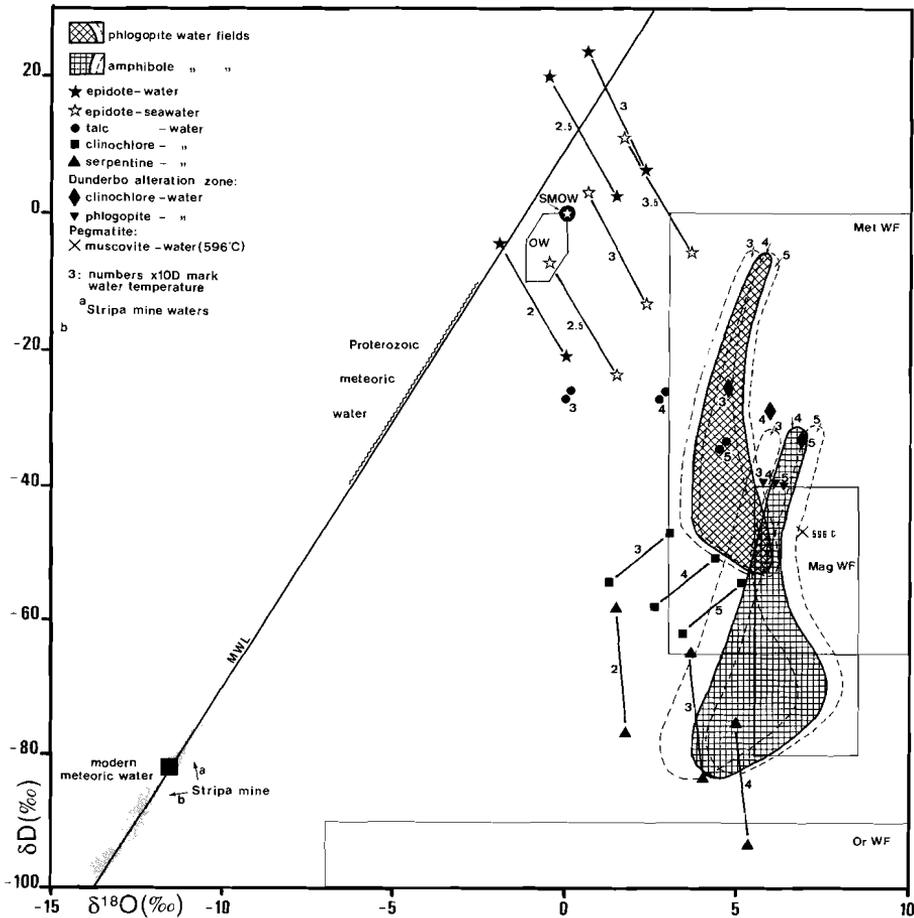
**Figure 3.** Oxygen isotopic compositions of quartz, pyroxene and albite mineral separates from skarns, and quartz, microcline, muscovite and biotite from granites and a pegmatite.

### Results

Hydrous skarn minerals were analysed both for hydrogen and oxygen isotopes. Results are given in table 2 and figure 2.  $\delta^{18}\text{O}$  values of all minerals are concentrated in a rather narrow range of 1 to 6‰, while the  $\delta\text{D}$  values show a wide range of nearly 100‰, subdivided into smaller ranges for separate minerals: amphibole: -55 to -105‰, phlogopite: -42 to -90‰, serpentine: -92 to -111‰, talc: -53 to -55‰, epidote: -13 to -30‰.

$\delta^{18}\text{O}$  values of the non-hydrous minerals quartz, pyroxene and feldspar are shown in figure 3. Quartz, pyroxene and albite show ranges of 7.4 to 10.3‰, 3.4 to 4.7‰ and 7.7 to 7.8‰ respectively.

Samples from the Hjulsjö (Baker, 1985b) and Västra Gråshöjden (Baker et al., 1987) granites and from the Rebuda pegmatite were analysed to obtain



**Figure 4.** A  $\delta^{18}\text{O}$  versus  $\delta\text{D}$  diagram for fluids calculated at a temperature range of  $200^\circ$  -  $500^\circ\text{C}$  from isotopic values of skarn minerals, minerals from the Dunderbo alteration zone and a pegmatite sample (no. 15 of Fig. 1 and Table 2). Phlogopite and amphibole fluid fields, and separate points for epidote, talc, clinocllore, and serpentine fluid values, connected by tie lines for the same temperature, are shown. Points for clinocllore and phlogopite from the Dunderbo alteration zone, and a muscovite from a pegmatite, which is in equilibrium with pegmatite quartz at  $596^\circ\text{C}$ , are also shown.

Marked boxes are: OW = Ocean Water Field; Met WF = Metamorphic Water Field; Mag WF = Magmatic Water Field; Or WF = Organic Water Field (All water fields after Sheppard, 1986). MWL = Meteoric Water Line (Craig, 1961); SMOW = Standard Mean Ocean Water. The Proterozoic meteoric water range marked on the MWL is estimated from Dansgaard (1964) for coastal low latitude regions on earth. Modern meteoric water and the fields for the Stripa mine dripping waters (a) and groundwaters (b) were obtained from Moser et al. (1989). The isotopic values are in per mil relative to the SMOW standard.

**Table - 3.** Calculated oxygen isotopic values of waters in equilibrium with quartz, albite and pyroxene from western Bergslagen skarns.

sample	$\delta^{18}\text{O}$	equilibrium water $\delta^{18}\text{O}$ values in ‰.				
		mineral	temperature:			
		300	400	500	600°C	
<b>QUARTZ:</b>						
Adg 1	9.43	0.59	4.04	6.24	7.74	
Sir 8	7.59	-1.23	2.21	4.41	5.90	
Öb 2	8.23	-0.59	2.85	5.05	6.54	
Öb 6 [light]		7.75	-1.07	2.39	4.39	6.06
Öb 6 [dark]		7.40	-1.41	2.02	4.22	5.71
Sk P1	8.89	0.06	3.50	5.71	7.20	
Sk P2	8.85	0.02	3.46	5.67	7.16	
Sk P3	8.80	-0.03	3.42	5.62	7.11	
Sk P4	8.92	0.09	3.53	5.74	7.23	
Sp BJ1	10.51	1.67	5.12	7.32	8.81	
W 71	7.70	-1.12	2.32	4.52	6.01	
Yx AM2		8.11	0.28	3.73	5.93	7.42
Yx HW3		7.93	-0.89	2.55	4.75	6.24
<b>ALBITE:</b>						
Sk BJ1	7.91	2.05	4.68	6.36	--	
Sk BJ3	8.02	2.16	4.79	6.47	--	
W P5	7.92	2.06	4.69	7.37	--	
<b>PYROXENE:</b>						
Rr 19	4.71	4.08	5.28	6.08	6.56	
HW HG2		3.77	3.14	4.34	5.10	5.62
Sk P2	4.52	3.89	5.09	5.85	6.37	
Sk P7	4.83	4.20	5.40	6.16	6.68	
W P7	3.55	2.92	4.12	4.88	5.40	
Yx AM2		4.11	3.48	4.68	5.44	5.96

$\delta^{18}\text{O}$  values for waters in equilibrium with quartz, albite and pyroxene are calculated for 300, 400, 500 and 600°C respectively (fractionations from Bottinga and Javoy, 1973, 1975). All values are in per mil (‰) relative to the SMOW standard. -- = not calculated. Compared with the mean  $\delta^{18}\text{O}$  water value obtained from hydrous skarn minerals (5.5‰), it may be concluded that either quartz and pyroxene formed at a 450 - 600°C and a 400 - 600°C temperature range respectively, and albite around 450°C, or quartz and pyroxene formed in equilibrium with a fluid with lower oxygen isotopic values, while fluids forming albite are in reasonable accordance with those forming the hydrous minerals.

representative magmatic isotope values. Results are shown in table 2 and on figures 2 and 3.

The isotopic compositions of water in equilibrium with amphiboles, phlogopites, talc and serpentines, at temperatures of 300°, 400°, and 500°C, were calculated and are shown in figure 4. The same figure shows water in isotopic equilibrium with serpentine at 200°C and waters in equilibrium with epidotes between 200° and 350°C.

## Discussion

Skarn mineralization in the western Bergslagen region probably took place over a temperature interval from 600 to 200°C. Fluid inclusion thermometry on pegmatite related skarns of the Gåsborn region (Damman, 1989) gave an upper limit of 560°C, a temperature confirmed by thermometry based on mineral compositions (Outhuis, 1989). This temperature is assumed to be an upper limit for skarn formation in the western Bergslagen region. Lower temperatures were found in alteration zones, which are interpreted as conduit zones for skarn forming fluids (Baker and De Groot, 1983; De Groot and Baker, 1992) and by fluid inclusion thermometry (Van Campenhout, in: Helmers, 1984). Thermodynamic calculations (De Groot, 1990) suggest temperatures between 400° and 550°C for these conduit zones. The mineralogy of the skarns is related to the temperature range in which they formed. Most skarns are formed between 300° and 500°C, and comprise amphibole, phlogopite, Mg-rich chlorite, and quartz as the major silicate minerals and calcite/dolomite (e.g. Adamsgård, Dunderbo, Killingberget, Sirsjöberg-Ösjöberg, Sparrbergsgruvan, Stolpberget (Sikfors), Timansberg). Skarns including pyroxene and garnet (e.g. Hörken, Hultagruvor, Skropen, Ställdalen, Yxsjöberg) formed at higher temperatures (400° - 600°C). Epidote (Adamsgård, Sirsjöberg-Ösjöberg) in Bergslagen could both be formed as an early or late phase at relatively low temperatures. A lower limit of 200°C for epidotes is suggested by Matthews et al. (1983). Serpentine minerals (chrysotile, lizardite) of the Sparrbergsgruvan also formed at relatively low temperatures, but their retrograde character excludes them from the major skarn history.

The mean  $\delta^{18}\text{O}$  value for water in equilibrium with hydrous skarn minerals (Fig. 4) over the temperature range of 300° - 500°C is 5.5‰, with a total range of 4.2 - 6.7‰. This  $\delta^{18}\text{O}$  is at the lower end of the  $\delta^{18}\text{O}$  range of 5 - 9‰, which is found for fluids in many skarns related to felsic magmatic rocks (Taylor, 1987).

Oxygen isotopic values of fluids in equilibrium with quartz, albite and pyroxene are calculated for 300°, 400° and 500°C, and are shown in table 3. Compared with the hydrous silicates, the quartz and pyroxene must have either formed at higher temperatures (450° - 600°C and 400° - 600°C respectively) or at similar temperatures but from fluids having lower  $\delta^{18}\text{O}$

values. Albite is formed at approximately the same temperatures and from the same type of fluids as the hydrous silicates.

Differences in  $\delta^{18}\text{O}$  of the calculated skarn-forming fluids may be explained by:

- a) fluids which had different interaction histories passing through the supracrustal and/or intrusive rocks before reaching the site of skarn formation,
- b) changes of temperature during skarn formation,
- c) uncertainty in temperature estimates of skarn mineral formation,
- d) disequilibrium between minerals and fluids in the skarn forming system.

In spite of these variations we may conclude that much of the high-temperature alteration took place by interaction with a fluid which had a  $\delta^{18}\text{O}$  close to 5.5‰. This is in contrast with the hydrogen isotope values of the fluids, which show quite a wide range of more than 90‰.

### The highest $\delta\text{D}$ values

The highest  $\delta\text{D}$  values of the ore-forming fluids, around -15‰ (if epidote is excluded) can be derived from various sources of water. Metamorphic - or connate water is an unlikely source, because the supracrustal rocks of the western Bergslagen region are mainly felsic volcanics in a post consolidation state, which are considered poor carriers of such fluids (Defenition of fluids after Sheppard, 1986).

The  $\delta\text{D}$  values of around -15‰ are higher than those considered to be normal for magmatic fluids. Some magmatic fluid could have been mixed with other fluids, but the trends of the skarn fluids in figure 4 show no evidence for such mixing. Sea water or meteoric water are the more likely sources of the skarn-forming fluids.

The fluids in equilibrium with silicates have been calculated as pure waters, while sea water, a possible fluid source, is a saline solution. The salinity of any fluid probably increases after prolonged exchange with rocks in a hydrothermal system. The salinity does not drastically change the oxygen isotope fractionation in the system (Truesdell, 1974; Stewart and Friedman, 1975; Koehler et al., 1981; Horita and Matsuo, 1986), but it may decrease the hydrogen isotopic fractionation by 7‰ or more (Stewart and Friedman, 1975; Horita and Matsuo, 1986; Horita and Gat, 1988). Sheppard (1981) reports lower fractionations in saline fluids only at temperatures below 550°C. Saline fluids in equilibrium with the skarn-minerals must be corrected for this effect and the calculated  $\delta\text{D}$  of waters may be decreased by  $\leq 7\%$ . The  $\delta\text{D}$  of the corrected fluids in the Bergslagen skarns is then around -20‰, which is 15 to 20‰ lower than modern sea water.

Mg-enrichment in altered rocks provides the strongest evidence for sea water involvement in the hydrothermal systems (Baker and De Groot, 1983). Additional support for a sea water source for the skarn-forming

fluids is given by the  $\delta D$  of epidote, which at 200° - 350°C is in equilibrium with fluids which have a  $\delta D$  of about zero (Fig. 4). These fluid values are comparable to the isotopic compositions of fluids calculated from epidotes in the 2.65 Ga old Canadian Shield (Kerrick, 1987). These Canadian Shield fluids probably represent modified Archean seawater (Kerrick, 1987). The talc  $\delta^{18}O$  values (5.24 and 5.42‰) from the Stolpberget skarn are in the same range as talc  $\delta^{18}O$  values (5.2 to 6.6‰) found in a submarine hot fluid (300°C) discharging system (Costa et al., 1980).

### **Proterozoic isotopic sea water composition**

The isotopic composition of Proterozoic sea water cannot be measured directly; it can only be derived from materials that exchanged with Proterozoic sea water, or from (undisturbed) fluid inclusions in minerals formed in contact with this sea water. The oxygen isotopic composition of ancient sea water has been more extensively reviewed than the hydrogen isotopic composition. Oxygen isotopic compositions from the Archean onwards, were probably not drastically different from the present value and have been buffered by sea floor alteration at oceanic ridges (Muehlenbachs and Clayton, 1976; Gregory and Taylor, 1981; Muehlenbachs, 1986; Gregory, 1991). The hydrogen isotopic value of sea water in Precambrian times is poorly known. Sheppard (1986) tentatively proposed that  $\delta D$  values of ancient oceans varied between 0 and -25‰. If escape of hydrogen gas from the atmosphere into space is considered, we may conclude that the sea water  $\delta D$  must have increased with time (e.g. Holland, 1984; Knauth and Roberts, 1991). The magnitude of this escape, which is related to the atmospheric water content, was negligibly small compared with the total water content on the earth's surface (Kasting and Ackerman, 1986). Mantle degassing, bringing hydrogen gas and water contained in mantle derived melts or minerals (Fukai, 1984; Bell, 1992; Bell and Rossman, 1992; Bai and Kohlstedt, 1992) to the earth's surface, may also have an effect on the  $\delta D$  balance of the hydrosphere.

Fluids calculated for skarn minerals with the highest  $\delta D$  values could either be derived from sea water or from Proterozoic meteoric waters circulating through the crust. Fluids from both sources are modified in oxygen isotopic composition by exchange with felsic volcanic and intrusive rocks in the hydrothermal systems, as generally is reported for deep crustal fluids (e.g. Sheppard, 1986). The fluids show increased  $^{18}O$  while the exchanged minerals are decreased in  $^{18}O$ . Hydrogen isotopes do not show such isotope shifts since they are dominated by the fluids under the high water/rock ratios in the Bergslagen hydrothermal systems (Baker and De Groot, 1983). The consequences of the low latitude position of the Bergslagen region for the isotopic composition of meteoric waters has already been discussed in

an earlier section. If we assume that the oxygen isotopic composition of the 1.9 - 1.8 Ga sea water was similar to the present value (see above), and if we also accept a  $\delta^{18}\text{O}$  range of -2.5 to -6‰ for low latitude meteoric waters (Dansgaard, 1964), than a  $\delta\text{D}$  range of -10 to -40‰ is obtained for meteoric waters if the oceanic  $\delta\text{D}$  is similar to the present value (Craig, 1961). Considering the highest  $\delta\text{D}$  values of the calculated fluids and assuming a sea water or meteoric water source for these fluids, it may be concluded that the Proterozoic  $\delta\text{D}$  value of sea water was < 20‰ lower than the present day value.

No conclusion can be drawn regarding the Proterozoic oxygen isotopic composition of sea water on the basis of our results.

### **The low $\delta\text{D}$ values**

The large range in  $\delta\text{D}$  values from -10‰ to -100‰, without a concomitant change in  $\delta^{18}\text{O}$ , is most simply explained by mixing of two end member fluids. Candidates for the high- $\delta\text{D}$  fluids have been discussed above, but it is not so simple to find suitable candidates for the low- $\delta\text{D}$  fluids. The  $\delta\text{D}$  values are too low for magmatic fluids, and Proterozoic meteoric fluids are excluded because of the low latitude geographical position of Bergslagen, implying relatively high isotopic values for meteoric fluids as discussed in earlier sections.

Organic fluids are possible (Sheppard, 1986; Charef and Sheppard, 1987) but unlikely for this highly active volcanic region. However, the occurrence of stromatolites (Boekschoten et al., 1988) and of possible bacteriological activity in manganese deposition (Oen et al., 1986) show that organic material existed and include organic fluids as a hypothetical source.

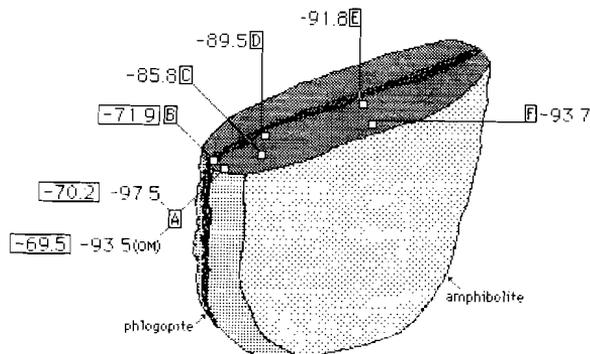
No other commonly accepted sources of low- $\delta\text{D}$  fluids are known.

### **Exchange with present day meteoric water**

Low- $\delta\text{D}$  mineral values are tentatively explained by exchange of skarn minerals, formed originally in equilibrium with the high- $\delta\text{D}$  fluids, with relatively low- $\delta\text{D}$  (and  $\delta^{18}\text{O}$ ) present day meteoric waters. Shifts in  $^{18}\text{O}$  correlating with the hydrogen isotopic shift are not found. Hydrogen isotopes, however, exchange much more easily than oxygen isotopes (e.g. Taylor, 1977), and therefore the lack of  $^{18}\text{O}$  shifts does not exclude this explanation of the low  $\delta\text{D}$  values.

To test this exchange theory, fresh and severely altered samples were compared (Table 4). Careful separation of minerals from the respective samples was made to make sure that the selected minerals were not altered

into weathering products. All samples were controlled by X-ray diffraction for their mineralogical composition. Also, in the weathered samples, organic material was carefully avoided during hand picking of the mineral separates.



**Figure 5.** The lower half of a large amphibolite block of the Dunderbo skarn. The block is 30 cm thick and has a diameter of 70 cm. A phlogopite vein (in black) cuts through the block, dividing it in sheets of 10 and 20 cm thick. Sample points are marked by squares in this section, and are connected by lines with their sample number and hydrogen isotopic values. Normal numbers are amphibole, and numbers in boxes are phlogopite  $\delta D$  values. Sample A is divided in two sub-samples; the unmarked sample is collected from the solid edge of the block and the sample marked with (OM) is scraped from the same side as loose and weathered material.

Results on a large amphibolite block from the Dunderbo skarn cut by a phlogopite vein are shown in figure 5 and tables 4 and 5. Samples were collected from the most weathered outside and the freshest inside of the block. Sample "a" is split into two subsamples; one sample scraped from the surface and consisting of loose material (marked OM), and the other sample from the solid edge of the block at about the same place.  $\delta^{18}O$  values are very consistent throughout the block. Phlogopite  $\delta D$  values are also similar throughout the block, but are lower than the  $\delta D$  of phlogopites in fresh samples from the same skarn. Amphibole  $\delta D$  values show a difference of 10‰ between the outside (-97.5 to -93.5‰) and the inside (-89.5 to -85.8‰) of the block. An intermediate amphibole  $\delta D$  (-91.8‰) is found near the phlogopite vein in the centre of the block. The highest value in central part of the block is comparable with the value of a fresh sample (Db 3) from the same skarn.

Similar relations between low- $\delta D$  in severely weathered samples and higher  $\delta D$  in fresh samples are found in several skarns (Table 4). Phlogopite and amphibole in the Stolpberget skarn show  $\delta D$  shifts of 15 - 20‰ and 10‰ respectively. In contrast, both weathered and fresh amphiboles and talcs,

from Sparrbergsgruvan and Stolpberget respectively, show a similar  $\delta D$ . A phlogopite sample from the alteration zone surrounding the Dunderbo skarn shows the same value as altered phlogopites within the skarn, and thus seems to have exchanged hydrogen with the low deuterium meteoric water. A clinocllore sample from the same alteration zone, however, has a high- $\delta D$  and clearly retained its original isotopic composition. Two other clinocllore samples from the Ösjöberg skarn have probably been shifted towards lower  $\delta D$  values. Figure 6 clearly illustrates the isotopic relations between fresh and altered samples.

TABLE - 4;  
Hydrogen isotopic values of fresh and weathered samples

FRESH	WEATHERED
<b>DUNDERBO</b>	
Db 3, amph. [-83.7]	Db 91-1A/OM, amph. [-93.5]
Db 91-1C, amph. [-85.8]	Db 91-1A, amph. [-97.5]
Db 4, phlog. [-44.7]	Db 91-1E, amph. [-91.8]
Db 5, phlog. [-66.8]	Db 91-1F, amph. [-93.7]
	Db 91-1A/OM, phlog. [-69.5]
	Db 91-1A, phlog. [-70.2]
	Db 91-1B, phlog. [-71.9]
	Db 91-1D, amph. [-89.5]
<b>STOLPBERGET</b>	
St 3, amph. [-55.2]	St 91-2, amph. [-65.5]
St 4, phlog. [-54.1]	St 91-1A, phlog. [-70.7]
St 6, phlog. [-51.6]	St 91-2, talc [-53.2]
St 5, talc [-54.4]	
<b>SPARRBERGSGRUVAN</b>	
Sp 2, amph. [-90.2]	Sp 91-1A/I, amph. [-91.0]
	Sp 91-1A/II, phlog. [-83.0]
	Sp 91-4, phlog. [-88.4]
<b>TIMANSBERG</b>	
	Tb 91-1, phlog. [-71.1]
	Tb 91-2, phlog. [-81.8]
	Tb 91-2, amph. [-88.3]

amph. = amphibole; phlog. = phlogopite. Hydrogen isotopic values ( in brackets ) are in per mil.

**Table - 5.** Hydrogen and oxygen isotopic values and relative water contents of amphibole and phlogopite samples from W. Bergslagen skarns.

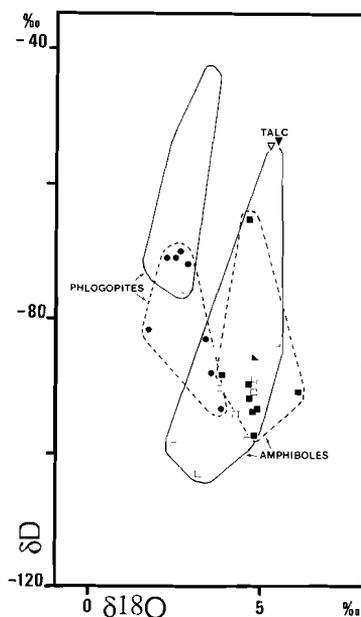
AMPHIBOLE:			PHLOGOPITE:				
samples	$\delta D$	$\delta^{18}O$	H <sub>2</sub> yield mb/mg	samples	$\delta D$	$\delta^{18}O$	H <sub>2</sub> yield mb/mg
Db 3	-83.7	5.69	8.08	Db 4	-44.7	3.74	8.65
Db 91-1A/OM	-93.5	5.00	6.63	Db 5	-66.8	2.84	9.79
Db 91-1A	-97.5	4.90	6.73	Db 91-1A/OM	-69.5	3.00	13.88
Db 91-1C	-85.8	5.05	5.37	Db 91-1A	-70.2	2.80	11.52
Db 91-1D	-89.5	4.87	6.36	Db 91-1B	-71.9	3.00	10.30
Db 91-1E	-91.8	4.89	6.01	BJ 118KB	-76.1	2.95	9.22
Db 91-1F	-93.7	4.96	5.88	Sp 91-1A/II	-83.0	3.51	11.31
BJ 118	-84.9	3.80	8.15	Sp 91-4	-88.4	3.73	21.50
BJ 118KB	-98.0	4.74	6.53	St 4	-54.1	2.84	8.36
Sp 2	-90.2	3.91	12.70	St 6	-51.6	3.28	8.61
Sp 91-1A/I	-91.0	6.28	6.16	St 91-1A	-70.7	2.71	9.52
W P1	-103.1	3.37	6.77	Tb 91-1	-71.1	2.43	11.90
St 3	-55.2	5.58	11.55	Tb 91-2	-81.8	1.86	17.19
St 91-2	-65.5	4.83	6.09	Yx HW2	-74.1	2.03	8.51
Tb 91-2	-88.3	4.04	6.18				
Yx AM1	-91.0	4.97	4.27				
Yx HW1	-94.5	4.64	3.52				

Values in italic writing stand for weathered samples (solid symbols in figure 7) and values in normal writing for fresh samples (open symbols in figure 7). H<sub>2</sub>yield represents a value based on the yield-measurement during hydrogen isotopic analyses. The yield was recorded in millibars in a constant volume and normalized against atmospheric pressure expressed in millibars. The water content of the minerals is expressed in millibars per milligram (mb/mg).

Samples from the Yxsjöberg mine are all in the low- $\delta D$  range, although they look fresh and were collected from a part of the mine which was then in operation. The water contents of these samples are relatively low (Table 5; Fig. 7) and they are outside the fields characteristic for the weathered samples. Meteoric water has probably circulated deep into the mine and the wall rocks, and may have exchanged hydrogen isotopes with the minerals in the rocks. From a study on the Stripa mine (Moser et al., 1989) it is known that present day meteoric waters circulate deep into the mine, moving through the wall rocks and dripping down the shafts. The migration of meteoric water into the rocks is drastically enhanced by mining activity (Frape et al., 1984; Moser et al., 1989, and references therein).

Oxygen and hydrogen isotopic exchange in clay minerals and serpentines is extensively reported (e.g. Lawrence and Taylor, 1972; Wenner and Taylor, 1973, 1974; O'Neil, 1987; Savin, 1990; Yui and Jeng, 1990).

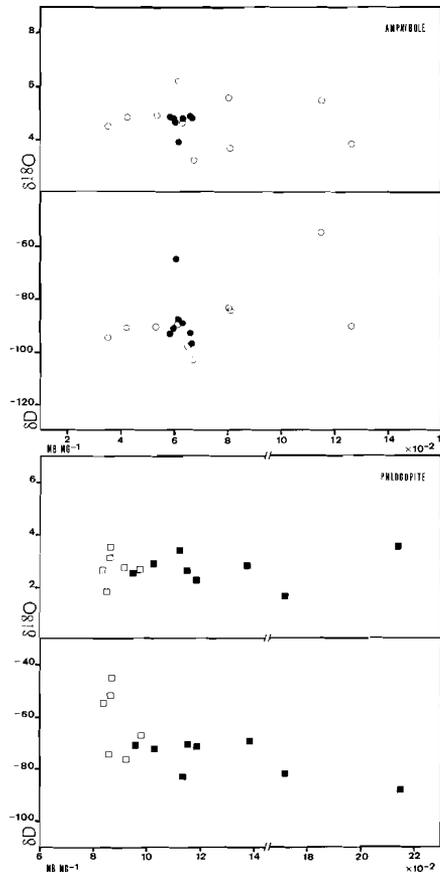
However, oxygen and hydrogen isotopic exchange between other silicate minerals and water at low temperatures is generally considered to be negligible. We know of only one report describing a  $\delta D$  and  $\delta^{18}O$  shift during weathering of biotite (Clauer et al., 1982). These authors observed that although X-ray diffraction, chemical analysis, and microscopic study show no change in the mineral, a negative  $\delta D$  shift of about  $-25\text{‰}$  and a positive  $\delta^{18}O$  shift of  $1.5 - 3\text{‰}$  occur during weathering. The only observed change is an increase in the water content of the biotite, which correlates with the isotope shift.



**Figure 6.** An oxygen versus hydrogen isotope diagram showing the difference between fresh (open symbols) and altered (solid symbols) mineral samples. The half open symbol is an intermediate sample. Circles are phlogopites, squares are amphiboles and triangles are talc. Fresh samples are encircled by a solid line and altered samples by a broken line. Isotopic values are in per mil relative to the SMOW standard.

Yield measurements during the hydrogen isotope analyses give information on the water contents of the minerals analysed. The yields are measured as millibars  $H_2$  gas at a constant volume (precision  $\pm 10\%$ ) and the results are given in table 5.

Figure 7 shows the hydrogen yields ( $mbar H_2$  per  $mgr$  mineral:  $mb.mg^{-1}$ ) plotted against  $\delta D$  and  $\delta^{18}O$ . The fresh phlogopites have a relative wide  $\delta D$  range and a narrow range of low water contents, while the weathered phlogopites have a narrow and low  $\delta D$  range and a wide range of water



**Figure 7.** Diagrams of water content (expressed in mb. mg<sup>-1</sup>) versus δD and δ<sup>18</sup>O values of phlogopites and amphiboles. Phlogopites are squares and amphiboles are circles in the diagram. Open symbols are fresh- and solid symbols are altered samples. For further explanation see text.

contents which are substantially higher than those of the fresh phlogopites. Oxygen isotopic compositions of the phlogopites show no relation to the water contents.

A remarkably wide range of water contents is found in fresh amphiboles, while altered amphiboles show a narrow range of 6 to 7.10<sup>-2</sup> mb.mg<sup>-1</sup> (Fig. 7). No correlation is found between the water content of the amphiboles and either δD or δ<sup>18</sup>O. The amphiboles, in contrast with the phlogopites, do not

seem to have increased in water content during alteration. The wide scatter of the water contents in fresh amphiboles may be related to local differences in conditions of amphibole formation in the skarns or, alternatively to a wide range of F or Cl replacing the OH-group in the minerals. A possible explanation for the narrow range of water contents in the altered amphiboles is removing F or Cl from the minerals. It is possible that this narrow range represents the equilibrium content of water in the structure of the amphiboles under low temperature weathering conditions, which were very uniform over the different skarn sites.

Fluid-amphibole or fluid-phlogopite oxygen isotope fractionations at ambient temperature are not known. If a comparison is made with hydrated minerals formed at low temperatures, e.g. clay minerals, then a large positive fractionation of 20 to 40‰ is expected. The variation in water content of the amphiboles and phlogopites is very large (up to more than 140%). Coupled with such large variations in water content we expect large oxygen isotopic shifts in these minerals. However, no large  $\delta^{18}\text{O}$  shifts are found in the altered skarn minerals. The phlogopites show a systematic decrease in  $\delta\text{D}$  in the altered samples, suggesting hydrogen exchange between the mineral and modern meteoric fluid, while the oxygen is not exchanged. In contrast to the phlogopites, the amphiboles show similar  $\delta\text{D}$  in both fresh and altered samples. This is possibly explained by the smaller water contents of the amphiboles compared to the phlogopites, so that the influence of fluid exchange is detected easier. No other satisfactory explanation for this observation is found.

Fresh and altered mineral pairs from the same location show  $\delta\text{D}$  differences not exceeding 20‰, but the total  $\delta\text{D}$  range in the skarns is much larger. Single mineral isotopic fields cover only part of the hydrogen isotopic range. The various water fields in equilibrium with different minerals (Fig. 4) may be explained by the different water contents of the minerals and differences in mineral resistivity against exchange with fluids.

### **Intrusives**

Minerals from two granites and a pegmatite from the western Bergslagen area were analysed for oxygen and hydrogen isotopes in order to characterize the magmatic fluid composition. Coexisting quartz and microcline of the Västra Gråshöjden granite are in isotopic equilibrium at 600°C, but biotite - quartz gives a rather low oxygen isotope temperature of 495°C. Biotite of the Hjulsjö granite gives even a lower temperature, and is considered to be out of equilibrium with the bulk granite. These biotites probably exchanged isotopes with a hydrothermal fluid; they plot in the same  $\delta\text{D} - \delta^{18}\text{O}$  field as the phlogopites in the skarns (see Fig. 2 and 4).

Magmatic fluids are best characterized by the muscovite (Rb Pegm; Table 2). This sample is taken from the center of a large muscovite crystal, and

interaction with hydrothermal fluids after its crystallization is not expected. This muscovite is in equilibrium with quartz from the granites at 596°C, and at this temperature it defines a fluid  $\delta D$  and  $\delta^{18}O$  composition in the middle top part of the magmatic water field (Fig. 4);  $\delta D$  and  $\delta^{18}O$  values to be expected in felsic intrusives (Taylor, 1974).

### Conclusions

Minerals of a selection of Fe  $\pm$  Mn and W - Mo skarns from western Bergslagen were analysed for hydrogen and oxygen isotopes. Fluids in isotopic equilibrium with the skarn minerals were calculated for appropriate temperatures of skarn formation. A wide range of hydrogen isotope values and a narrow range of oxygen isotope values is obtained for these fluids.

High- $\delta D$  fluids, corrected for the effects of salinity on isotopic fractionations, are in the range of -15 to -20‰, and were most probably (modified) Early Proterozoic sea water or meteoric water. Epidote related fluids were close to the present day sea water isotopic values.

Early Proterozoic sea water or meteoric water sources both lead to the conclusion that 1.90 - 1.86 Ga sea water had a  $\delta D$  composition between 0 and -20‰.

Low- $\delta D$  fluid sources are very rare for the proposed geographical position of the 1.90 - 1.86 Ga Bergslagen region. Meteoric waters and organic fluids, the most probable candidates for low- $\delta D$  fluids, are both excluded.

A tentative explanation of the low- $\delta D$  values is exchange of the skarn minerals with modern low- $\delta D$  meteoric waters. This explanation is supported by the lower  $\delta D$  values in weathered samples compared to fresh samples from the same skarns and by the very humid conditions of the region. Water contents in the weathered minerals compared to the fresh minerals are not conclusive.

Additional studies on the tentatively proposed low temperature exchange are desirable before a firm conclusion can be reached.

### Aknowledgements

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## Chapter 10

### ARE LOW $\delta^{18}\text{O}$ VALUES IN PRECAMBRIAN CARBONATES RELATED TO RESTRICTED VOLCANO-SEDIMENTARY BASINS HEATED BY HYDROTHERMAL ACTIVITY ?

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#### Carbonates formed in restricted hot marine basins

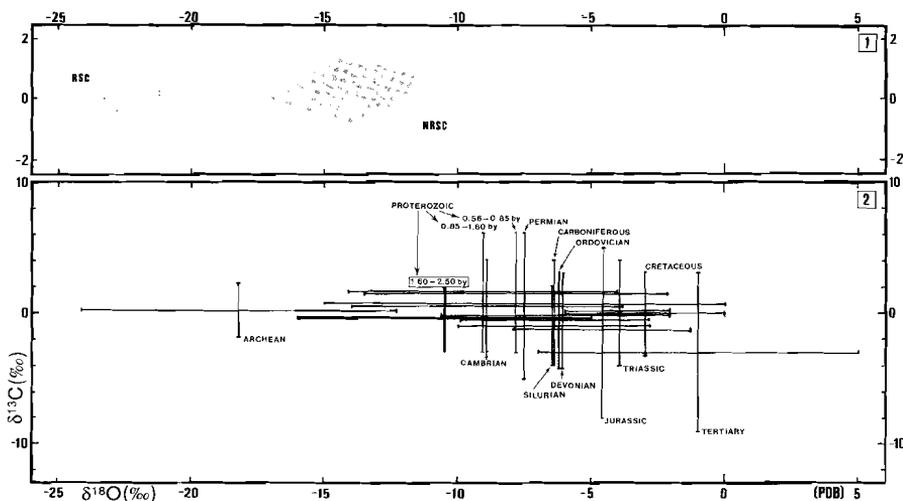
A stable isotope study of stratabound carbonates in the Early Proterozoic volcano-sedimentary belt of W. Bergslagen, Central Sweden, shows  $\delta^{13}\text{C}$  values in the range of normal marine carbonates (De Groot and Sheppard, 1988). Two groups of marine carbonates were distinguished:

- 1) carbonates which are related to exhalative mineralizations (RSC), and
- 2) carbonates which are not related to exhalative mineralizations (NRSC)(Fig. 1).

Both groups have lower  $\delta^{18}\text{O}$  values (RSC: 6.8 to 10.7‰; NRSC: 12.5 to 19.6‰) than would be expected for Proterozoic  $\delta^{18}\text{O}$  carbonate values (Early Proterozoic dolomites: 21 to 25‰; Veizer and Hoefs, 1976), while the RSC are 6 to 13‰ lower in  $\delta^{18}\text{O}$  than NRSC (Fig. 1). Both groups are interpreted as probably having exchanged with hot fluids after their deposition; NRSC with fluids at temperatures 15° - 60°C higher, and RSC at 100° - 250°C higher than those exchanging with most Proterozoic carbonates (De Groot and Sheppard, 1988). Hot fluids could be derived from exhalative systems at the sea floor (Baker and De Groot, 1983).

#### Precambrian carbonates

Considering the sample locations of the Precambrian carbonates, most, if not all, were collected from greenstone belts (Schidlowski et al., 1975; Veizer and Hoefs, 1976). Greenstone belts represent volcano-sedimentary basins (Windley, 1976, 1977; Condie, 1981) where volcanism and magmatic intrusions generated enormous amounts of heat. This heat led to extensive fluid circulation in the crust and the exhalation of hot fluids at the basin floors. Ore mineralizations (e.g. Volcanogenic Massive Sulphides, Banded Iron Formations) are common in this sort of settings (Condie, 1981; Trendall and Morris, 1983). A relationship is proposed between marine deposited carbonates and the subsequent lowering of  $\delta^{18}\text{O}$  values of the carbonates in the greenstone basins due to exchange with hot exhalative



**Figure 1.**  $\delta^{18}\text{O}$  versus  $\delta^{13}\text{C}$  diagram for carbonates from Bergslagen, central Sweden. Dark field NRSC, represents marine carbonates not related to mineralizations, and stippled field SRC, represents marine carbonates related to mineralizations. Oxygen and carbon isotopes relative to PDB standard in per mil. Data from De Groot and Sheppard (1988).

**Figure 2.** Compilation of oxygen and carbon isotopic values of marine carbonates (Data after Veizer and Hoefs, 1976). Crosses indicate the spread of isotopic values for specific geological periods. The thick-lined cross with connected age (shown in a box) are carbonate data of approximately the same Proterozoic age as are the Bergslagen carbonates shown in figure 1.

fluids at the sea floor, similar to the relationship in the W. Bergslagen basins as described above.

### Hydrothermal exhalative processes in precambrian marine basins

Exhalative activity of hydrothermal fluids on the sea floor is well documented (e.g. Boström and Peterson, 1966; Corliss, 1971; Wolery and Sleep, 1976; Edmond et al., 1979; Michard et al., 1983; Lonsdale and Becker, 1985; Rona and Clague, 1989; Nelsen and Forde, 1991). Exhaling fluids brought Ca, Fe, Mn, and Si into the basins (Veizer et al., 1982, 1989; Elderfield and Rudnicki, 1992; Sugitani, 1992), although they could also, together with Mg, be brought to the sea basins from erosion of the continents (e.g. Holland, 1973; Garrels, 1987). The high atmospheric  $p\text{CO}_2$  level and a sea water pH of  $\approx 7$  (Walker, 1983; Holland, 1984) in Precambrian times favours high concentration of bicarbonate ions in sea water (Walker, 1983). Fluids exhaling from hydrothermal vents at the sea floor will have increased the sea water temperature in the vicinity of the venting systems. Local depressions may have contained hot brines similar to the Atlantis II and Thetis Deeps in the Red Sea (Cronan et al., 1977;

Shanks and Bischoff, 1977; Hartmann, 1983; Scholten et al., 1991). Cyclic exhalative activity may explain the interlayering of carbonates, chert and/or iron (manganese) oxides. Precambrian oceans were close to saturation in respect to  $\text{CaCO}_3$  (Walker, 1983) and amorphous silica (Holland, 1973; Veizer, 1973). Higher temperatures decrease the solubility of  $\text{CaCO}_3$  (e.g. Fyfe et al., 1978) and promote the crystallization of calcite on the basin floors. Silica material became supersaturated in the sea water during cooling, after a less active period of exhalation, and precipitated as opal. Flocculant iron-(Mn)-hydroxides could form by supersaturation in a similar way as the opal (e.g. Holland, 1973; Anbar and Holland, 1992), or alternatively by photonactivity (Cairns-Smith, 1978; Braterman et al., 1983; Anbar and Holland, 1992). A relationship between BIF deposition and hydrothermal activity is suggested by Derry and Jacobsen (1990) and Sugitani (1992). Extensive Precambrian hydrothermal sea floor activity is highly compatible with chemical buffering of the oceans by the mantle (Veizer et al., 1982, 1989).

Figure 3 shows a compilation of the processes in the Precambrian hydrothermally active marine basins after the model proposed above.

### **Precambrian atmosphere and sea water compositions**

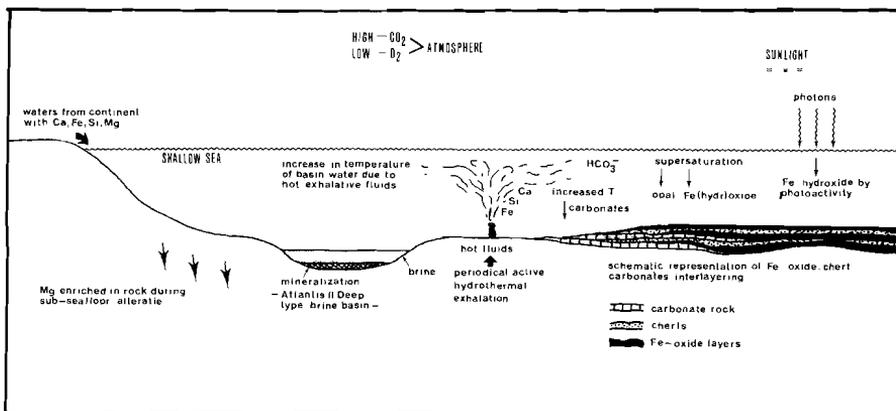
An important aspect of this discussion is the oxygen isotope composition of Precambrian sea water, which is still under debate (see discussions in Muehlenbachs, 1986, 1987; Sheppard, 1986; Gregory, 1991).

Carbonates, cherts and phosphates show a secular increase in  $^{18}\text{O}$  with time (Muehlenbachs, 1986, 1987; Veizer and Hoefs, 1976; Gregory, 1991; Fig. 2), and controversies concentrate on the following alternative interpretations:

- 1) Precambrian sea water had a lower  $\delta^{18}\text{O}$  than present sea water,
- 2) Precambrian sea water had a  $\delta^{18}\text{O}$  similar to the present value, but either temperatures were substantially higher, or carbonates have exchanged oxygen isotopes with groundwaters progressively with time.

Evidence has been presented to show that sea water  $\delta^{18}\text{O}$  has not changed from the Archean onwards, because it is buffered by hydrothermal sub-sea floor alteration, as exemplified by Archean greenstones, Cretaceous ophiolites and modern ocean floor alteration (Muehlenbachs and Clayton, 1976; Gregory and Taylor, 1981; Beatty and Taylor, 1982; Stakes and O'Neil, 1982; Smith et al., 1984). This leads us to the second interpretation: a hot ocean or post-depositional isotope exchange with groundwaters. However, a hot ocean interpretation is not compatible with models of the evolution of the atmosphere on the early Earth (Walker et al., 1981; Marshall et al., 1988; Kuhn et al., 1989; Tajika and Matsui, 1992). Solar luminosity probably was 20 to 30% less than at present (Sagan and Mullen, 1972; Newman and Rood, 1977; Rowley et al., 1980; Gough, 1981) implying temperatures below zero at the surface of the early Earth (Sagan

and Mullen, 1972; Kuhn and Kasting, 1983). The common occurrence of sedimentary rocks (e.g. Condie, 1981; Lowe, 1980) are clear evidence that oceans were not frozen in those times (Sagan and Mullen, 1972; Kuhn and Kasting, 1983; Kasting, 1989), and the ancient atmosphere required greenhouse conditions to keep the temperature above zero at the Earth's surface (Sagan and Mullen, 1972; Kuhn and Kasting, 1983; Kasting, 1987). An atmosphere with high  $\text{CO}_2$  concentrations, 500 - 1000 times PAL (Present Atmospheric Level), could have caused the greenhouse conditions (Kasting and Ackerman, 1983; Kuhn and Kasting, 1983).  $\text{CO}_2$ -feedback models (Walker et al., 1981; Marshall et al., 1988; Kuhn et al., 1989; Worsley and Kidder, 1991; Tajika and Matsui, 1992) relate temperatures and  $\text{CO}_2$  levels in the atmosphere, concluding that the Earth's surface temperature was buffered at  $\pm 10^\circ\text{C}$  over geological history. Existence of Precambrian glaciations (Schenk, 1965; Church and Young, 1970; Frarey and Roscoe, 1970; Windley, 1977; Frakes, 1979; Marshall et al., 1988) is in favour of this model.



**Figure 3.** A schematic diagram shows different processes leading to carbonate, chert, and Fe-oxide deposition. Interlayering of different compositions could be due to cyclic hydrothermal activity. Not shown in the diagram is the possible exchange of carbonate, chert, and Fe-oxide with warm/hot fluids shortly after their deposition, explaining lowering of the oxygen isotopic composition in these rocks.

The surface temperature of the early Earth was not much higher than at present times, while sea water  $\delta^{18}\text{O}$  was approximately zero. A possible way out of this dilemma is that increased temperatures occurred only locally in sea basins, where the carbonates (and cherts/iron oxides/phosphates) were deposited. Exchange with heated sea water shortly after deposition explains a negative  $\delta^{18}\text{O}$  shift in the carbonates. This explanation is comparable to that of post-depositional oxygen isotopic exchange between carbonates and groundwater with time (Degens and Epstein, 1962; Keith and Weber, 1964; Savin, 1980; Veizer et al., 1986). A major difference,

however, is the quick exchange with heated fluids at the sea floor proposed here, instead of a later exchange with groundwaters as in the other model.

The smooth, secular trend of decrease in carbonate  $\delta^{18}\text{O}$  values with time is very coincidental, and it is hard to imagine that all carbonate rocks had a similar post-depositional history, or exchanged with the same kind of fluids. This seriously questions the last model, but does not conflict with the model presented in this paper.

### **conclusions**

A model is proposed whereby Precambrian carbonate, chert and iron-(Mn) oxide are deposited in restricted hot marine basins. Local heating of marine basins, instead of global elevated temperatures, explains the conflicting evidence of moderate Precambrian surface temperatures and carbonates formed in warm oceans.

The proposed model is compatible with oxygen isotopic compositions of Precambrian sea water being around zero, with models of a high  $\text{CO}_2$  greenhouse atmosphere compensating for a lower solar luminosity, with the buffering effect of silicate alteration by atmospheric  $\text{CO}_2$  controlling the global surface temperature, with the occurrence of glaciations in the Precambrian, and with the chemical buffering of Precambrian oceans by the mantle through hydrothermal activity.

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## Chapter 11

### ALTERATION ZONES IN WEST BERGSLAGEN - A STABLE ISOTOPE APPROACH

After earlier petrographic and chemical studies on hydrothermal alteration zones in chapters 3 - 6, a stable isotope approach is presented. Different types of hydrothermal alteration are described in chapter 3 and a selection for the stable isotope study was made as follows:

- 1) the relatively deep Hjusjö zones, representing a group of conduits cutting the supracrustal rocks,
  - 2) the relatively shallow Fogdhyttan zone,
  - 3) sharply bordered and pervasive alterations in granitic intrusions
- From the earlier descriptions it is clear that fluids play an important role in the hydrothermal systems, and it is the aim of this chapter to trace the source and the development of fluid(s) in the systems.

#### 11.1 - THE HJULSJÖ ZONES

The Hjusjö alteration zones (Fig. 1) are chemically and mineralogically described by Baker and De Groot (1983a/chapter 4) and De Groot and Baker (1992/chapter 5). Thermodynamic calculations for mineral stability fields in a sea water-derived fluid - felsic rock exchange system are presented by De Groot (1990/chapter 6). In addition to these studies, oxygen and hydrogen isotopic analyses on silicates from the alteration zones were carried out.

##### Quartz oxygen isotopic values

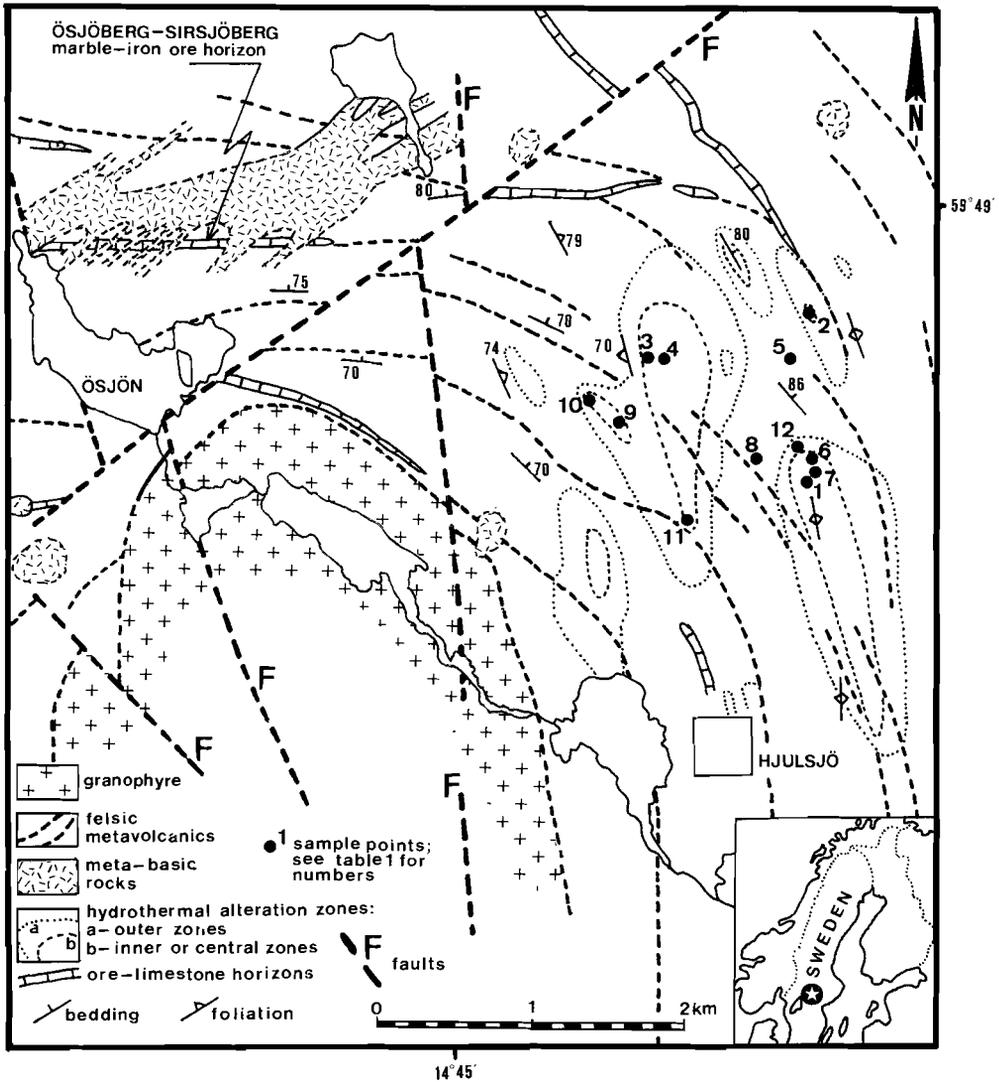
Quartz grains collected from:

- 1) metavolcanics outside the Hjusjö alteration zones (MV),
- 2) the outer alteration zones (OZ),
- 3) the inner zones (IZ),
- 4) the most altered inner zones (MAIZ),

are analysed for oxygen isotope values. A clear decrease in  $^{18}\text{O}$  values is found going from the least altered metavolcanics to the most altered inner zone (Fig. 2a; Table 1).

##### Whole rock hydrogen isotopic values

Five whole rock samples from the metavolcanics and alteration zones were analysed for hydrogen isotopic values. Results are shown in table 1 and figure 2b. The lowest  $\delta\text{D}$  value is found in the metavolcanics (MV), while the inner zones (IZ) and most altered inner zones (MAIZ) have  $\delta\text{D}$  values between -52 and -59‰. One sample from the inner zones (BRIZ) has a low  $\delta\text{D}$  value (-78‰), and is close to the metavolcanic  $\delta\text{D}$  value (-84‰).



**Figure 1.** The Hjulsjö alteration zones and surrounding geological situation (after Baker and De Groot, 1983a). Results are reported in Table 1, together with data for the Dunderbo (see Appendix) and Annehill alteration zones and for a shear zone at Bastnässet ( $\pm 2$  km E. of the Finnän granite; see Fig. 10).

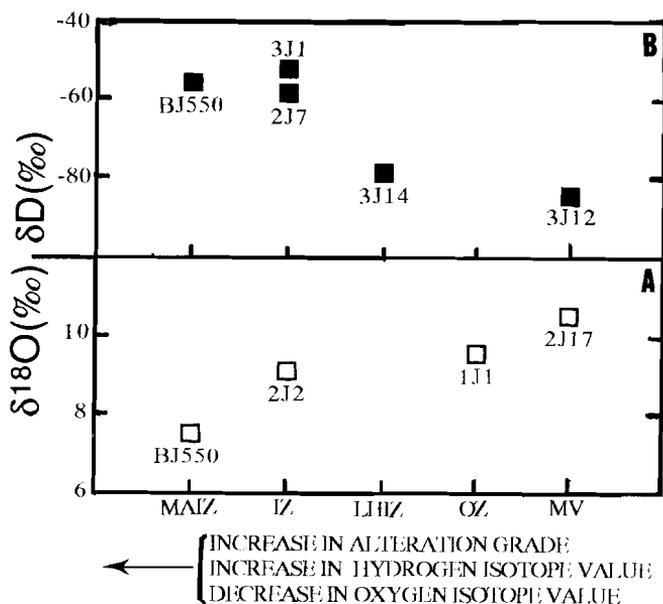
### Oxygen- and hydrogen isotopic values from alteration zone silicates

Oxygen- and hydrogen isotopic values are determined on muscovite, phlogopite and high-Mg chlorite (sherdanite) from the alteration zones (Fig. 3; Table 1). Isotopic compositions for fluids in equilibrium with these silicates are calculated for 300°, 400° and 500°C (Fig. 4; Fractionations

**Table 1.** Stable isotopic values of the Hjulsjö, Dunderbo and Annehill alteration zones and a shear zone at Bastnässet, West Bergslagen belt, central Sweden.

Nr	SAMPLE	MINERAL	MEAN $\delta D_{\text{‰}}$	$\delta D$ $\pm\text{‰}[N]$	MEAN $\delta^{18}\text{O}_{\text{‰}}$	$\delta^{18}\text{O}$ $\pm\text{‰}[N]$
<b>HJULSJÖ ALTERATION ZONES :</b>						
1	BJ550	Quartz			7.58	7.70
		Muscov/Mg-chlor	-55.9	-55.9	7.82	$\pm 0.12[2]$
			-56.2	$\pm 1.2[5]$	3.53	3.51
			-56.4		3.48	$\pm 0.03[2]$
			-56.4			
			-54.7			
2	1J1	Quartz			9.73	9.73
		Phlogopite	-67.3	-67.4	3.57	3.57
			-67.5	$\pm 0.1[2]$		
3	2J2	Quartz			9.23	9.23
		Phlogopite	-68.0	-68.0	8.43	8.43
		Muscovite	-66.1	-66.1	8.38	8.38
4	2J7	wr	-58.9	-58.9		
5	2J17	Quartz			10.79	10.72
					10.65	$\pm 0.07[2]$
6	3J1	wr	-52.2	-52.2		
7	3J2	Clinochlore	-55.3	-56.7	2.47	2.36
			-55.2	$\pm 3.0[3]$	2.25	$\pm 0.11[2]$
			-59.7			
8	3J12	wr	-82.8	-84.2		
			-85.5	$\pm 1.4[2]$		
9	3J14	wr	-78.3	-78.3		
10	3J15	Muscovite	-67.3	-66.7	5.31	5.46
			-66.0	$\pm 0.7[2]$	5.60	$\pm 0.15[2]$
11	4J4	Clinochlore	-95.5	-92.4	5.71	5.71
			-89.3	$\pm 3.1[2]$		
12	GP85/23B	Clinochlore	-61.8	-60.9	1.84	1.78
			-59.9	$\pm 1.0[2]$	1.71	$\pm 0.07[2]$
<b>DUNDERBO ALTERATION ZONE :</b>						
	1L2	Phlogopite	-76.1	-76.1	3.99	3.99
	1L3	Clinochlore	-61.8	-60.0	4.86	4.88
			-58.1	$\pm 1.9[2]$	4.90	$\pm 0.02[2]$
<b>ANNEHILL ALTERATION ZONE :</b>						
	2L2	wr	-41.5	-41.5		
<b>BASTNÄSSET SHEAR ZONE :</b>						
	BN BS1	Phlogopite	-68.9	-68.9	3.17	3.12
					3.06	$\pm 0.06[2]$

Hydrogen and oxygen isotopic values are related to the SMOW standard. Numbers in italics are measurements made at CRPG, Vandoeuvre-lès-Nancy, France. Clinochlore is standing for a high-Mg chlorite variety (sheridanite). [N] = number of measurements. wr = whole rock. The numbers in front of the Hjulsjö samples refer to the sample points marked on figure 1. Dunderbo samples are marked on figure 2 of the appendix, showing the Dunderbo skarn and alteration zone region.



**Figure 2.** A- Oxygen isotopic values of quartz separates (open squares) from different parts of the Hjulsjö alteration zones, B- Hydrogen isotopic values of whole rock samples (solid squares) from different parts of the Hjulsjö alteration zones. Sample numbers are marked in the diagrams. MAIZ = most altered inner zone; IZ = inner zone; BRIZ = border region inner zone; OZ = outer zone; MV = metavolcanics. Isotopic values relative to the SMOW standard.

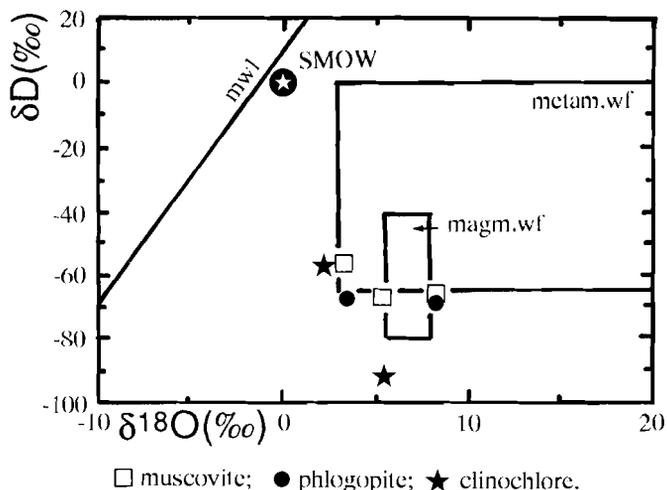
One sample (GP85/23B; clinocllore) from a skarn mineralization situated within the alteration zones close to a most altered inner zone (MAIZ) was analysed for oxygen and hydrogen isotopes. The isotopic values are comparable with sample 3J2 (see Table 1 and Fig. 4), which is collected in the MAIZ near this skarn.

**Dunderbo and Annehill alteration zones; Bastnässet shear zone**  
These alteration zones and shear zone in general show isotopic values comparable with those of the Hjulsjö alteration zones described above. The Dunderbo phlogopite has a more negative  $\delta\text{D}$  value than Hjulsjö zone phlogopites; the Annehill whole-rock  $\delta\text{D}$  is the highest value found for all the alteration zone rocks.

## Discussion

The hydrous minerals (Fig. 4) show a similar, but less smooth,  $^{18}\text{O}$  decrease with alteration grade in the zones as does the quartz (Fig. 2). Fluids in equilibrium with the hydrous minerals at temperatures of  $300^\circ - 500^\circ\text{C}$  have  $\delta^{18}\text{O}$  between 3 and 8‰ (Fig. 5), and are similar or lower than typical magmatic fluids (e.g. Sheppard, 1986).

The lowest measured  $\delta^{18}\text{O}$  of quartz in the alteration zones and the the hydrous minerals are approximately in equilibrium with the same fluid at temperatures between  $450^\circ$  and  $700^\circ\text{C}$ . This suggests a cogenetic formation of quartz with the hydrous minerals in the zones while even in the most altered parts of the zones a small percentage of quartz from the volcanic rocks is preserved unchanged. Old quartz grains were recrystallized and in equilibrium with fluids in the alteration zones.

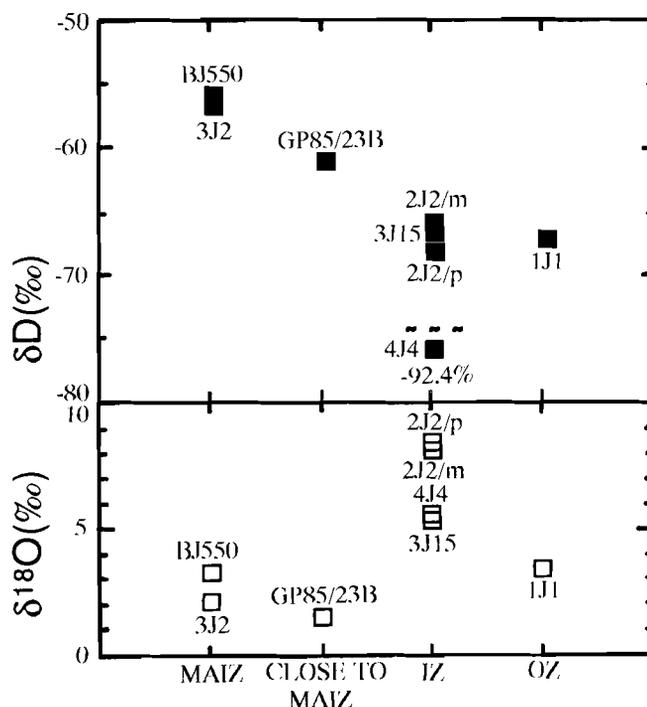


**Figure 3.** Oxygen against hydrogen isotopic diagram of muscovite, phlogopite and clinochlore (sheridanite) samples from the Hjulsjö alteration zones. mwl = meteoric water line; smow = standard mean ocean water; metam. wf = metamorphic water field; magm. wf = magmatic water field (definitions of water fields after Sheppard, 1986).

The increasingly lower oxygen isotopic values towards the centre of the alteration zones (Fig. 4) may be explained by the increasing formation of new quartz grains, or alternatively overgrowth of old grains. The proportion of newly formed low  $^{18}\text{O}$  quartz increases towards the central zones and therefore the total quartz isotopic value decreases. Oxygen isotopic exchange of quartz grains with a fluid at temperatures below about  $500^\circ\text{C}$  is a slow and non-equilibrium process, and is considered of minor influence on the Hjulsjö alteration zones.

The  $\delta\text{D}$  values of whole rock samples increase towards the most altered parts of the alteration zones, as is shown in figure 4. A similar increase is shown by  $\delta\text{D}$  of hydrous minerals in the alteration zones, with the exception of sample 4J4 which is abnormally low. Isotopic exchange between the regional metavolcanic rocks and relatively high D fluids leads to alteration products with increased  $\delta\text{D}$ .

Combining the quartz ( $\delta^{18}\text{O}$ ) and whole rock ( $\delta\text{D}$ ) data leads to the conclusion that the original volcanic rocks have interacted with a hydrothermal fluid of relatively low  $\delta^{18}\text{O}$  and high  $\delta\text{D}$  values. A fluid source showing such isotope characteristics is sea water, which may have been modified by exchange with volcanic rocks before reaching this level in the hydrothermal system. A sea water source is in good agreement with the inferred isotopic compositions of fluids during skarn formation in the western Bergslagen region (De Groot and Kreulen, 1993/chapter 9). Similar fluid compositions have also been determined for the Sirsjöberg-Ösjöberg skarn altered exhalative mineralizations, for which the Hjulsjö alteration zones were the feeder zones (Baker and De Groot, 1983a/chapter 4; De Groot and Baker, 1992/chapter 5).

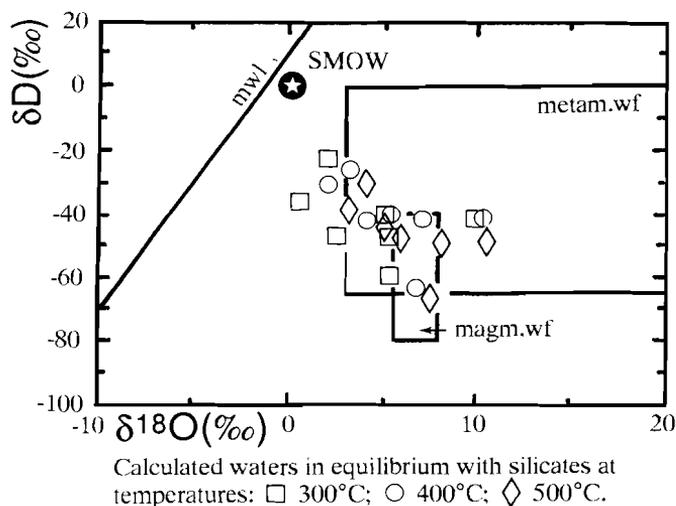


**Figure 4.** Oxygen and hydrogen isotopic values of hydrous silicates from the Hjulsjö alteration zones. The samples are arranged according to their place in the alteration zones. Sample numbers are marked. Open symbols are oxygen isotopic values and solid symbols hydrogen isotopic values. /p = phlogopite; /m = muscovite; MAIZ = most altered inner zone; CLOSE TO MAIZ = sample in IZ and close to the border with MAIZ; IZ = inner zone; OZ = outer zone.

The abnormally low  $\delta\text{D}$  value of sample 4J4 ( $-92.4\text{‰}$ ; Fig.4) can probably be explained by recent exchange with modern meteoric water as discussed by De Groot and Kreulen (1993/chapter 9).

The high  $\delta^{18}\text{O}$  of phlogopite of sample 2J2 is possibly due to the presence of some very fine grained clay in the rocks. Although such clay was not detected in the present sample, neither by microscope nor XRD-analysis, the occurrence of clay has been reported in the alteration zone enveloping the Dunderbo skarn (Baker and De Groot, 1983a/chapter 4).

High  $\delta^{18}\text{O}$  was found in quartz from veins in the Kidd Creek ore deposit, Ontario, Canada, showing evidence for high  $^{18}\text{O}$  ore fluids (Beaty et al., 1988). Evaporation leading to saline brines and enriched oxygen isotopic fluid values (comparable with present situations like the Salton Sea) was invoked as an explanation (Beaty et al., 1988). In the Bergslagen region not a single relict of any common evaporate mineral or structure as evidence for evaporitic processes is found, although evaporates are proposed by several workers (e.g. Parr and Rickard, 1987; Hellingwerf, pers. com.). Because this lack of evidence evaporation is not considered to be an explanation here.



**Figure 5.** Waters in equilibrium with the minerals of figure 3, calculated for 300°, 400°, and 500°C. Abbreviations and definitions as in figure 3.

The interpretation of isotopic results on the Dunderbo and Annehill alteration zones is the same as for the Hjulsjö zones. The clinocllore sample from the Dunderbo zone (1L3) has a high oxygen isotopic value, comparable with that of the clinocllore sample (4J4) from the Hjulsjö zones. The explanation of an increased  $\delta^{18}\text{O}$  caused by dispersed clay is more convincing here, because in this same alteration zone feldspar replacement by clay (meta-halloysite), followed by replacement of clay by chlorite is described by Baker and De Groot (1983a/chapter 4; De Groot, 1985).

The Bastnässet shear zone phlogopite has a comparable hydrogen isotopic value as the Hjulsjö alteration zone phlogopites. The oxygen isotopic value is relatively low. It is therefore suggested that a fluid which was closer to its primary sea water isotopic composition (less exchange with wall rocks) passed through the Bastnässet shear zone.

### **Water-rock ratios in the alteration zones**

Calculation of water-rock ratios using stable isotopes generally leads to minimum values (Taylor, 1977). Application of this method on the Hjulsjö alteration zones is complicated, because some parameters can't be determined very precise. Although uncertainties, a calculation based on oxygen isotopes is carried out for the most altered parts of the Hjulsjö zones. Sea water is assumed to be the initial fluid ( $\delta^{18}\text{O} = 0\text{‰}$ ). Fluids in equilibrium with hydrous minerals and quartz, at  $400^\circ - 500^\circ\text{C}$  have a mean  $\delta^{18}\text{O}$  value of  $5,5\text{‰}$ , and are taken as final fluid. There are no initial or final whole rock  $\delta^{18}\text{O}$  values available. The initial rock is a felsic volcanic of rhyolitic composition;  $\delta^{18}\text{O}$  of such rocks is around  $8\text{‰}$  (e.g. Taylor, 1974). The final rock composition is estimated from the altered minerals, and is  $5\text{‰}$ . Using these parameters, a water/rock ratio of 0.55 is obtained, which must be considered as a minimum ratio.

Water-rock ratios were determined based on chemical data by Baker and De Groot (1983a/chapter 4) calculating Mg exchange between the altered rocks and a sea water derived fluid. This calculation gave a water/rock ratio of approximately 100, which later was corrected to 20 (Baker and De Groot, 1983b), and must also be considered as a lower limit.

A large difference exist between the two methods given above, and the largest minimum ratio from these two methods may still be a low estimate.

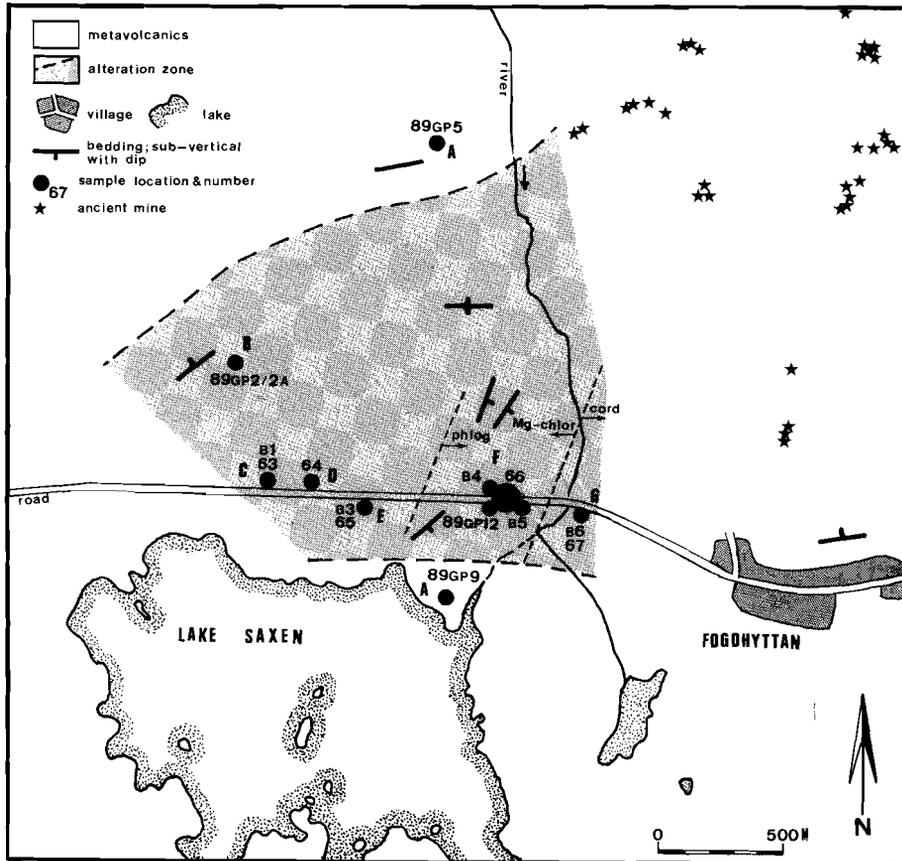
Another method to estimate water/rock ratios, which was not employed until recently, is based on the high rare earth element (REE) mobility in the alteration zones (Baker and De Groot, 1983a/chapter 4; De Groot and Baker, 1992/chapter 5). Preferential leaching of light REEs, especially Eu, by hydrothermal fluids produces negative light REE anomalies in the rocks. The resulting REE pattern of the hydrothermal fluids is comparable to that measured in exhaling fluids at mid-oceanic ridges (Michard et al., 1983; Michard and Albarède, 1986; Michard, 1989). Michard and Albarède (1986) and Michard (1989) reason that, with the very low REE concentrations in the exhaling fluids, extreme high water-rock ratios ( $> 10^6$ ; Michard and Albarède, 1986) are required to cause the reported leaching of REE from the rocks. Water-rock ratios in the order of  $10^6$  are not considered impossible in view of the very high grade of alteration in the Hjulsjö alteration zones, and other comparable highly altered zones in the Bergslagen region.

In systems with high water/rock ratios ( $\gg 1$ ) the fluids completely determine the isotopic composition of the system. This apparently raise a

contradiction between the oxygen isotopic composition of a sea water source (0‰) and the calculated alteration fluids (3 - 8‰) in a high water/rock system. The Hjulsjö zones are part of a larger hydrothermal system (Baker and De Groot, 1983a/chapter 4; De Groot and Baker, 1992/chapter 5). Before fluids arrive at the Hjulsjö zones, they started in a low temperature part of the system with low water/rock ratios and were transported further in the system with increasing temperatures and water/rock ratios. Finally, when they reach the Hjulsjö alteration system, they have exchanged extensively with the supracrustal sequence at far lower water/rock ratios and their  $^{18}\text{O}$  composition is increased. It thus may be concluded that an original sea water source for the Hjulsjö alteration zones fluids is not contradicted.

## 11.2 - THE FOGDHYTTAN ZONE

The Fogdhyttan zone (Fig. 6) is an East-West orientated alteration zone with poorly defined borders because of poor rock exposure. The zone consist of hydrothermally altered felsic volcanics showing banded and foliate structures, which are clearly not primary volcano-sedimentary, but of later alteration origin. The bands show a white, green or pink colour. Quartz veins with irregular shapes cut through the altered rocks. Near the village of Fogdhyttan a red and striated granite is exposed.

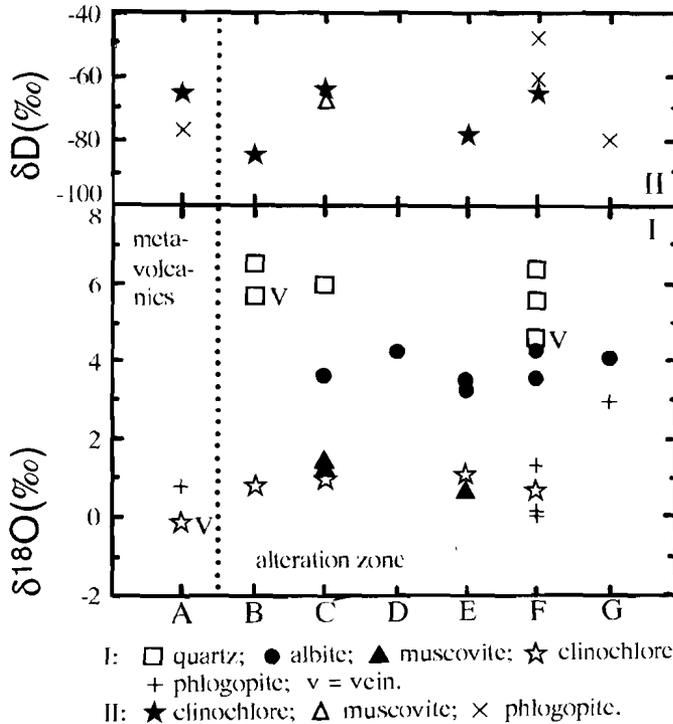


**Figure 6.** Map of the Fogdhyttan alteration zone and surroundings. Sample points are marked on the map. Thin broken lines are mineral stability boundaries in section C to G; arrows direct into the stability field of the marked mineral. phlog = phlogopite; Mg-chlor = Mg-chlorite; cord = cordierite. For A - G marks, see figure 7.

The sampled section of the Fogdhyttan zone is about 2 km long and several hundred meters wide (see Fig. 6). The mineralogy changes with distance from the granite. The samples furthest from the granite consists of quartz, albite, sericite and/or clay minerals and Mg-rich chlorite (sherdanite)

containing rutile needles (samples: 63a,b, 64a, 65a,b, 83GP-B1,B3,89GP-2; see Table 2, Fig. 6). Towards the granite the mineralogy changes to an assemblage of quartz, albite, phlogopite (with intergrown sheridanite) and calcite veins (samples: 66a-d, 83GP-B4,B5; Table 2, Fig. 6). At 5 m from the contact with the granite the sheridanite disappears and cordierite is present in reddish flecks on outcrop surfaces. Quartz, albite, phlogopite complete the mineralogy of this part of the zone (samples: 67r, 83GP-B6; Table 2, Fig. 9).

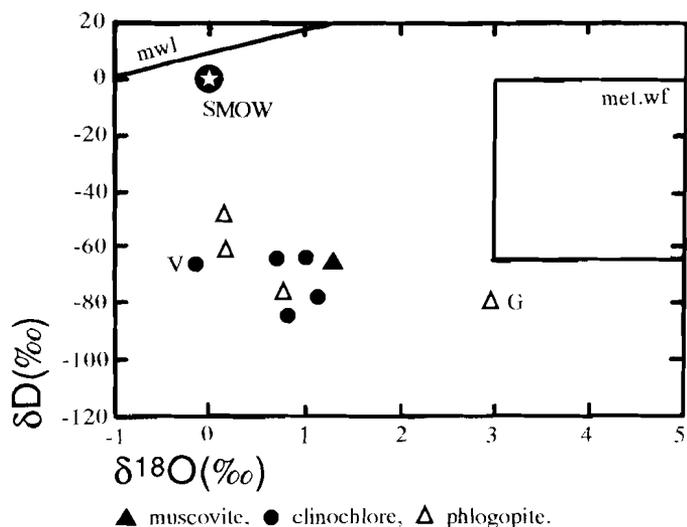
Stable isotopic (O, H) analyses were made on mineral separates from the different parts of the alteration zone and from two metavolcanic samples outside the zone (samples: 89GP-5 and 9).



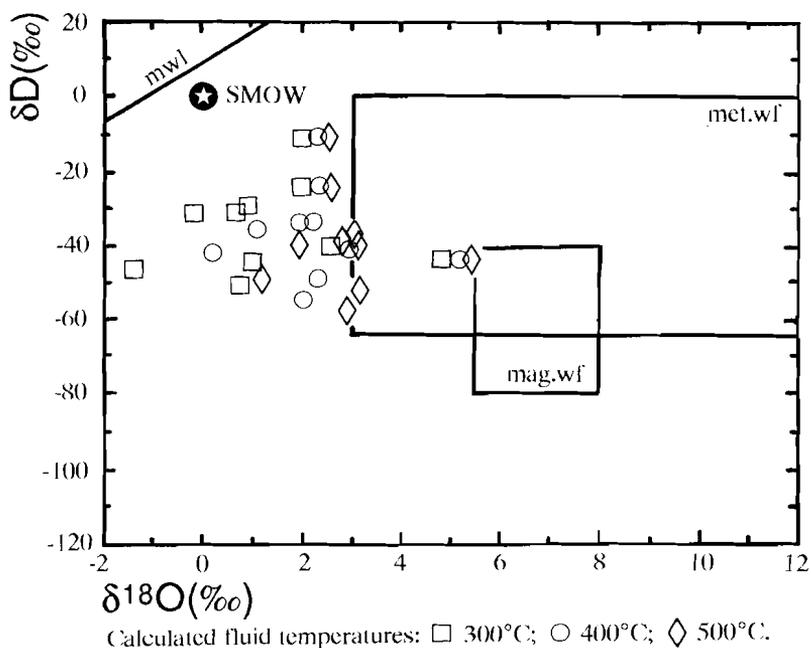
**Figure 7.** I) Oxygen isotopic values of quartz, albite, muscovite, clinocllore, and phlogopite relative to their position in the Fogdhyttan section. II) Hydrogen isotopic values for clinocllore, muscovite, and phlogopite relative to their position in the Fogdhyttan section. Abscissa of diagram: A = metavolcanics (outside section); B - F = different parts of section going in the direction of the Fogdhyttan granite; G = Fogdhyttan granite.

Oxygen and hydrogen isotope values are given in table 2. Figure 7 shows the oxygen and hydrogen isotope values along the sampled section. Isotopic data of hydrous minerals are plotted in a  $\delta^{18}\text{O} - \delta\text{D}$  diagram (Fig. 8).

Fluid compositions in equilibrium with these hydrous minerals are calculated for 300°, 400° and 500°C and shown in figure 9. (Fractionations



▲ muscovite, ● clinocllore, Δ phlogopite.  
**Figure 8.** Oxygen - hydrogen isotope diagram of muscovite, clinocllore and phlogopite in the Fogdhyttan alteration zone. G = granite; V = vein; SMOW = standard mean ocean water; mwl = meteoric water line (after Craig, 1961); met. wf = metamorphic water field (After Sheppard, 1986).



Calculated fluid temperatures: □ 300°C; ○ 400°C; ◇ 500°C.  
**Figure 9.**  $\delta D$  -  $\delta^{18}O$  diagram showing water values in equilibrium with Fogdhyttan zone muscovite, clinocllore, and phlogopite at 300°, 400°, and 500°C. SMOW = standard mean ocean water; met. wf = metamorphic water field; mag. wf = magmatic water field; mwl = meteoric water line (mwl after Craig, 1961; water fields after Sheppard, 1986).

Table 2. Fogdhyttan alteration zone stable isotopic data.

sample	mineral mean[±n]	$\delta D_{\text{‰}}$		$\delta^{18}O_{\text{‰}}$	
		meas.	mean[±n]	meas.	
63A	Quartz			6.10	6.05
				6.20	±0.05[2]
	Albite			3.79	3.77
				3.74	±0.03[2]
63B	Muscovite			1.72	1.66
				1.59	±0.07[2]
	Albite			3.79	3.79
				3.78	±0.01[2]
64A	Muscovite	-66.3	-66.3	1.48	1.48
	Albite			4.47	4.47
65A				4.47	±0.00[2]
	Albite			3.51	3.61
				3.70	±0.10[2]
65B	Muscovite			0.87	0.85
				0.82	±0.03[2]
	Albite			3.50	3.44
66A	Albite			3.38	±0.06[2]
	Quartz			6.58	6.52
66D				6.45	±0.07[3]
				6.52	
	Albite			4.39	4.45
				4.51	±0.06[2]
	Phlogopite			1.27	1.50
				1.72	±0.23[2]
67R	Quartz			5.90	5.79
				5.67	±0.12[2]
	Albite			3.76	3.74
				3.72	±0.02[2]
83GP-B1	Phlogopite	-48.5	-48.2	0.32	0.30
		-48.3	±0.3[3]	0.27	±0.03[2]
		-47.9			
	Albite			4.40	4.29
83GP-B2				4.18	±0.11[2]
	Clinochlore	-62.4	-63.6	1.17	1.17
83GP-B3					
	Clinochlore	-64.8	±1.2[2]	1.16	1.28
83GP-B4				1.40	±0.12[2]
	Clinochlore	-76.9	-78.1		
83GP-B5					
	Biotite	-78.4	±1.2[3]	0.88	0.88
83GP-B6				0.14	0.34
				0.53	±0.20[2]
	Biotite	-60.9	-61.0		
89GP-2					
	Quartz	-60.1	±1.9[4]	3.15	3.15
89GP-9[vein]				6.68	6.68
	Clinochlore	-62.9	-79.6	0.98	0.98
89GP-12[vein]					
	Quartz	-83.6	-84.0	5.86	5.80
89GP-5				5.74	±0.06[2]
	Phlogopite	-84.5	±0.5[3]	0.92	0.92
89GP-9[vein]				0.04	0.04
	Clinochlore	-83.8			
89GP-12[vein]				4.84	4.81
	Quartz			4.78	±0.03[2]

Isotopic values are in per mil (‰) relative to the SMOW standard. Clinochlore is standing for a Mg-rich chlorite which may represent sheridanite.

from: Wenner and Taylor, 1971; Bottinga and Javoy, 1973, 1975; Suzuoki and Epstein, 1976; Graham et al., 1987; Hoefs, 1987).

From studies on the Hjulsjö zones alterations (chapters 4, 5 and 6) a sequence of mineral formation in a prograde alteration system is obtained. This sequence for the Fogdhyttan zone is expected to be: albite + muscovite (sericite) - Fe-rich clinocllore - Mg-rich clinocllore + phlogopite.

### Oxygen isotope values

Albites show a narrow range of  $\delta^{18}\text{O}$  values from 3.44 to 4.47‰. Calculated fluids in equilibrium with the albites, have a  $\delta^{18}\text{O}$  range between -2.6 and -1.6‰ at 300°C, 0.05 and 1.1‰ at 400°C, and 1.7 and 2.75‰ at 500°C. Fluids calculated for muscovite are -0.43 and 1.40‰ at 400° and 500°C respectively, and for Fe-rich (dark green) clinocllore in a vein outside the alteration zone -0.19‰ at 300°C and 1.12‰ at 400°C. Fluids in equilibrium with phlogopite between 300° - 500°C and Mg-rich (light green) clinocllore between 400° - 500°C have a  $\delta^{18}\text{O}$  range of 1.5 - 3.5‰, some per mil higher than the fluids in equilibrium with the earliest formed minerals.

A phlogopite from the granite is clearly enriched in  $^{18}\text{O}$  compared with the other hydrous minerals in the alteration zones and is consistent with magmatic  $\delta^{18}\text{O}$  fluid values at 500° - 600°C.

Quartz  $\delta^{18}\text{O}$  values show a narrow range from 4.81 to 6.86‰, which is 2 - 3 per mil lower than  $\delta^{18}\text{O}$  of quartz in normal rhyolites. Hydrothermal alteration caused a decrease in  $\delta^{18}\text{O}$ , probably by partial recrystallization in the presence of a fluid. Vein quartz is in the same isotopic range as the quartz in the alteration zones.

The oxygen isotopic values of the calculated fluids increase from close to present day seawater values (around 0‰) at early stages of the Fogdhyttan alteration, to values in the range of 1.5 to 3.5‰ at later stages. I suggest a shallow hydrothermal system, at 300° - 400°C, with nearly unmodified seawater during early alteration. With increasing temperature and alteration the oxygen isotopic value of the fluid is shifted towards positive values due to exchange with the rocks.

### Hydrogen isotope values

The hydrous minerals of the Fogdhyttan zone show a  $\delta\text{D}$  range between -48 and -84‰. Calculated hydrogen isotope values of fluids in equilibrium with the hydrous minerals range from -10.6 to -58.0‰, with most values between -30 and -50‰ (Fig 9). Combining the hydrogen and oxygen isotopic values of the fluids shows that magmatic or metamorphic water can not be the source of the alteration fluids. Proterozoic sea water or low-latitude meteoric water origin, with positive shift of the oxygen isotopic

composition of the fluids during the alteration are suggested. Hydrous alteration minerals were then in isotopic equilibrium with a sea water or low-latitude meteoric water. Calculated fluids in equilibrium with the hydrous minerals show a range of  $\delta D$  at the highest end (-10 to -30‰) of the present isotopic range (Fig. 9). The  $\delta D$  range of fluids as presented above, may be explained by present exchange of the hydrous mineral with present day meteoric water ( $\delta D = -82‰$ ). An extended explanation of this exchange is given in chapter 9.

A seawater origin of the fluid phase is in agreement with explanations for the origin of fluids in the Hjulsjö alteration zones (section 11.1), fluids from skarn mineralizations (De Groot and Kreulen, 1993/chapter 9) and with the strong Mg-enrichment in the alteration systems of West Bergslagen in general (Baker and De Groot, 1983a/chapter 4). In comparison, the Fogdhyttan zone is a relatively shallow hydrothermal system with moderate temperatures, while the Hjulsjö zones formed in deeper systems at higher temperatures. Nearly unmodified seawater was involved in the Fogdhyttan zone, while the fluid in the Hjulsjö zones was a strongly modified fluid, probably of seawater origin.

### 11.3 - ALTERATION OF GRANITIC INTRUSIONS

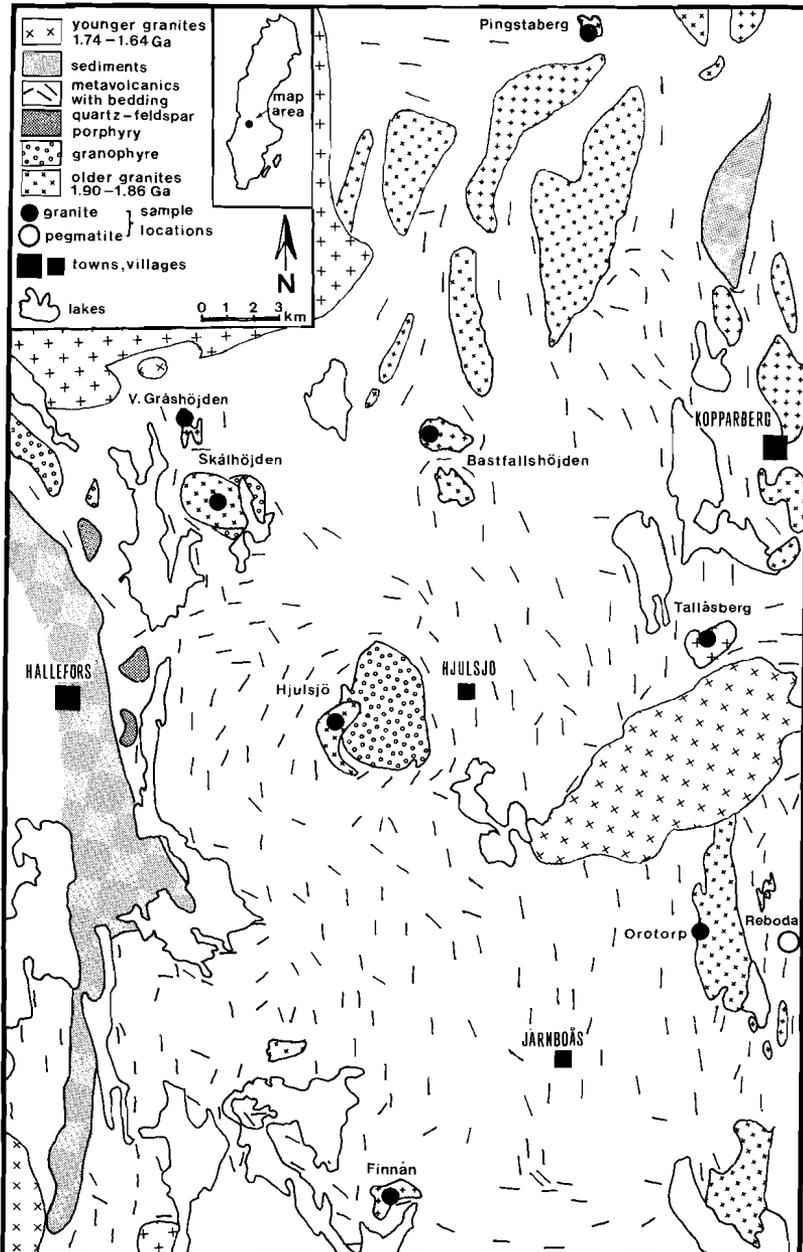
The Svecofennian granites in the western Bergslagen region have grain-sizes of mm to several cm scales, with the most common size between 0.5 and 1 cm. They mostly have a light to dark pink colour, or white to greyish-white in some places. The pink colour is caused by alteration of the feldspars, which contain small particles of Fe-oxides giving a clouded appearance in thin sections under the microscope. Sometimes the feldspars contain very thin "Fe-particle" coatings on their grain boundaries. During alteration the granites are bleached and show a white appearance. Bleaching is generally restricted to distinctive zones varying from a few dm to several m wide, and from a few m to several km length (e.g. Baker, 1985b), but can also be seen as pervasive alteration with irregular or gradual transitions with the pink granite. In extreme cases the pink-coloured granite is bleached first and subsequently altered into a light-grey mica-quartz schist zone, as is seen in the Orotorp and Finnån granites (see Fig. 10).

Quartz samples from a selection of granites (locations shown in Fig. 10) and bleached alteration zones were analysed for oxygen isotopic values. In addition one microcline was analysed for oxygen, and two biotites, two muscovites and one edenite were analysed for oxygen and hydrogen isotopic values. Results are given in table 3 and plotted in figure 11.

From figure 11 it can be seen that practically non-altered quartz (NAQ) shows a narrow  $\delta^{18}\text{O}$  range between 8.1 - 9.2‰; mean  $\delta^{18}\text{O} = 8.6‰$  (n=12). An exception is the Orotorp granite with  $\delta^{18}\text{O}$  values of 10.12 and 10.52‰. Quartz in the highly altered zones (AQ) has lower  $\delta^{18}\text{O}$  values between 7.5 and 8.1‰; mean  $\delta^{18}\text{O} = 7.75‰$  (n=4). The difference in  $\delta^{18}\text{O}$  between the Orotorp granite and the other granites is probably due to different crustal source compositions. The Orotorp granite probably formed by remelting of crust containing primarily continental components (S-type granite: see Baker, 1985a) while the other granites formed by remelting of magmatic components of mantle origin (I-type granites; Baker, 1985a).

It is important to note that the quartz  $\delta^{18}\text{O}$  in the strongly altered zones is the same for all granites, including the Orotorp granite. The  $\delta^{18}\text{O}$  range is similar to that of quartz in the most altered parts of the Hjulsjö alteration zones. This suggests that similar type of fluids exchanged with granites and volcanic rocks. This also suggests that the system was fluid dominated (high water/rock ratios), while quartz was mobilized to a high extent.

Quartz-fluid exchange is discussed in more detail in sections 11.1 and 11.2. The microcline from sample VG4 may be in isotopic equilibrium with the quartz from the same sample at magmatic temperatures ( $\Delta[\delta^{18}\text{O}_{\text{quartz}} - \delta^{18}\text{O}_{\text{microcline}}] = 1.25‰$ ; e.g. see Taylor, 1974).



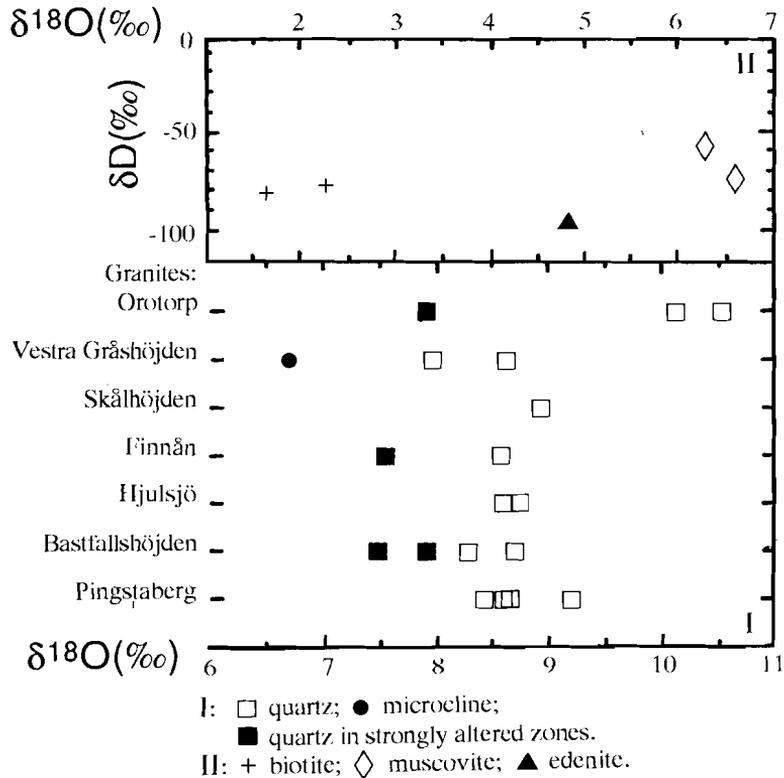
**Figure 10.** Map of W. Bergslagen showing different felsic intrusives and sample locations (see also Table 3).

The isotopic composition from muscovite of the Reboda pegmatite is comparable with magmatic muscovite at  $500^{\circ}$  -  $600^{\circ}\text{C}$  (Fig. 12), suggesting that it is a primary mineral in the pegmatite. This is also in accordance with observations in the field.

**Table 3.** Isotopic data of minerals from granites in western Bergslagen.

sample	description	quartz		mineral	$\delta D$	$\delta^{18}O$	
		$\delta^{18}O$	$\pm\%o[n]$			$\pm\%o[n]$	
PINGSTABERG GRANITE:							
GP85-12A	pink	8.41	0.16[2]				
GP85-12C	aplite	8.60					
GP85-12F	coarse pegmatitic	8.65					
GP85-20	pale-pink	9.19					
BASTFALLSHÖJDEN GRANITE:							
GP85-17	white-bleached	7.47	0.03[2]				
GP85-18A	red	8.70					
GP85-18C	white-bleached	7.91	0.08[2]				
BJ1069	red	8.28					
HJULSJÖ GRANITE:							
BJ51	red	8.74					
BJ392	red	8.61		biotite	-80.9	1.82	0.07[2]
FINNÅN GRANITE :							
GP86-2	red	8.59					
GP86-4	white-bleached	7.54					
SKÅLHÖJDEN GRANITE:							
BJ451	red	8.93					
VESTRA GRÅSHÖJDEN GRANITE:							
GP WG2	pink	8.63					
VG4	pink	8.13*	0.10[2]	microcline biotite	-76.7	6.88 2.45	0.10[2]
TALLÅSBERG GRANITE:							
GP85-10F	dark schist zone			edenite	-96.8	5.02	0.22[2]
OROTORP GRANITE:							
GP85-A1	white schist	8.09*					
GP85-A2	white-bleached	10.12	0.13[2]				
GP85-A3	red	10.52	0.05[2]				
GP85-13C	white schist			muscovite	-73.3	6.76	
REBODA PEGMATITE:							
Rb Pegm				muscovite	-56.3	6.44	0.19[2]

All the isotopic values are in per mil related to the SMOW standard. Quartz samples, except those marked with an asterix, are analysed at the Centre des Recherches Pétrographiques et Géo-chimiques (CRPG), Vandoeuvre-lès-Nancy, France. The other minerals, including the asterix marked quartz samples, are analysed at the University of Utrecht (RUU), The Netherlands. If more than one analysis is made of the same sample, the mean value is given with the range in  $\pm\%o[n]$ , where [n] refers to the number of analyses. All granites are of 1.90-1.86 Ga age, except Tallåsberg granite and Reboda pegmatite (1.74-1.64 Ga); the Orotorp granite may represent both granite generations.

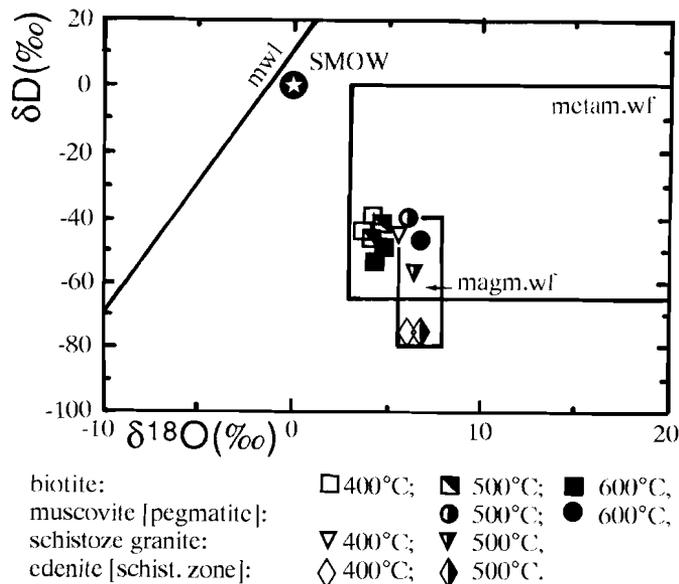


**Figure 11.** Oxygen isotopic data of quartz and microcline from granites, quartz from altered zones in granites, oxygen and hydrogen isotopic data from biotite, muscovite and edenite from altered granites.

Muscovite from the Orotorp schist formed in a strongly altered granite by hydrothermal processes. The muscovite formed in isotopic equilibrium with the hydrothermal fluid at 400° - 500°C (Fractionations from Bottinga and Javoy, 1973; Suzuoki and Epstein, 1976). Edenite of the Tallåsberg granite formed in a sheared fault zone. Both these minerals, although the water fields in equilibrium with these minerals are situated in the magmatic water field, correlate well with isotopic values of minerals formed in equilibrium with hydrothermal fluids in skarns as described in De Groot and Kreulen (1993/chapter 9), suggesting they were formed in contact with the same hydrothermal fluid as were the skarns. A magmatic water origin can not be rejected here, although magmatic water may be represented by water from another source which has extensively exchanged with magmatic rocks and was shifted isotopically towards a magmatic water composition.

The biotites (Figs. 11, 12) may have formed primarily in the plutons and subsequently exchanged with the hydrothermal fluids, or they may have formed as secondary phases during alteration. Their oxygen isotopic

compositions are several per mil lower than those of normal magmatic biotites because they have exchanged with the hydrothermal fluids at 400° - 500°C. They have similar isotopic values as the skarn phlogopites reported by De Groot and Kreulen (1993/chapter 9)(Fractionations from Bottinga and Javoy, 1973, 1975; Graham et al., 1984; Hoefs, 1987).



**Figure 12.**  $\delta^{18}\text{O}$  -  $\delta\text{D}$  diagram for calculated waters in equilibrium with biotite, muscovite and edenite from altered zones and a pegmatite in the Bergslagen granites. SMOW = standard mean ocean water; mwl = meteoric water line (Craig, 1961); metam. wf = metamorphic water field; magn. wf = magmatic water field (water fields from Sheppard, 1986).

## 11.4 - SEA WATER - A MAJOR SOURCE OF THE HYDROTHERMAL FLUIDS

In chapters 3, 4, 5, 8, 9, and sections 11.1/3 a sea water source for hydrothermal fluids in the Bergslagen belt is involved. The composition of Proterozoic sea water is not well known, but several attempts were made to estimate its chemical and isotopic composition. Holland (1978, 1984), based on well-founded reasoning, concluded that the major element chemistry of sea water did not change much from the late Archean till the present. The trace element composition of ancient sea water is more difficult to estimate. Baker and De Groot (1983a/chapter 4) for instance, tentatively proposed similar heavy rare earth element patterns in Proterozoic and present times. Based on the foregoing work, the Proterozoic sea water chemistry is assumed to be similar to the present chemistry. This is important for comparison of chemical trends in sea water - rock exchange processes.

The stable isotopic composition of sea water through geological history is reasonably well established for the oxygen isotopes but less well for hydrogen isotopes. Muehlenbachs (1986) reviewed the sea water oxygen isotope evolution, and Sheppard (1986) gave a short review of the hydrogen isotopic composition of sea water in Precambrian times.

Oxygen isotopes, although not unanimously agreed upon (see Muehlenbachs, 1986, 1987; and Gregory, 1991), probably were unchanged from early Precambrian ages till the present. This view is based on the consistency of isotopic values in sea floor alteration processes over this period;  $\delta^{18}\text{O}$  of sea water seems to be buffered by oceanic crust alteration to a  $\delta^{18}\text{O}$  of zero (Gregory and Taylor, 1981; Veizer et al, 1982; Muehlenbachs, 1986; Gregory, 1991). Small fluctuations, however, are possible, caused for example by (de-)glaciation processes.

Hydrogen isotopic compositions are expected not to have changed much through geological history (Sheppard, 1986), although they are not well established for Precambrian ages. Kerrich (1987) reports epidote formed 2.65 Ga ago in equilibrium with sea water having a modern  $\delta\text{D}$  value. In chapter 9 evidence is presented for a similar  $\delta\text{D}$  during early to middle Proterozoic ages.

In chapter 10 the negative oxygen isotopic values shift in carbonate rocks and cherts back into Proterozoic time is discussed. The possibility is proposed that this decreasing oxygen isotopic trend is due to elevated temperatures in the heated waters of active volcano-sedimentary basins (greenstone basins). In this model, the oceanic water wasn't necessarily heated on a global scale, but rather in restricted basins, allowing for co-existence of glaciations on the continental crust. This model is compatible with a constant  $\delta^{18}\text{O}$  of sea water from early Precambrian ages till present.

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## Chapter 12

### EXHALATIVE, SKARN AND EPIGENETIC MINERALIZATIONS IN BERGSLAGEN

As a conclusion to this thesis, a model is presented which summarizes the different type of ore mineralizations in West Bergslagen. The subject of this concluding chapter should be considered as the final link in the chain of the hydrothermal systems. Material transported by the fluids in these hydrothermal systems can be redeposited. Mineralizations may be enriched in ore minerals if the fluids were able to deliver the building stones for them. Study on the hydrothermal history of the alteration systems and the related mineralizations, with the emphasis on the fluid genesis, is leading to an improvement of the knowledge of the mechanisms of ore mineralization. This knowledge may be advantageous in exploration for new deposits in the future.

#### **The ore mineralizations of West Bergslagen**

Classification of the ore mineralizations of the Bergslagen region in central Sweden is given on a genetic basis. A classification based on metal-type is rejected because such a division leads to a long list of types with numerous sub-types, while nothing is said about their process of formation.

Koark (1962) proposed exhalative marine processes for the sulphides of the Falun mineralizations, placed by Rickard (1987) in a volcanogenic sedimentary setting. Schermerhorn (1978) compared the Bergslagen and southern Finnish belt mineralizations with the Spanish pyrite belt, developed in a marine environment. Boström et al. (1979) proposed an exhalative deposition in a marine marginal basin environment for the Långban mineralizations. Oen et al. (1982) presented a model of exhalative ore formation in marine rift basins.

Only relatively small volumes of the exhalative deposits in Bergslagen, after their burial by volcano-sediments, escaped reworking and mobilization by hydrothermal and metamorphic processes.

Hydrothermal activity related to the mineralizing processes were described by Boström et al. (1979), Baker and De Groot (1983/chapter 4), Hedström (1984), Vivallo (1984, 1985b), and Lagerblad and Gorbatshev (1985).

A volcanogenic origin of the mineralizations was proposed by Koark (1962), Oen et al. (1982), Frietsch (1982a,b), Vivallo (1985a), Rickard (1987), and Oen (1987).

Extended descriptions of Fe-(Mn-) stratiform exhalites and skarns in the Bergslagen region are given by: Geijer and Magnusson (1944, 1952), Magnusson (1970), Grip (1978), Boström et al. (1979), Frietsch (1982a,b), Loberg and Horndal (1983), Oen (1987), Damman (1988); of



sulphide mineralizations by: Koark (1962), Grip (1978), Frietsch (1982a,b), Vivallo (1985a), Hellingwerf (1984), Wolter and Seifert (1984), Hedström (1984), Kresten (1986), Oen (1987), Rickard (1987), Hellingwerf et al. (1988), Oen and Hellingwerf (1988); of W-Mo skarns by: Magnusson (1940), Hübner (1971), Ohlsson (1979), Hellingwerf and Baker (1985), Baker and Hellingwerf (1988a,b) and Cheilletz (1988); of Ni-Cu mineralizations by: Baker et al. (1988), Zakrzewski (1988). Completely different from the former mineralization types is the diagenetic-bacteriological Mn-oxide and sulphide mineralization in the upper slate layers of the supracrustal sequence near the village of Grythyttan (Oen et al., 1986).

A classification, based on own observations, oral communication and the literature, is proposed as follows (Fig. 1):

- Exhalative sedimentary mineralizations:
  - a- oxidic phase (Fe,  $\pm$ Mn)  
[iron formation types]
  - b- sulphidic phase (base metals, Fe, Ag)  
[volcanogenic massive sulphide types: VMS]  
- and intermediates between oxidic and sulphidic phases
- Skarn mineralizations:
  - a- remobilized and skarn altered exhalative sedimentary mineralizations (Fe, Mn, base metals, W, Mo, Ag, Co, Ni)
  - b- skarns formed by reaction of hydrothermal fluids with marbles or diabase dykes-sills (Fe, base metals, W, Mo)  
[included are the biotite sköls (Fe, Mo -bearing) and mineralized quartz veins related to the conduit zones connected with the skarn mineralizations]
- Epigenetic mineralizations:
  - stratiform mineralizations; replacement of preferred layers in a bedded sequence (mainly Pb, Zn sulphides)
- Magmatic mineralizations:
  - magmatic crystallization of ore pegmatites and pneumatolites.
- Diagenetic - bacteriologic Mn-oxide mineralization in clastic sediments.

Figure 2 is a  $\delta^{18}\text{O}$  -  $\delta^{13}\text{C}$  diagram showing a compilation of isotopic data of stratabound and skarn related calcite and dolomite from W. Bergslagen (De Groot and Sheppard, 1988/ chapter 8). The same diagram shows a collection of trends for "normal marine deposited carbonates" to skarn

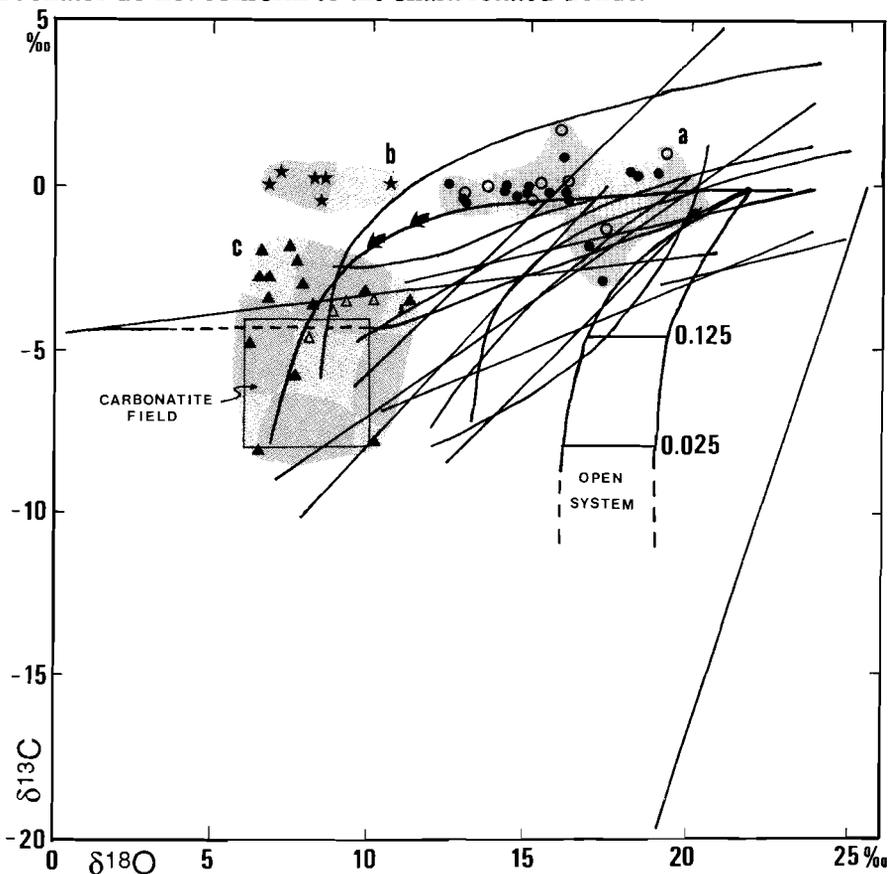
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< **Figure 1.** Schematic representation of different mineralization types in the West Bergslagen region, Central Sweden. See text for classification of the mineralizations.

carbonates as presented in Valley (1986, Fig. 6, p. 455).

Skarn carbonate C and O isotopes in general follow a trend from sedimentary carbonate values to values in the same range as that of magmatically formed carbonates, represented by the carbonatite box in figure 2.

The W. Bergslagen skarn carbonate values (shaded field c in Fig. 2), while ranging up to more positive values of both oxygen and carbon isotopes, cover the carbonatite isotope box. Arrows between the shaded fields a and c in figure 2 mark the West Bergslagen trend from sedimentary carbonates to skarn carbonates. This trend fits well with "normal trends" shown by Valley (1986) in his figure. Shaded area b (Fig. 2) represents the isotopic data of carbonates related to sea floor exhalative sedimentary deposits; these carbonates do not conform to the skarn related trends.



**Figure 2.**  $\delta^{18}\text{O}$  -  $\delta^{13}\text{C}$  diagram of skarn related carbonates from Bergslagen (after Valley, 1986). The lines marked as "open system" show the isotopic trend in an open system Rayleigh distillation process. Other lines in the diagram represent coupled  $\delta^{18}\text{O}$  -  $\delta^{13}\text{C}$  trends of normal marine limestones to contact metamorphic skarns. See text for further explanation.

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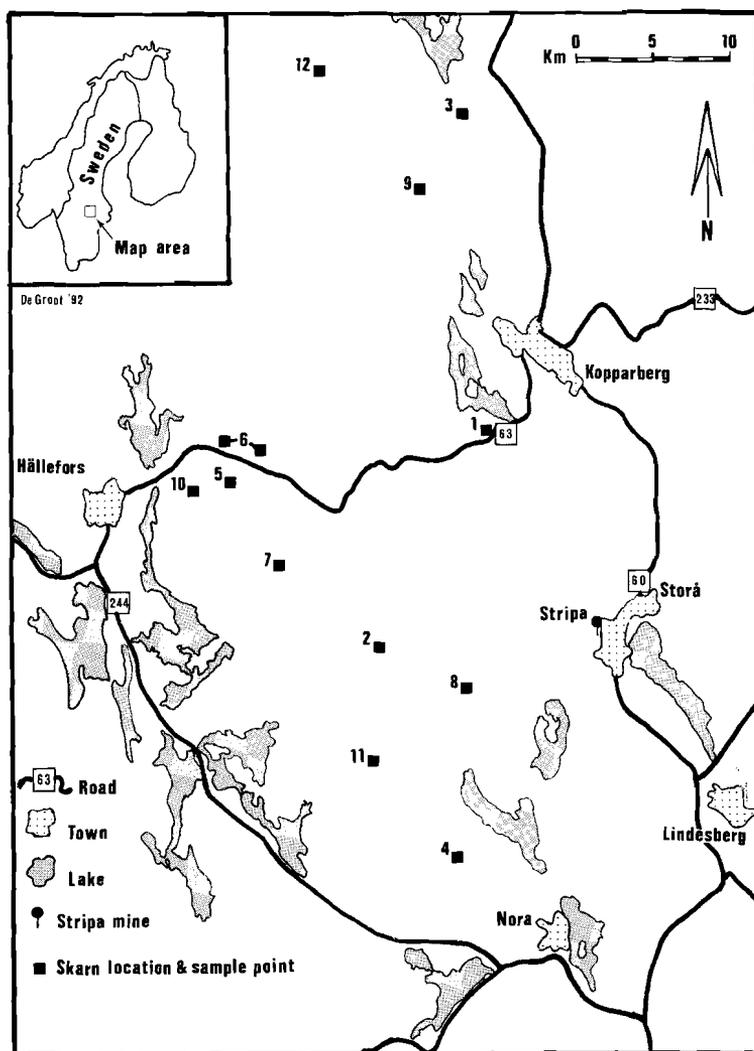
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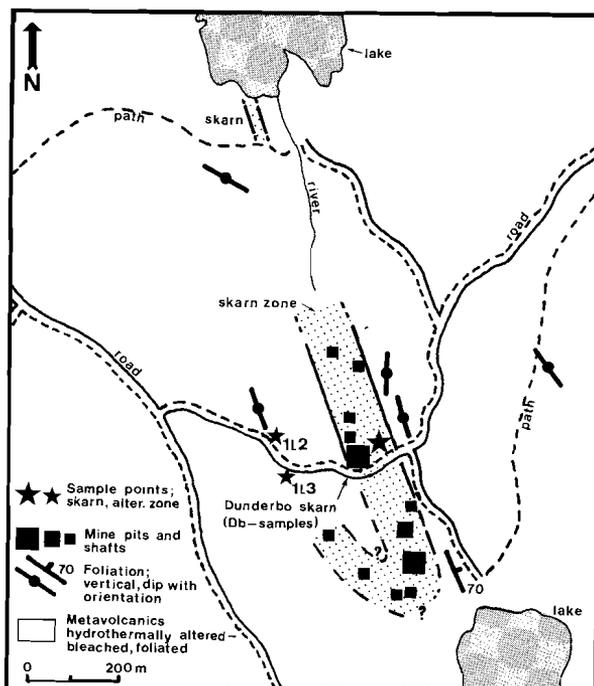
## Appendix

### DESCRIPTION OF SKARN DEPOSITS

Figure 1 shows a map with the locations of the skarns described below.



**Figure 1.** Map showing the locations of the skarns described in this chapter. 1 = Adamsgård; 2 = Dunderbo; 3 = Hörken; 4 = Hultagruvor; 5 = Killingberget; 6 = Sirsjöberg - Ösjöberg; 7 = Skropen; 8 = Sparrbergsgruvor; 9 = Ställdalen; 10 = Stolperget (Sikfors); 11 = Timansberg; 12 = Yxsjöberg.



**Figure 2.** Geological map of the Dunderbo region.

### Dunderbo

The Dunderbo region is characterized by a wide zone of highly altered and bleached felsic volcanics of the Bergslagen supracrustal sequence (Fig. 2). A (sub-)vertical bedding strikes approximately N340E. Foliation is parallel with this bedding.

A zone of skarn mineralizations is approximately parallel to the bedding/foliation and is completely surrounded by highly altered metavolcanics. Although no carbonate horizon is found in this zone, relict blocks of layered carbonate and the distribution of skarn mineralization in a specific horizon strongly suggest the former existence of a carbonate horizon. A series of old mine pits and dumps are situated in this skarn horizon. Samples were collected from the dump of the major mine-pit in this zone, marked on figure 2. Oxygen and hydrogen isotopic analyses were carried out on two silicate mineral samples from the alteration zone surrounding the skarn zone (Fig. 2; Table 1). Whole rock chemical analyses (XRF and INAA) for samples from the alteration zone are presented in table 2, including sample DU from Baker and Hellingwerf (1988).

Minerals in the skarn are: actinolite, calcite, dolomite, edenite, fluorite, magnetite, Mg-arfvedsonite, molybdenite, monazite, orthite, phlogopite, quartz (veins), scheelite, sulphides (minor), talc, tremolite.

### Sirsjöberg-Ösjöberg

The Sirsjöberg-Ösjöberg horizon comprises layers of Fe-(Mn-) oxides, marbles and skarn minerals (Fig. 3)(Baker, 1985b).

This horizon is parallel with the bedding of the felsic volcanics of the Bergslagen supracrustal sequence. It forms part of the volcanic sequence in the sub-circular Hjulsjö complex (Fig. 3; Baker, 1985a). An intrusive system of metabasic sills and dykes is parallel with, and cutsthrough this horizon. The intrusives of the Hjulsjö complex were assumed to have been the motor of the hydrothermal processes leading to the mineralizations.

**Table 1.** Compilation of the Dunderbo skarn isotopic data.

sample	mineral	$\delta D$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
Db1	dolomite			-4.65	8.11
Db2	dolomite			-3.53	9.28
Db-S	dolomite			-3.85	8.92
Db3	tremolite	-83.7	5.69		
Db4	phlogopite	-44.7	3.74		
Db5	phlogopite	-66.8	2.84		
Db91-1A/OM	edenite	-93.5	5.00		
	phlogopite	-69.5	3.00		
Db91-1A	edenite	-97.5	4.90		
	phlogopite	-70.2	2.80		
Db91-1B	phlogopite	-71.9	3.00		
Db91-1C	edenite	-85.8	5.05		
Db91-1D	Na-tremolite	-89.5	4.87		
Db91-1E	Mg-arfvedsonite	-91.8	4.89		
Db91-1F	edenite	-93.7	4.96		
DUNDERBO ALTERATION ZONE:					
GP1L2	phlogopite	-76.1	3.99		
GP1L3	clinochlore	-60.0	4.88		
ANNEHILL ALTERATION ZONE:					
GP2L2	whole rock	-41.5			

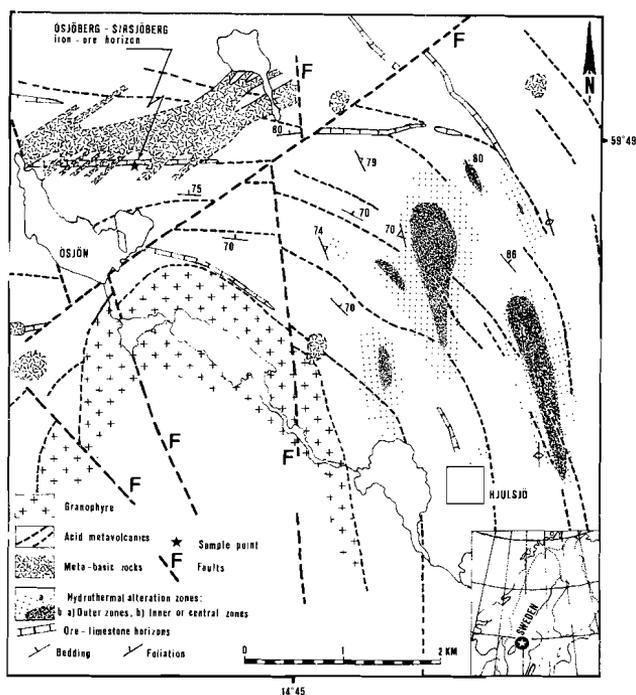
Isotopic values in per mil (‰) related to the SMOW standard (O, H) and PDB standard (C). Explanation of the isotopic data is given in chapters 8 and 9.

The Sirsjöberg-Ösjöberg mineralizations were primarily deposited as exhalative sea floor deposits and, after burial by volcanics, were skarn altered by later hydrothermal fluids, while tectonic processes have deformed, folded and faulted the horizon. The nearby Hjulsjö alteration

**Table 2.** Chemical data of the Dunderbo alteration zone and skarn mineralization.

	1L1	1L2	1L3	1L4	1L5	DU
SiO <sub>2</sub>	77.57	78.42	76.24	78.46	78.36	56.68
TiO <sub>2</sub>	0.07	0.08	0.07	0.07	0.09	0.02
Al <sub>2</sub> O <sub>3</sub>	12.4	12.85	12.12	13.05	11.93	1.33
Fe <sub>2</sub> O <sub>3</sub> *	0.34	0.20	0.52	0.13	0.84	5.42
MnO	0.002	0.002	d.l.	0.002	d.l.	0.012
MgO	2.49	0.72	5.25	0.48	3.48	25.35
CaO	0.15	0.14	d.l.	0.17	d.l.	5.57
Na <sub>2</sub> O	5.88	7.09	0.27	7.24	0.13	0.15
K <sub>2</sub> O	1.02	0.36	3.65	0.25	3.20	0.60
P <sub>2</sub> O <sub>5</sub>	0.029	0.034	0.029	0.041	0.028	0.017
Cr <sub>2</sub> O <sub>3</sub>	0.006	0.005	0.006	0.007	0.005	--
total	99.95	99.91	98.15	99.88	98.06	95.14
Ni	2.85	3.31	3.51	3.19	2.26	15.8
Cu	4.41	6.46	4.12	5.57	6.84	7.7
Zn	11.2	12.9	9.17	11.1	8.82	8.5
Ga	9.61	17.2	10.0	12.8	12.8	21.3
Rb	44.4	18.4	92.4	14.8	85.9	41.8
Sr	17.0	19.8	6.45	22.0	d.l.	6.8
Y	55.1	62.4	41.7	24.5	27.8	1130.0
Zr	87.6	90.8	89.3	91.4	84.7	13.5
Nb	7.09	8.67	12.6	9.61	14.7	--
Ba	87.4	34.8	173.0	69.8	d.l.	--
Pb	8.24	5.75	8.41	8.07	3.90	17.5
Th	16.5	15.7	19.7	18.5	13.6	--
Sc	--	--	--	--	1.75	4.79
Cr	--	--	--	--	10.53	--
Co	--	--	--	--	0.13	5.21
As	--	--	--	--	0.86	--
Sb	--	--	--	--	0.63	0.72
Cs	--	--	--	--	0.81	1.02
Hf	--	--	--	--	4.04	--
Ta	--	--	--	--	1.22	--
W	--	--	--	--	4.29	--
U	--	--	--	--	0.74	--
F	--	--	--	--	--	6840.0
La	--	--	--	--	5.93	940.0
Ce	--	--	--	--	11.02	2040.0
Sm	--	--	--	--	1.10	341.9
Eu	--	--	--	--	0.105	12.19
Tb	--	--	--	--	0.37	64.81
Yb	--	--	--	--	3.43	69.64
Lu	--	--	--	--	0.68	9.62
ΣREE	--	--	--	--	22.63	3478.16

Major elements in percentages. Trace elements in parts per million (ppm). Fe<sub>2</sub>O<sub>3</sub>\* = total iron. Analyses by XRF and INAA methods on whole rock samples. Analysis of F by ion selective anode technique. ΣREE = total rare earth elements. d.l. = detection limit. -- = not analysed. DU from Baker and Hellingwerf (1988b).



**Figure 3.** Geological map of the Hjulsjö region, including the Sirsjöberg - Ösjöberg iron-oxide mineralized horizon (After Baker and De Groot, 1983).

zones (Baker and De Groot, 1983/chapter 4; De Groot and Baker, 1992/chapter 5) could have been the conduit zones for fluids which transported the ore-forming elements to the surface. A compilation of isotopic data of minerals from the skarn is given in table 3. The carbonates represent sedimentary, stratabound carbonates, carbonates related to exhalative sea floor processes, and carbonates formed as late phases in the skarn mineralization.

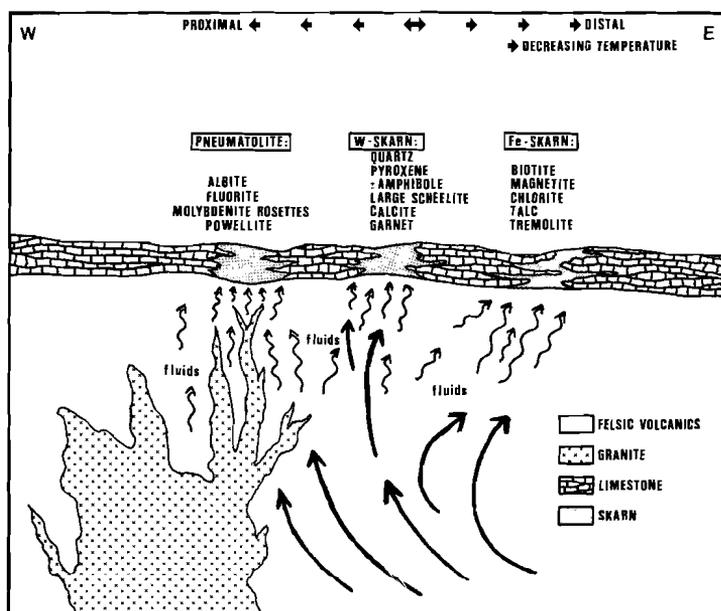
### Skropen

Two parallel carbonate horizons are interbedded in (sub-)vertical felsic volcanics with an E - W orientation (Fig. 4). Skarn mineralizations are formed in both carbonate horizons. In the western extension, pneumatolytic albite, fluorite, molybdenite (rosettes), and powellite mineralizations are most probably related to a granitic intrusion. Going eastwards hydrothermal fluid reacted with the carbonate horizon and formed skarns with garnet, pyroxene, scheelite (crystals of 5-6 cm size), and locally amphibole. At the eastern extension of the mineralized zone hydrothermal fluids reacted with an exhalative Fe-oxide and carbonate horizon to a Fe-skarn with magnetite, biotite, chlorite, tremolite, and talc. The West to East changing mineralogy reflects a decrease in temperature and increasing distance from the assumed granitic heat-source of the hydrothermal skarn forming system.

**Table 3.** Compilation of the Sirsjöberg - Ösjöberg skarn isotopic data.

sample	mineral	$\delta D$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
Cab1B-S	calcite			-2.87	17.59
Sir2-S	calcite			0.01	6.83
Sir3-S	calcite			-2.01	6.60
Sir7-S	quartz		7.59		
Sir8-S	piemontite	-12.8	2.86		
Öb2-Ö	calcite			-2.24	7.77
	quartz		8.23		
	clinocllore	-87.9	1.48		
Öb3-Ö	calcite			-3.47	6.86
	albite		6.15		
	Mg-hornblende	-90.1	4.98		
Öb4-Ö	clinocllore	-80.0	3.25		
Öb5-Ö	calcite			0.39	7.05
Öb6-Ö	quartz[light]		7.75		
	quartz[dark]		7.40		

Isotopic values in per mil (‰) related to the SMOW standard (O, H) and the PDB standard (C). S = Sirsjöberg; Ö = Ösjöberg. Explanation of the isotopic data is given in chapters 8 and 9.

**Figure 4.** Schematic representation of the Skropen skarn mineralizations (After Baker, pers. com.).

**Table 4.** Compilation of the Skropen skarn isotopic data.

sample	mineral	silicates:		carbonates:	
		$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	
BJ Sk1	calcite		-5.70	7.55	
	albite	7.91			
BJ Sk2	calcite		0.30	14.89	
BJ Sk3	albite	8.02			
Sk P1	quartz	8.89			
	Fe-pargasite	3.98			
Sk P2	quartz	8.85			
	hedenbergite	4.52			
Sk P3	quartz	8.80			
Sk P4	quartz	8.94			
Sk P7	diopside	4.83			

Isotopic values in per mil (‰) related to the SMOW standard (O) and the PDB standard (C). Explanation of the data is given in chapters 8 and 9.

**Table 5.** Compilation of the Sparrbergsgruvan skarn isotopic data.

sample	mineral	$\delta\text{D}$	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
Sp1	calcite			-3.51	11.37
	dolomite			-3.51	10.17
	chrysotile	-92.5	3.88		
Sp2	pargasite	-90.2	3.91		
Sp3	lizardite	-110.5	4.24		
Sp BJ1	quartz		10.51		
Sp91-1A/I	edenite/pargasite	-91.0	6.28		
Sp91-1A/II	phlogopite	-83.0	3.51		
Sp91-4	phlogopite	-88.4	3.73		

Isotopic values in per mil (‰) related to the SMOW standard (O, H) and PDB standard (C). Explanation of the data is given in chapters 8 and 9.

The chemical composition of a sample from the skarn was analysed by Baker and Hellingwerf (1988). A compilation of the isotopic data from the Skropen skarn is given in table 4.

Minerals: albite, biotite, calcite, chlorite, diopside, Fe-pargasite, fluorite, grossular, magnetite, molybdenite, powellite, scheelite, talc, tremolite, quartz, zircon.

### Sparrbergsgruvan

The bedding of the felsic metavolcanic sequence of the Sparrbergsgruvan area is steeply dipping westward. The strike is North - South with slight bendings resulting in a concave form towards the East (Fig. 5). Thin layers (up to 10 m thick) of limestone and skarn are interbedded. The skarn is divided in a magnetite skarn which contains garnet, amphibole and epidote, and a scheelite skarn which contains epidote, garnet, hornblende and clinopyroxene. They are marked with *m* and *s* on figure 5 respectively. Former mineshafts with dumps are marked on the map and are named Sparrbergsgruvan and Vintergruvan. The samples collected for this study are from the Sparrbergsgruvan dumps. A compilation of the isotopic data is given in table 5. One sample from the Sparrbergsgruvan skarn was chemically analysed by Baker and Hellingwerf (1988).

Minerals: calcite, chrysotile, diopside, dolomite, edenite, epidote, fluorite, garnet, kaoline, lizardite, magnetite, microcline, oligoclase, relict olivine (Geijer and Magnusson, 1944), pargasite, phlogopite, plagioclase, quartz, scheelite, sericite, talc, tremolite, vesuvianite.

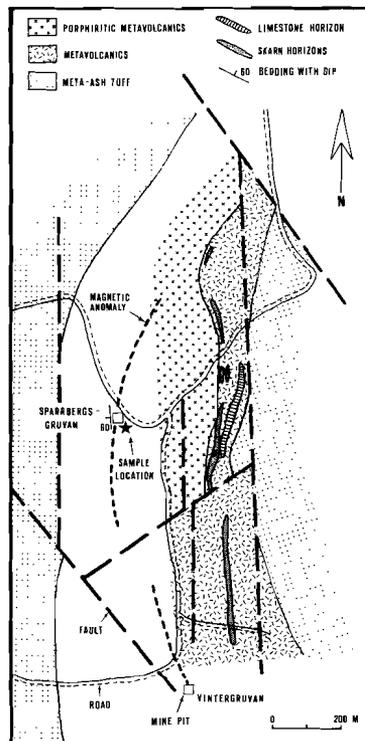


Figure 5. Geological map of the Sparrbergsgruvan area (After K.-A. Sandahl, unpubl.).

### Stolpberget (Sikfors)

A sequence of rhyolitic flows is covered by felsic ash tuffs (Fig. 6). The tuff intercalates a horizon of thin marble lenses (maximum thickness: 5 m) just above the flow - tuff contact. Bedding of the volcanics and marble strikes N020-040E, bends to a N060-080E strike in the North, and is positioned sub-vertically. Several metabasic dykes, most with a N340E orientation, crosscut the volcanics and the marble. Skarn mineralization (Fe) took place in metabasic dykes at and near the contact with the marble. Old mine pits and shafts are situated in lines parallel with the mineralized metabasite. The wide angle between the mineralized dykes and the bedded supracrustals characterizes a non-stratiform skarn. A compilation of isotopic data is given in table 6.

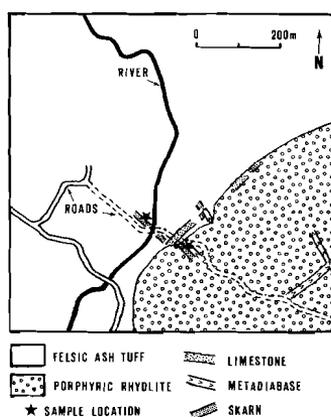


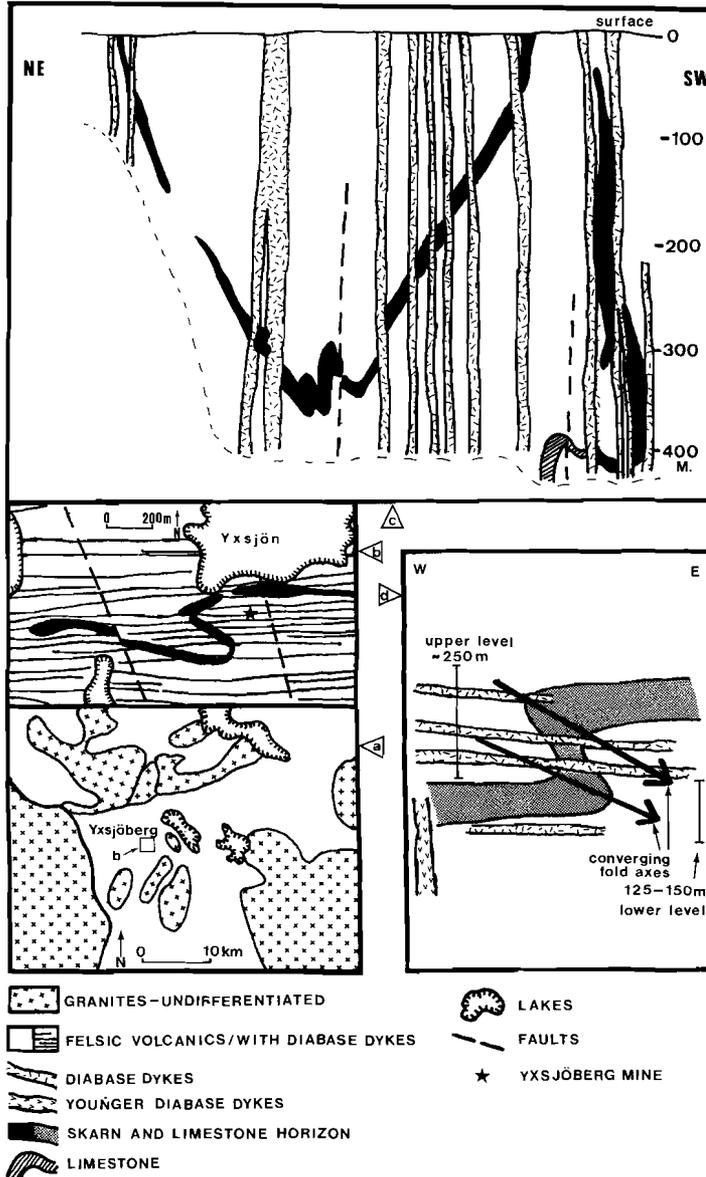
Figure 6. Geological map of the Stolpberget (Sikfors) area.

Table 6. Compilation of the Stolpberget (Sikfors) isotopic data.

sample	mineral	$\delta D$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
St1	calcite			0.49	16.65
St2	calcite			-1.91	7.60
St3	edenite	-55.2	5.58		
St4	phlogopite	-54.1	2.84		
St5	talc(pyrophyllite)	-54.4	5.42		
St6	phlogopite	-51.6	3.28		
St91-1A	phlogopite	-70.7	2.71		
St91-2	Na-tremolite	-65.5	4.83		
	talc	-53.2	5.60		

Isotopic values in per mil (‰) related to the SMOW standard (O, H) and PDB standard (C). Explanation of the data is given in chapters 8 and 9.

Minerals: biotite, calcite, chlorite, edenite, epidote, hematite (minor, secondary), hornblende, magnetite, Na-tremolite, phlogopite, pyrite (minor), pyrophyllite, quartz, sericite, talc.

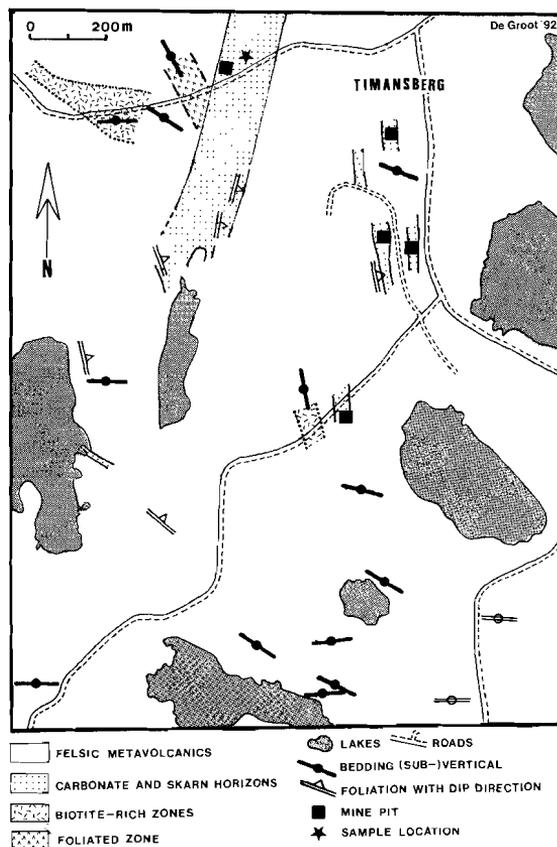


**Figure 7.** a) Geological map of the Yxsjöberg area, b) Geological map of the surroundings of the Yxsjöberg mine (marked with a star on the map); showing the outcrop pattern of the skarn, c) NE - SW section of the Yxsjöberg skarn, d) Horizontal section of the S-pattern folded skarn. Maps a-c after Ohlsson (1979) and map d by pers. com. S. Månson (1988).

**Table 7.** Compilation of isotopic data of samples from the Yxsjöberg mine.

sample	mineral	$\delta D$	$\delta^{18}O$
Yx AM1	edenite	-91.0	4.97
Yx AM2	hedenbergite		4.11
	quartz		9.11
Yx HW1	Mg-hornblende	-94.5	4.64
Yx HW2	quartz		7.93
	phlogopite	-74.1	2.03
Yx HW3	Mg-hornblende	-94.5	4.58

Isotopic values in per mil (‰) related to the SMOW standard. Explanation of the isotopic data is given in chapters 8 and 9.



**Figure 8.** Geological map of the Timansberg area.

### Yxsjöberg

The tungsten mine of Yxsjöberg started operation in 1971 and was closed in 1989. Earlier mining activity concentrated on Cu extraction (Ohlsson, 1979; S. Månson, pers. com.). The geological situation is shown in figure 7a-d and is described in Ohlsson (1979). The samples collected for this study were taken in August 1988, at the active mining level, 575 m below surface, with the kind permission of mine chief-engineer S. Månson.

Cheilletz (1988), reviewing stratiform tungsten deposits, classifies the Yxsjöberg (and Sandudden) deposits as concordant replacement epigenetic deposits formed in calc-silicate bands. A compilation of the isotopic data from samples of the Yxsjöberg mine is given in table 7.

Minerals: andradite, calcite, chalcopyrite, diopside, edenite, fluorite, grossularite, hedenbergite, magnetite (minor), Mg-rich hornblende, phlogopite, pyrrhotite, quartz, scheelite; accessory: apatite, Bi-sulphides, helvite, molybdenite, sphalerite, sphene, wolframite.

### Timansberg

An approximately N-S striking sequence of sub-vertically placed felsic volcanics bends to an E-W strike within a distance of 1 km south of the Timansberg mine (Fig. 8). Several levels of stratiform carbonate layers follow the bedding. The skarn mineralizations of this site are formed in or near the N-S carbonate horizons. The mineralizations cannot be followed after the volcanics bend to an E-W orientation. The mine dump sample location is marked with a star on the map. A compilation of the isotopic data is given in table 8.

Minerals: actinolite, chlorite, epidote, garnet, hornblende, magnetite, phlogopite, pyrite (minor), talc.

**Table 8.** Compilation of the Timansberg isotopic data.

sample	mineral	$\delta D$	$\delta^{18}O$
Tb91-1	phlogopite	-71.1	2.43
Tb91-2	Mg-arfvedsonite	-88.3	4.04
	phlogopite	-81.8	1.86

Isotopic values in per mil (‰) related to the SMOW standard. Explanation of the isotopic data is given in chapters 8 and 9.

### Adamsgård, Hörken, Hultagruvor, Killingberget, Ställdalen

These skarns are not discussed separately. Their location in the Bergslagen region is shown in Figure 1. Isotopic data are listed in Table 1, chapter 9. The isotopic data are also explained in chapter 9. Baker and Hellingwerf

(1988; see their Table 2) produced chemical analyses of samples from the Adamsgård, Hultagruvor, and Killingberget skarns.

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**Curriculum Vitae:**

Pier Anne de Groot, auteur van dit proefschrift, werd geboren op 19 Oktober 1950 te Eindhoven. Tussen 1963 en 1970 werd de B-richting van de Hogere Burger School (H.B.S.-B) van het Gemeentelijk Lyceum te Eindhoven doorlopen. Na 14 maanden militaire dienst, volgens de gebruikelijke Nederlandse normen, van September 1970 tot Januari 1972, werd een study geologie aangevangen aan het Geologisch Instituut van de Universiteit van Amsterdam. Begin 1976 wordt het kandidaatsexamen behaald in de richtingen G3 (algemeen geologie) en G5 (geochemie). Na het kandidaatsexamen wordt gekozen voor de richting petrologie, mineralogie, ertskunde. De studie van het Bergslagen gebied, Centraal Zweden, wordt begonnen. Dit is tevens het gebied van onderzoek voor dit proefschrift. Het doktoraalexamen in de petrologie, met bijvak mineralogie, werd behaald aan de Universiteit van Amsterdam in 1985. Hierna volgt, op een beurs van de Franse C.N.R.S. organisatie, een verblijf van 16 maanden aan het Centre de Recherches Pétrographiques et Géochimiques, Vandoeuvre-lès-Nancy, Frankrijk. Uiteindelijk is de auteur op het Instituut voor Aardwetenschappen, Universiteit van Utrecht, bij de vakgroep Geochemie in het stabiele isotopen laboratorium terechtgekomen. Na een beginperiode, waarin hij als part-time werkkraft bij de posterijen helpt voorzien in het onderhoud van zijn gezin, wordt een twee-jarig AIO-schap aangeboden om het proefschrift af te maken. Aan de Universiteit van Utrecht wordt het proefschrift verder voltooid, met een verdediging van dit proefschrift op 22 Februari 1993.

## ERRATA

- Page 73 / line 6 -** Formula:  $\delta (\text{‰}) = \{(R_{\text{sample}} - 1)/R_{\text{standard}}\} \cdot 10^3$  should be  $\delta (\text{‰}) = \{(R_{\text{sample}}/R_{\text{standard}}) - 1\} \cdot 10^3$ .
- Page 126 / figure 3 -** At lower left corner of figure: "sub-seafloor alteratie" should be "sub-seafloor alteration".
- Page 160 / figure 1 -** Bottom of figure: "DEEP FLUIDS" should be "DEEP FLUIDS (seawater origin)".
- Page 161 / line 14 -** Exhalative sedimentary mineralizations are not SEDEX in the classical sense of the term.