

**GEOLOGICA ULTRAIECTINA**

Mededelingen van het  
Instituut voor Aardwetenschappen der  
Rijksuniversiteit te Utrecht

No. 37

**MAGMAS AND INCLUSIONS  
OF MONTE AMIATA VOLCANO,  
TUSCANY, ITALY**

**MANFRED J. VAN BERGEN**

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**MAGMA'S EN INSLUITSELS  
VAN DE VULKAAN MONTE AMIATA,  
TOSCANE, ITALIË**  
(met een samenvatting in het Nederlands)

**PROEFSCHRIFT**

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN  
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN  
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**MANFRED JULES VAN BERGEN**

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**PROMOTOR: PROF. DR. R.D. SCHUILING**



*- E c'è chi dice che, al pari di tutte le cose toscane,  
nasce di sotterra, o, come credevan gli etruschi,  
dall'inferno -  
(Curzio Malaparte: Maledetti toscani)*

Met dank aan al degenen die de totstandkoming van dit proefschrift  
mogelijk hebben gemaakt

## SUMMARY

Mt. Amiata, a Pleistocene volcanic complex in south Tuscany consists mainly of silicic (62-67 wt.% SiO<sub>2</sub>) lavas and domes, many of which contain abundant metamorphic and mafic igneous inclusions. The results of a detailed geochemical and petrological study indicate a bimodal magmatic system where magma-mixing and wall-rock assimilation were the main pre-eruptive processes in a reservoir underlying the volcano. The metamorphic inclusions are fragments of a contact aureole that formed around the magma chamber in regionally metamorphosed rocks, predominantly schists, gneisses and minor quartzites of the pre-Mesozoic crystalline basement. Aluminous, silica-deficient inclusions that form the largest group, are considered to originate from quartz-poor mica-schists by complex assimilation processes involving extraction of partial melt, interdiffusion between co-existing liquids and mineral-liquid reactions. The igneous inclusions represent blobs of hybrid magma, and form, together with some subordinate intermediate lavas and the host lavas an almost complete mixing array, as a result of the inflow of mafic magma into the acid reservoir. Processes of selective chemical exchange superimposed on mixing were probably of little importance. Consequently, the end-members can be identified as an acid Tuscan-type magma of crustal anatectic origin, and a primitive mafic Roman-type magma of the high-K series that is commonly considered to be derived from the upper mantle. This separated origin and the fact that both magmas have some chemical characteristics in common (an enrichment in potassium and a number of related elements) could imply that portions of the lower crust and upper mantle were metasomatized by the same fluid prior to melting.

## SAMENVATTING

De Monte Amiata, een Pleistoceen vulkanisch complex in zuid Toscane, bestaat voornamelijk uit zure (62-67 gew.%  $\text{SiO}_2$ ) lava's en dômes, waarvan vele rijk zijn aan metamorfe en basische magmatische insluit-sels. De resultaten van een gedetailleerde geochemische en petrologi-sche studie wijzen op een bimodaal magmatisch systeem waar magmavermen-ging en assimilatie van het nevangesteente de voornaamste pré-eruptieve processen waren in een reservoir onder de vulkaan. De metamorfe in-sluit-sels zijn fragmenten van een contact-aureool dat ontstond rond de magmakamer in regionaal metamorfe gesteenten, voornamelijk schisten, gneizen en in mindere mate kwartsieten van de pré-Mesozoïsche kristal-lijne ondergrond. Alumineuze, silica-deficiente insluit-sels die de grootste groep vormen, worden beschouwd te zijn ontstaan uit kwarts-arme glimmerschisten als gevolg van ingewikkelde assimilatieprocessen. Hierbij speelden extractie van partiële smelt, interdiffusie tussen smeltfasen en mineraal-smelt reacties een rol. De magmatische insluit-sels vertegenwoordigen 'druppels' gemengd magma, en vormen tezamen met enige ondergeschikte intermediaire lava's en de gastheer lava's een vrijwel volledige mengserie als gevolg van de instroming van ba-sisch magma in het zure reservoir. Processen van selectieve chemische uitwisseling gesuperponeerd op de vermenging waren waarschijnlijk van weinig belang. De eindleden kunnen derhalve geïdentificeerd worden als een zuur magma van het Toscaanse type, ontstaan door anatexis in de korst, en een primitief basisch magma van het Romaanse type en wel van de kalium-rijke serie die algemeen beschouwd wordt afkomstig te zijn van de bovenmantel. Deze gescheiden oorsprong en het feit dat beide magma's enige chemische kenmerken gemeen hebben (een aanrijking in ka-lium en een aantal verwante elementen), kunnen een aanwijzing zijn dat delen van de onderkorst en bovenmantel vóór opsmelting een metasomato-se hebben ondergaan door één en dezelfde fluïde fase.

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## CHAPTER I

### INTRODUCTION

#### REGIONAL SETTING

The northern part of the young magmatic belt that extends along the Tyrrhenian side of the Italian peninsula comprises rock-types that belong to the two magmatic provinces that are commonly distinguished in Central Italy (fig. 1). In Tuscany, northern Lazio and on islands of the Tuscan archipelago, predominantly acid intrusive, subvolcanic and volcanic occurrences form the Tuscan Magmatic Province (TMP), whereas large potassic-alkaline volcanic centres in Lazio belong to the Roman Magmatic Province (RMP) which stretches further southwards to still active centres such as Vesuvius in the Campanian region. The Pleistocene complex of Mt. Amiata is the youngest of the TMP occurrences. These have mostly Pliocene ages that decrease from west to east, while the neighbouring Roman centres are Pleistocene and younger.

The magmatic activity developed in the internal parts of the Northern Apennines which are characterized by a pile of nappes transported in northeastern and eastern directions during the Miocene compressional stage of the Apennine orogenesis. As a rule, more external Umbro-Tuscan units that consist of Mesozoic and Cenozoic sediments typical for deeply submerged continental platforms ('miogeosynclinal' facies) underly more internal Ligurian units of 'oceanic' sediments and ophiolites ('eugeosynclinal' facies) of the same age. On the Tyrrhenian side, the substratum of these more or less allochthonous units is known to be formed by a Hercynian or older crystalline basement.

Although compressional movements are presumably still active in the easternmost part of the Northern Apennines, the internal areas have been subject to distensive tectonics with strong vertical movements since the end of Miocene times, which led to the development of horst-

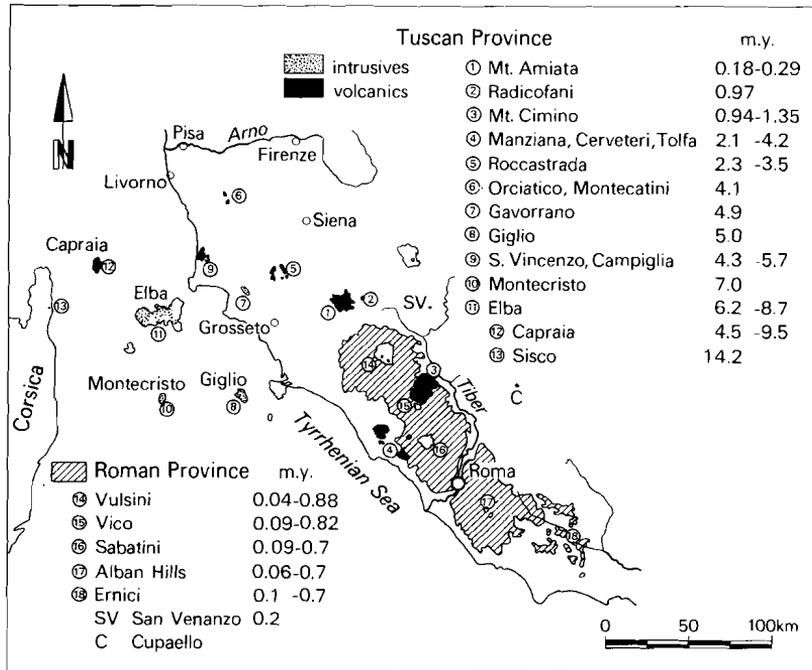


Fig.1. Occurrences of the Tuscan and Roman magmatic provinces in Central Italy (modified after Pichler, 1970). Ages are from Barberi et al. (1971), Marinelli (1975), Locardi et al. (1975), Civetta et al. (1978) and others.

graben structures parallel to the Tyrrhenian coast (fig. 2). In Tuscany and northern Lazio, considerable amounts of clastic sediments were deposited in marine and continental basins, the formation of which gradually proceeded from west to east, in the same direction as the magmatic activity. Transverse structures dissect these basins. Complicated vertical movements continue till present and have caused a general regional uplift marked by high topographic elevations of Neogene sediments. The emplacement of magma, a high heat-flow anomaly and ore-forming mineralization further characterize the entire region.

The geotectonic setting of the Northern Apennines is a matter of discussion consequent on the complexity of the geodynamics of Italy. Several hypotheses, applying plate-tectonic mechanisms in order to solve problems such as those concerning the relationships between the Western Alps, the Corso-Sardinian continental fragment and the Adria-

tic microplate, as well as the formation of the Tyrrhenian Sea, invoke west- and/or east-directed subduction zones under the Northern Apennines at various stages of their orogenic evolution. Some authors fit the TMP in a trench/arc/back-arc model with a westward dipping Benioff zone, whereas others consider it as a calcalkaline system related with an eastward dipping zone caused by the anti-clockwise rotation of the Corso-Sardinian microplate. The latter model accounts for the migration of the activity in the TMP which has also been explained as a result of a westward movement of the Tuscan continental lithosphere over a hotspot and of the anti-clockwise rotation of the Apennines.

Different opinions on the deep crustal structure in this region have been put forward as well, but recent geophysical studies, combining seismic and gravimetric data, provide strong indications for the presence of two crust/mantle boundaries under Elba and western Tuscany

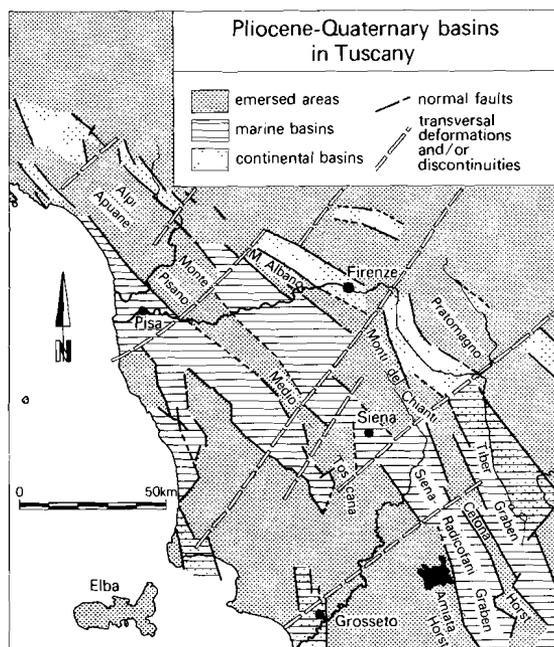


Fig.2. Fault-tectonics and distribution of main sedimentation basins in Tuscany, formed in Pliocene and Quaternary times (redrawn after Bartolini et al., 1982). Mt. Amiata volcanics indicated in black.

(fig. 3). The deeper boundary (40-60 km) is considered to be part of the Corso-Sardinian block, whereas the shallow one (20-30 km) belongs to the Adriatic microplate. This configuration is compatible with the hypothesis of a continental collision between Corsica and the Northern Apennines and underthrusting of the (thinned) Adriatic plate-margin by the Corsican front.

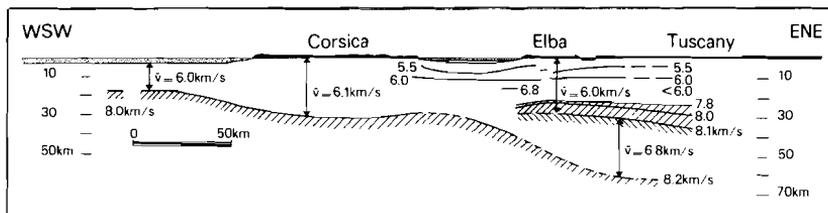


Fig.3. Seismic refraction velocities in a cross-section showing doubling of the crust-mantle transition in Tuscany (redrawn after Morelli et al., 1977).

Most magmas of the TMP undoubtedly have a crustal anatectic origin, given the presence of solid relicts of partial fusion, the high degree of silica-saturation, the frequent excess of aluminium and the available O, Sr and Nd isotope data, the latter being also compatible with large-scale assimilation of sediments. Hence, these magmas clearly differ from typical calcalkaline series commonly associated with converging plate-boundaries. Minor amounts of more mafic volcanic and sub-volcanic rocks also occur and have characteristics tending towards potassic series. These chemical variations have been ascribed to heterogeneous crustal source-rocks and to different degrees of partial melting of an homogeneous source, but interaction of crustal melts with subcrustal components seems another important alternative.

The potassic volcanics of the RMP which comprises high-potassic series (HKS) and (low-)potassic series (LKS or KS), are, on the other hand, considered to have a subcrustal origin, as the Mg/Fe ratio, Ni and Cr contents and phenocryst compositions of the most primitive lavas are in accordance with a primary mantle-derived liquid. Isotope systematics and high abundances of incompatible elements are explained in terms of interaction with crustal material (mixing with TMP magma

or assimilation) and by a metasomatic enrichment of the upper mantle prior to melting. The chemical evolution of both series is largely controlled by low-pressure fractional crystallization in shallow magmachambers, with magma mixing and assimilation as possible accompanying processes. Whether the RMP volcanism is related to a Benioff zone or to the initial stages of continental rifting is not clear.

Summarizing, the magmatic activity in Tuscany and Lazio is associated with distensive tectonics superimposed on a previous compressional stage. Siliceous crustal magmatism of the TMP generally preceded potassic subcrustal magmatism of the RMP, but both provinces overlap in space and time.

A general outline of the geology of Italy is to be found in Squyres (1975), which contains a chapter on the magmatic evolution by Marinelli. A review of the TMP is given by Barberi et al. (1971) and a good impression of the various aspects of the RMP can be obtained from recent publications on Vulcini, the Roman centre closest to Mt. Amiata (Varekamp, 1979, 1980; Holm and Munksgaard, 1982; Holm et al., 1982). Relevant papers discussing tectonic models include those by Alvarez (1972), Boccaletti and Guazzone (1972), Elter et al. (1975), Reutter et al. (1978) and Kligfield (1979). Morelli et al. (1977) presented recent geophysical data. Other references are given in the next chapters.

#### MT. AMIATA

Mt. Amiata complex, located on the boundary between the provinces of Siena and Grosseto in southern Tuscany, occupies an area of about 85 km<sup>2</sup> and has an approximately rectangular shape with radially trending offshoots (fig. 4). In the accidented central part a number of domes occur of which Amiata (1738 m.) is by far the highest summit in the wide mountainous surroundings. Around the more gently undulating peripheral parts, several villages are situated at elevations between 600 and 850 m.

Up to 1000 m. thick volcanic products with a total volume of some 25-30 km<sup>3</sup> cover a substratum of mainly Cretaceous-Eocene formations of the allochthonous 'Alberese-Pietraforte' Group which consists of a

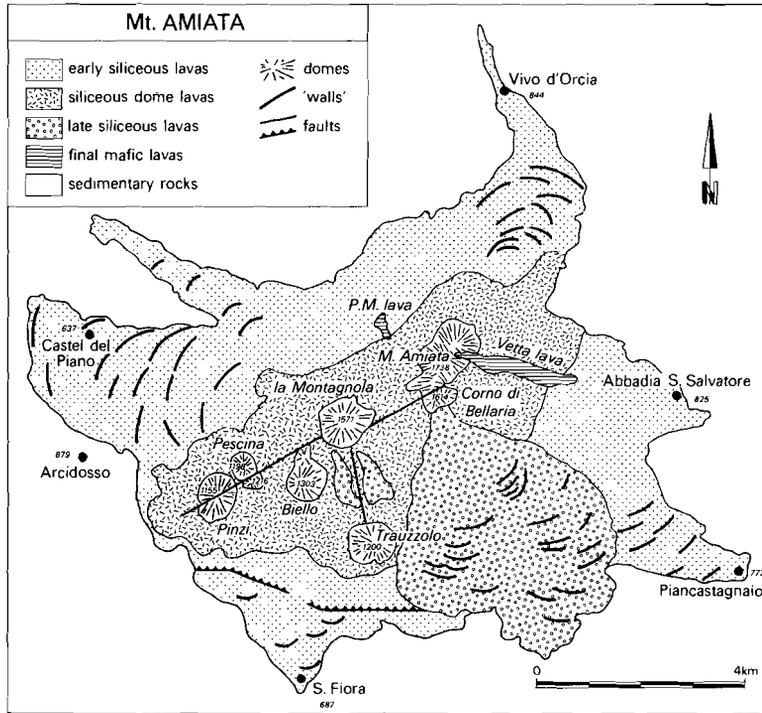


Fig.4. Geological map of Mt. Amiata complex (after Marinelli, 1961 and Mazzuoli and Pratesi, 1963). Indented fault possibly of volcano-tectonic origin. 'Walls' (see text) are exaggerated. P.M. lava: Pian delle Macinate lava.

variety of shales, calcareous rocks and sandstones (Calamai et al., 1970). These rocks, as well as tectonically reduced older Mesozoic sediments that belong to the so-called Tuscan Formations, outcrop in an uplifted structure bounded on the east by the NW-SE trending Radico-fani Graben (fig. 2) which was filled with thick clastic sediments after the early Pliocene marine transgression.

As a result of the vertical movements characteristic for the post-Miocene tectonic regime in this part of the Northern Apennines, the area of Mt. Amiata was already emerged when the volcanic activity started. Lavas were emplaced on an eroded surface and filled existing depressions, which eventually led to a morphological inversion of the landscape.

Eruption points are difficult to trace in the field, but probably coincide with the positions of the domes, most of which are aligned according to NE-SW (anti-apenninic) directions. Bifid summits of several domes point to post-volcanic tectonic activity possibly resulting from reactivation of older dislocations. Faults connected with a caldera-type collapse appear to be absent or inconspicuous on the surface, except for one in the southern part that may be interpreted as such (fig. 4). A series of faults with a roughly concentric trend dissect the substratum, however, and mark a depression in the central part of the volcano (Calamai et al., 1970). Also, sparse diatomaceous deposits are thought to have formed in small intra-calderic lakes.

The collapse structures suggest the partial emptying of a magma-chamber, independent evidence for the presence of which is given in Chapter II. The emplacement of magma at depth may explain the recent upheaval (up to 900 m.) of certain Pliocene sediments, a local strong negative Bouguer anomaly and very high heat flow (Marinelli, 1963; Calamai et al., 1970). Geothermal steam is exploited at several localities in the area (see Cataldi, 1967), which is also known for important mineralizations of cinnabar. Further details on the geological setting of Mt. Amiata are to be found in Calamai et al. (1970) who presented excellent geological, geophysical and hydrogeological maps. More information concerning the local subsurface geology is discussed at the end of Chapter II.

#### PREVIOUS STUDIES

Since Mt. Amiata was described as an extinct volcano for the first time in the 18th century by Micheli (1773, reference in Rodolico, 1935), numerous researchers have been occupied with its rocks including the unusual variety and abundance of igneous and metamorphic inclusions. In most of the existing literature (which is almost exclusively in Italian), emphasis was laid on petrographical aspects, and much attention was paid to the eruption sequence and mode of emplacement of the volcanic products. The following list is a selection of the most important studies (note that originally used rock-names are maintained):

Williams (1887), who divided the volcanics into trachytes with limpid glass and small phenocrysts, and trachytes with turbid glass and large phenocrysts, believed in only one single eruption for the whole complex.

Sabatini (1910, 1912) considered the possibility that the volcanics were welded tuffs, given the analogy with certain products of Mt. Cimino, and made a subdivision into four major eruptions.

Rodolico (1934, 1935), in a study which also included the xenoliths, distinguished hypersthene-bearing trachyte, hypersthene and augite-bearing trachyte and augite-bearing andesite (= Pian delle Macinaie lava). Observing the similarity of the igneous inclusions and the andesite, these relatively mafic rocks were interpreted as lavas that erupted earlier than the trachytes. Argillaceous sediments, possibly of Neogene age, were suggested to be parent rocks of the metasedimentary inclusions in which contact- and pyrometamorphic mineral-assemblages were recognized. The reader is referred to these papers for a bibliography of previous publications on Mt. Amiata.

Rittmann (1958, 1960, 1962), discussing eruption mechanisms, considered the trachytes as ignimbrites and mentioned Mt. Amiata as a good example for the occurrence of rheoignimbrites. These were thought to originate when ignimbrites are deposited on slopes sufficiently steep to induce a secondary flow, which would explain why the rocks have the textural aspect of normal rhyolitic lavas. A characteristic of this mechanism would be the formation of the abundant arcuate, wall-like structures (fig. 4) which are convex in the direction of flow and give the impression that still fluid basal flow-layers intruded the already cooled, practically solid and fractured cover as rootless dikes. These structures emerge like 'walls' in the terrain due to selective erosion. Rittmann also noted the existence of the second more mafic lava flow (Vetta lava).

Marinelli (1961), in a paper on the genesis and classification of the recent Tuscan volcanics, adopted Rittmann's hypotheses with minor modifications and distinguished the following types of undifferentiated acid products:

- normal ignimbrite cover with large phenocrysts of sanidine

- lavadomes with large phenocrysts of sanidine
- rheoignimbritic types emplaced directly on the sedimentary substratum or on the normal ignimbrites (e.g. the flow south of Corno di Bellaria), with broken sanidines
- small stratified lavas with large sanidines (e.g. south of La Montagnola).

The igneous inclusions and mafic lavas were considered to represent magma derived from the acid anatectic magma by means of a filtration process leading to an enrichment in K and other mobile elements (see also Marinelli and Mittempergher, 1966; Marinelli, 1967). These differentiates then erupted as lavas at the beginning and at the end of the volcanic activity. Marinelli (1975) abandoned the hypothesis as a general explanation for the origin of potassic mafic magmas in Italy.

Mazzuoli and Pratesi (1963a, see also 1963b) presented a comprehensive study of Mt Amiata. Based on field-observations, aerial photographs, petrographical and (major element) chemical data, these authors made a subdivision into:

- a quartz-latic complex with small or broken phenocrysts of sanidine
- a quartz-latic complex with large phenocrysts of sanidine
- quartz-latic lava flows (south of La Montagnola and Corno di Bellaria)
- trachytic lava flows (refers to the small, more mafic lavas).

They shared Rittmann's view on the mode of emplacement of rheoignimbrites but denied the presence of normal ignimbrites with large sanidines. Marinelli's ideas on the magmatic differentiation were also accepted.

Other recent work deals exclusively with petrological and geochemical aspects in a regional context:

Schiaffino (1963) noted the presence of cristobalite in addition to sanidine and plagioclase in the glassy groundmass and in spherulites.

Coradossi (1966) discussed K/Rb systematics.

Dupuy (1970) made an extensive geochemical study of the intrusive and extrusive occurrences in the TMP. He presented (see also Dupuy, 1967, 1968a, b, 1972; Dupuy and Allègre, 1972; Dupuy et al., 1973) major and trace element data (notably Li, Rb, Cs, Sr, Ba, Ga and Tl)

for Amiata rocks and separated feldspars, biotites and glasses (except for the igneous inclusions). Model calculations were used to show that the magmas originated by anatexis of granitic-gneissic crustal material, whereby the observed whole-rock compositional variations were explained in terms of partial fusion.

Ferrara et al. (1975, 1976) analysed rocks and glasses for U, Th, Zr, La and Ce, and confirmed the crustal anatectic origin.

Dostal and Capedri (1975) reported some concentrations and partition coefficients between phenocrysts and groundmass for U.

Balducci and Leoni (1981) studied sanidine megacrysts and discussed the crystallization of feldspars.

Limited isotopic data are available. Barberi et al. (1971) and Marinelli (1975) reported a range of  $\text{Sr}^{87}/\text{Sr}^{86}$  ratios between 0.711 and 0.715 in agreement with the results of three rock-samples in Hawkesworth and Vollmer (1979), two of which have  $\text{Nd}^{143}/\text{Nd}^{144}$  ratios of 0.51214 and 0.51216. Vollmer (1977) determined Pb-isotopes in the same samples. Taylor and Turi (1976) made one analysis of oxygen isotopes which yielded  $\delta\text{O}^{18} = 12.36$  for a quartz-lattice and 12.67 for the sanidine in it.

Bigazzi et al. (1981) provided recent geochronological data for Mt. Amiata. They found consistent K/Ar and fission-track ages between 0.18 and 0.29 m.y. (one anomalously high fission-track determination yielded 0.44 m.y.), which seems to invalidate a single K/Ar age of 0.43 m.y. reported by Evernden and Curtis (1965). With these ages Mt. Amiata is the youngest occurrence in the TMP.

#### STARTING POINTS AND SCOPE OF THIS STUDY

Current views on the emplacement mechanisms of volcanics preclude the presence of ignimbrites or rheoignimbrites at Mt. Amiata (e.g. Barberi et al., 1971; Marinelli, 1975), a concept that was already criticized in a general context by Pichler (1963) and others who noted that, from outcrop to thin section, rheoignimbrites cannot be distinguished from normal lavas. From my own observations in the field and

of thin sections there is no doubt that all acid volcanics of the complex are lavas (which display flow layering, blocky fronts and surfaces and sometimes fumarolic colorations). Due to the dense vegetation, the monotony of rock-types and the absence or poor development of paleosoils, field relations are, however, not sufficiently clear to establish a detailed stratigraphic sequence of flows. Taking the results of the present study into account, the following modified version of Mazzuoli and Pratesi's (1963) sequence and subdivision into main units is proposed (cf. fig. 4):

- early siliceous lavas, which form the base and outcrop in the peripheral area; these are the first products in the eruption cycle.
- siliceous dome lavas, present in the central part and apparently more viscous.
- late siliceous lavas (south of Corno di Bellaria and La Montagnola); these are identical to the early lavas and seem to partially cover the dome lavas.
- final more mafic lavas (Pian delle Macinaie lava and Vetta lava).

It should be noted that this eruption sequence is based mainly on superposition relations because the range of absolute ages is too narrow for an adequate discrimination in detail (see Bigazzi et al., 1981). This implies that there is no unequivocal proof that the mafic lavas actually erupted after the late siliceous lavas, but the analogy with Mt. Cimino complex, where these relations are more evident, makes it very likely. In fact, even the relationship between the units of siliceous lavas are not always as obvious in the field as fig. 4 suggests, hence some caution should be exercised. It can be safely stated, however, that the eruption of large volumes of more viscous dome lavas followed that of large volumes of the other siliceous lavas.

Despite the fact that a considerable amount of data has become available, no satisfactory genetic model for the evolution of Mt. Amiata has been proposed so far. Starting from the evidence for a crustal source of the dominant siliceous lavas, the present study attempts to integrate geochemical, petrological and volcanological information in order to assess which conditions and processes other than melting of crustal material have played a role. It is believed that a detailed

approach to the problems concerning single volcanic systems is a necessary complement to regional studies which aim to elucidate the complicated magmatic activity in Central Italy. Special attention is paid to the significance of the various types of rock-inclusions, because these turn out to provide strong evidence that, prior to eruption, two important processes were active in a magmachamber underlying the volcano, namely

1. mixing of two distinct magmas with a different origin,
2. assimilation of country rock.

The effects and implications of these processes are examined and discussed in both local and regional frameworks.

Chapter II treats the origin of the metasedimentary inclusions and shows that these represent fragments of the wall-rocks of a magmachamber.

Chapter III deals with the complex interaction between the metasedimentary inclusions and the enclosing magma.

Chapter IV describes the relationships between the igneous inclusions and the lavas, and indicates that the siliceous 'Tuscan' magmachamber was invaded by mafic 'Roman' magma.

Chapter V defines the chemical characteristics of the magmas that represent the end-members in the mixing process, and discusses their possible origin.

Two appendices give an account of the occurrence of rare minerals. Appendix A describes the boro-silicate grandidierite found in metasedimentary inclusions from Mt. Amiata and Mt. Cimino. Appendix B describes the REE-Ti silicate perrierite, present in the siliceous lavas as an accessory mineral.

#### Note on rock-nomenclature

Because of the ambiguous chemical affiliation and potassic (5-6 wt.%  $K_2O$ ;  $K_2O/Na_2O=2-3$ ) nature of both the silica-poor and silica-rich varieties, the rocks of Mt. Amiata are difficult to fit into common classification schemes, hence many rock-names have been used: trachyte, quartz-latite and rhyodacite for the siliceous lavas, andesite, trachyte and latite for the mafic lavas, and selagite for the igneous inclusions. Throughout this work (except in Appendix A) the siliceous lavas (62-67 wt.%  $SiO_2$ , often corundum-normative) are called rhyoda-

cites and the small, more mafic lavas (56-63 % SiO<sub>2</sub>) are called (mafic) latites. The use of the term 'minette' for the partially silica-under-saturated inclusions (48-59 % SiO<sub>2</sub>) is explained in Chapter IV, to which is referred for further chemical and mineralogical details. Average modal compositions of the lavas, presented by Mazzuoli and Pratesi (1963), are reproduced below.

	1	2	3	4
plagioclase	17.4	14.5	18.2	10.1
sanidine	15.1	10.9	15.7	4.2
pyroxene	3.3	3.9	4.3	8.6
biotite	2.3	3.3	3.1	2.4
quartz+access.	0.5	1.0	0.7	1.0
groundmass	61.4	66.4	58.0	73.7

Table 1. Modal composition (vol %) of: 1 - early siliceous lavas, 2 - siliceous dome lavas, 3 - late siliceous lavas, 4 - final, more mafic lavas.

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## CHAPTER II

### POLYPHASE METAMORPHIC SEDIMENTARY XENOLITHS FROM MT. AMIATA VOLCANICS (CENTRAL ITALY); EVIDENCE FOR A PARTIALLY DISRUPTED CONTACT AUREOLE

Manfred J. van Bergen

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#### ABSTRACT

Metasedimentary inclusions in the crustal anatectic rhyodacites of Mt. Amiata volcanic complex can be subdivided into a silica-poor group, rich in aluminous minerals, and a small silica-rich group containing abundant quartz. Textural observations, supported by mineral chemistry provide evidence for three metamorphic events. The regional metamorphic  $M_0$  is often associated with deformation, and two subsequent progressive thermometamorphic events,  $M_1$  and  $M_2$ , are caused by the magmatic heat. Mineral assemblages of  $M_1$  are indicative for the pyroxene-hornfels facies, and assemblages of  $M_2$ , in combination with evidence for partial melting and sanidinization, suggest sanidinite facies conditions. The inclusions are interpreted mainly as xenolithic fragments of a contact aureole, which were remetamorphosed after incorporation by the magma. The aureole formed in pre-mesozoic formations during accumulation of the melt in a magmachamber. Constraints on pressure conditions for  $M_1$  indicate the possibility of a fairly large depth of the heat-source giving rise to Mt. Amiata geothermal field.

#### INTRODUCTION

The lavas of Mt. Amiata, representing a young, isolated volcanic complex in southern Tuscany, have been known since long for their considerable content of both metasedimentary and igneous rock inclusions (Lacroix, 1893; Rodolico, 1935). The predominantly acid volcanics occur in one of the highly active geothermal areas in Central Italy where geothermal energy is successfully exploited. It has been suggested (Marinelli, 1963, 1967) that the presence of young, not yet completely

cooled intrusions are responsible for the actual thermal activity in these areas, and in the case of Mt. Amiata such an intrusion is supposed to be related to the recent volcanism. A study concerning the meta-sedimentary inclusions from the volcanic rocks has been undertaken because

1. the occurrence of a large variety and abundance of metasedimentary rock fragments is relatively uncommon for acid volcanics, in contrast to acid intrusive rocks, and provides an opportunity to set an example of the development of such inclusions in acid magmas.
2. the inclusions with their complex metamorphic history bear potential information on the local subsurface geology, and they could consequently contribute to the elucidation of characteristics of Mt. Amiata geothermal field.

In this paper, based on a petrographic study of a large collection of samples and on supporting microprobe data, an inventory and detailed description of the polyphase metamorphic sedimentary xenoliths from Mt. Amiata volcanics (Central Italy) metasedimentary rock fragments are presented. A synthesis of their metamorphic/magmatic evolution is given along with estimates on temperature and pressure conditions, and their origin in relation to Tuscan (subsurface) geology is discussed.

#### GEOLOGICAL SETTING

The volcanic complex of Mt. Amiata, having an age of 0.18-0.29 m.y. (Bigazzi et al., 1981), belongs to the Tertiary and Quaternary Tuscan-Latian magmatic province, which is characterized by acid intrusive rocks of crustal anatectic origin (Marinelli, 1975). The main occurrences, apart from Mt. Amiata, are the intrusives of the island of Elba and the volcanic centres of Mt. Cimino, San Vincenzo, Roccastrada and Tolfa.

Chemical and petrological data on the volcanics of Mt. Amiata have been presented by Mazzuoli & Pratesi (1963) and van Bergen et al. (1983). According to M & P the following subdivision can be made (cf. Fig. 1):

- early rhyodacitic lavas (QLA)

These consist of rocks originally described as (rheo-)ignimbrites and presently considered as perlitic lavas (Marinelli, 1975). They directly

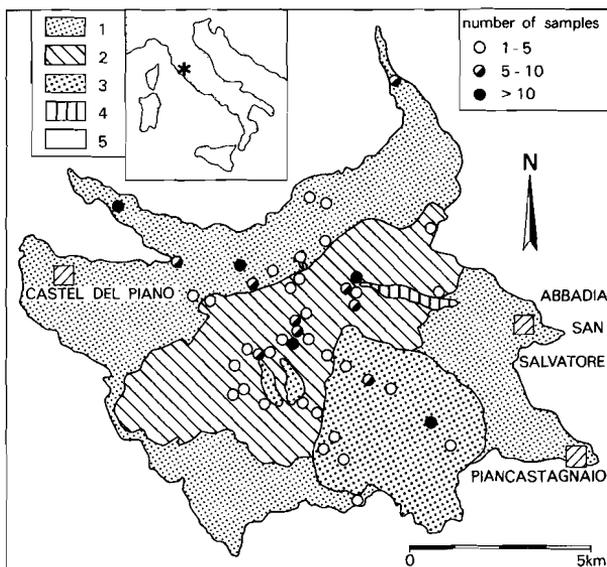


Fig.1. Geological map of Mt. Amiata (after Mazzuoli & Pratesi, 1963) with sampling localities. 1-early rhyodacitic lavas (QLA), 2-rhyodacitic dome lavas (QLB), 3-late rhyodacitic lavas (QL), 4-final mafic latitic lavas (TR), 5-sedimentary rocks. Codes refer to those used by M & P.

overlay late Cretaceous and early Tertiary sediments and occupy an area of appr. 55 km<sup>2</sup>. The average thickness varies around 200 meters. The mineralogical composition is uniform with phenocrysts of plagioclase, sanidine (both intensely fractured), pyroxene (mainly rhombic), biotite and sporadic quartz, set in a perlitic or microgranophyric groundmass.

- rhyodacitic dome lavas (QLB)

A renewed volcanic activity resulted in the emplacement of lavadomes which presently occupy an area of 35 km<sup>2</sup> in the central part. This complex is characterized by large unbroken sanidines. Phenocrysts are identical to those in QLA, while the groundmass is micro-crystalline with microliths of plagioclase, sanidine and clinopyroxene.

- late rhyodacitic lavas (QL)

One large and two small flows cover rocks of the QLB complex. The large flow, called after the Corno di Bellaria dome near its eruption centre, occupies 14 km<sup>2</sup>. The lavas are identical to QLA.

- final mafic latitic lavas (TR)

Two small flows mark the end of the volcanic activity. They show a

similar mineralogy and contain plagioclase, sanidine, ortho- and clinopyroxene, biotite and sporadic quartz as phenocrysts in a microcrystalline groundmass with microliths of plagioclase, sanidine, clinopyroxene and olivine.

The lavas of QLA, QLB and QL show limited chemical variation, that may be explained as the result of mixing with potassic alkaline magmas characteristic for the adjacent Roman magmatic province, whereas the more mafic TR lavas are more obviously hybrid products (van Bergen et. al., 1983).

#### THE INCLUSIONS

Metasedimentary inclusions are abundant in QLB, less abundant in QL, and relatively rare in QLA. A few specimen were found in the smallest of the TR lava-flows. The volcanics contain several other types of inclusions. Mafic igneous inclusions representing blobs of hybrid magma (van Bergen et.al., 1983) are abundant in QLB and sporadic in QLA and QL. They sometimes contain fragments of metasediments, and thus form double inclusions. Furthermore, a number of microgranitic inclusions were found in QLA and QLB, and a rare type, consisting of slightly or non metamorphic limestone and chert, was mentioned by Mazzuoli & Pratesi (1963).

More than 250 metasedimentary inclusions have been sampled from sites indicated in Fig.1. Although degree of exposure in the heavily afforested volcanic area, accessibility and state of weathering had their influence on the ultimate site distribution, Fig.1 gives an impression of the relative abundances of the inclusions in the different units. The peripheral QLA unit is somewhat underrepresented in the South and East, mainly as a consequence of weathering.

At each site all visible inclusions were sampled regardless of their size or nature, with an exception for fragments containing more than 50% graphite (less than 1% of the total volume of inclusions). The number of samples taken from one site may range from one to more than fifteen, while sizes of the sites may vary from several square meters to a few hundreds. There are no convincing indications for a preferent occurrence of one more (sub)groups of inclusions (see below) in a

certain area or in a specific unit or lavaflow. It is concluded therefore that the samples used in this study are representative for the metasedimentary inclusions of Mt. Amiata.

Two major groups of inclusions can be distinguished, based largely on the varying amounts of the most important minerals: a large silica-poor group A with spinel and andalusite/sillimanite as common constituents, and comprising about 90% of the total amount of inclusions sampled, and a small silica-rich group B with quartz as a dominant phase. Both groups can be subdivided further: the silica-poor group into a subgroup A<sub>1</sub> with major biotite and no corundum (except related to pseudomorphs after andalusite (see petrography) and a subgroup A<sub>2</sub> containing "free" corundum and little or no biotite; the silica-rich group into an aluminous subgroup B<sub>1</sub> with cordierite, a subgroup B<sub>2</sub> (siliceous s.s.), and a calcic subgroup B<sub>3</sub> characterized by clinopyroxene. Continuous transitions exist between different (sub)groups, mainly due to original compositional variations.

Qualitative mineral contents are listed in tables 1 and 2 in order to illustrate the large variety of mineral combinations found, and their frequency. It should be emphasized that only the presence of minerals is indicated, and that a given combination does not necessarily represent a stable assemblage.

## PETROGRAPHY

### Macroscopic appearance

The inclusions are irregularly rounded and often flattened parallel to a more or less pronounced schistosity. Inclusions in QLB are generally larger than those in QLA, but maximum sizes rarely exceed 20 cm. Colours vary from light to dark grey depending mainly on the graphite content. The quartz-rich rocks tend to be lighter coloured than other rocktypes. A mineralogical banding gives some inclusions a gneissic aspect, but more often irregular dark patches are observed in a pale matrix. The rocks are very fine to fine grained. A number of specimens belonging to the silica-poor group A are spotted hornfelses with brown spots in a dark matrix. Yellowish colours of some rocks or patches are due to the alteration of cordierite. The presence of relatively large

square prisms of pseudomorphs after andalusite, up to a few cm long, is particularly characteristic for group A. They often have a pale core of andalusite or sillimanite, a dark rim of spinel, and a thin, pale outer rim of feldspar. Biotite, sanidine, graphite and iron oxides are nearly always recognizable in the coarser crystalline inclusions. Quartz is sometimes visible in the silica-rich group B. Some samples show round, reddish garnet. Graphite-rich rocks are usually intensively micro-folded, sometimes with the development of crenulation cleavage. Sanidine veinlets are common. The inclusions usually show a parallel orientation to the pseudostratification of the volcanics, mainly present in the peripheral parts of the complex. Moreover, they tend to be concentrated at the contacts between the pseudostrata. In the central dome area the orientation appears to be more random.

#### Microscopic petrography

In thin sections both groups A and B are usually fine-grained hornfelslike rocks in which the following phases have been observed: quartz, sanidine, plagioclase, andalusite, sillimanite, cordierite, corundum, spinel, biotite, orthopyroxene, clinopyroxene, garnet, olivine, grandidierite, Fe-Ti oxides, apatite, zircon, rutile, graphite and glass.

The presence of pseudomorphs, coronas, ghost textures of pre-existing porphyro/poikiloblastic minerals and relict features indicate a complex metamorphic history. Relict microtectonic phenomena such as a more or less pronounced foliation, microfolds, crenulation cleavage, tectonic banding, fracture cleavage, microfaults, provide evidence of an early (multiple) deformation.

Detailed mineral descriptions are given below for subgroup A<sub>1</sub>, which is quantitatively the most important. With regard to the other subgroups only additional and/or deviating characteristics are mentioned if necessary.

Silica-poor subgroup A<sub>1</sub> (cf. table 1a)

By far the most rocks of this subgroup consist of sanidine + plagioclase + spinel + biotite + hypersthene. The former presence of andalu-

subgroup A 1	k-feldspar	plagioclase	and./sill/corund <sup>1)</sup>	cordierite	spinel	biotite	garnet	olivine	orthopyroxene	clinopyroxene	FREQUENCY
1	x	x			x	x			✓		abundant
2	x	x			x	x					abundant
3	x	x	x		x	x			x		abundant
4 <sup>2)</sup>	x	x	x		x	x					abundant
5	x				x	x			x		found once
6		x	x			x			x		found once
7	x	x			x	x			x	x	found once
8	x	x				x			x	x	found once
9	x	x				x			x		rare
10	x				x	x					rare
11	x		x		x	x					found once
12	x	x	x	x	x	x			x		rare
13	x	x	x	x	x	x					rare
14	x	x	x	x	x	x	x		x		found once
15 <sup>3)</sup>	x	x	x		x	x	x		x		rare
16	x	x			x	x	x				found once
17	x	x		x	x	x					found once
18	x	x			x	x	x		x		found once
19	x	x		x		x			x		found once
20	x	x			x	x	x		x		found once
21	x	x			x	x		x	x		rare
22	x	x	x		x	x		x	x		found once
23	x	x		x	x	x	x	x	x		found once
24	x				x	x		x	x		found once

subgroup A 2	k-feldspar	plagioclase	andalusite	sillimanite	corundum	cordierite	spinel	garnet	FREQUENCY
25	x	x	x			x	x		rare
26	x	x	x	x	x	x	x		rare
27	x		x	x	x	x	x		rare
28	x	x	x	x		x	x		found once
29	x		x		x	x			found once
30	x				x	?	x		found once
31	x			x	x		x		found once
32 <sup>4)</sup>	x	x	x			x	x	x	found once

Table 1 a and 1 b. Qualitative mineral contents of the silica-poor group A. <sup>1)</sup> in subgroup A<sub>1</sub> sillimanite and corundum occur only in para/pseudomorphs after andalusite. <sup>2)</sup> one sample with combination 4 contains grandidierite. <sup>3)</sup> some samples with combination 15 contain minor relictic quartz. <sup>4)</sup> minor biotite present.

site porphyroblasts is witnessed by the commonly occurring pseudomorphs and andalusite/sillimanite relicts. In addition to these minerals several inclusions contain cordierite and/or garnet, and in a few rocks olivine was found. The feldspars occur in varying ratios, but sanidine is generally dominant. Plagioclase is seldom completely absent and only two samples did not contain sanidine. Grandidierite and clinopyroxene are extremely rare. The pyroxene indicates a transition to the calcic subgroup B<sub>3</sub> of the quartz-bearing inclusions.

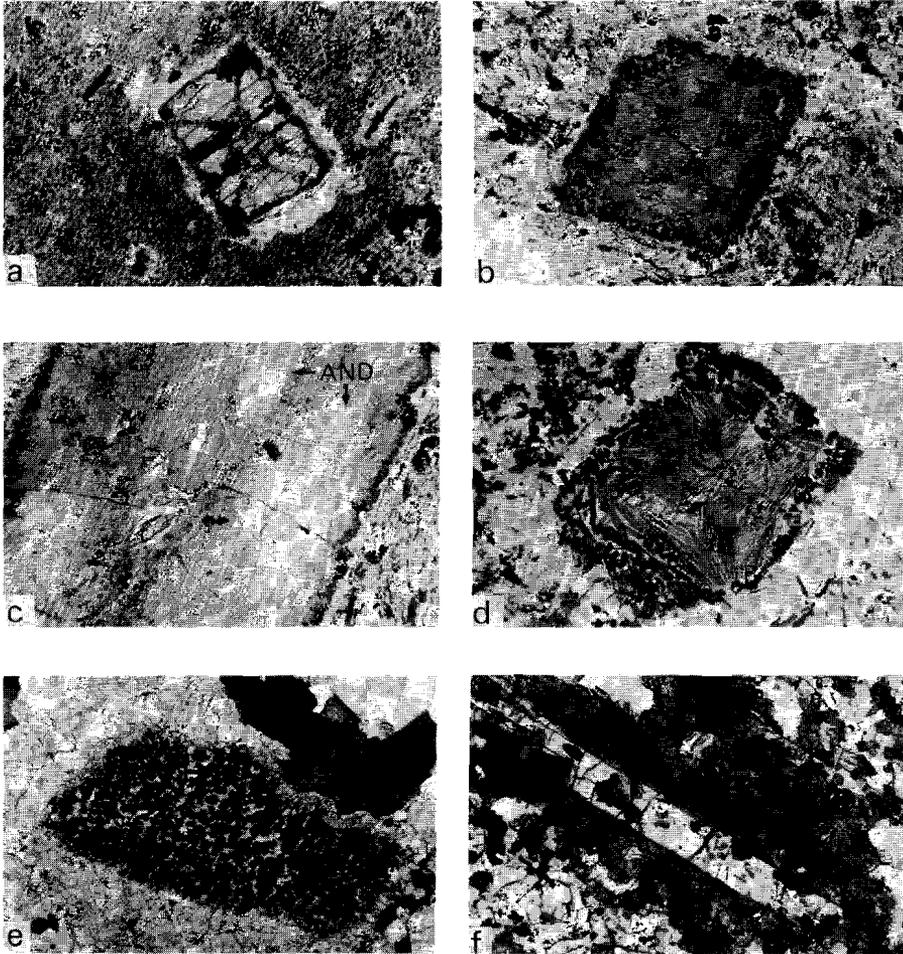
Many inclusions distinctly show leucocratic and melanocratic areas with irregular shapes. The former mainly consist of sanidine and may further contain plagioclase, biotite, hypersthene, olivine, glass and very rarely relictic quartz. Minerals representing the melanocratic areas are spinel, biotite, andalusite/sillimanite/corundum, cordierite, garnet, hypersthene, sanidine and plagioclase.

Pseudomorphs after andalusite. Pseudomorphism of spinel-rich aggregates after andalusite is well known for pelitic inclusions of volcanic rocks (e.g. Lacroix, 1893; Brauns, 1911) and has also been observed in similar inclusions from intrusive rocks (Didier, 1973). In the inclusions of Mt. Amiata the replacement of andalusite, leading to several endproducts after various intermediate stages, is particularly well demonstrated (Fig.2). The following types represent the final products:

- 1) spinel-plagioclase (common)
- 2) spinel-corundum, often with plagioclase only at the rim (common)
- 3) spinel-glass (rare)
- 4) spinel-grandidierite (found only once)

The original andalusite was long prismatic, square in cross section, with a maximum length of several cms. Entire crystals still occur mostly in graphite-rich rocks, and they often show chiasolite-type inclusion patterns. A pink pleochroism is sometimes visible. The mineral is clearly post-tectonic and may contain large elongated ilmenite grains, usually orientated parallel to the external foliation.

Corrosion along grain boundaries and the formation of minute spinel grains indicate incipient modification. This is followed by the formation of spinel-plagioclase coronas advancing towards the centre and gradually consuming the andalusite. At the same time sillimanite may form in small areas inside the crystal, which continues until the



*Fig.2. Pseudomorphism after andalusite porphyroblasts. a. chiascolitic andalusite with green spinel along rims and cleavage planes, surrounded by sanidine; note parallel orientation of elongated ilmenites in the groundmass; fieldwidth 2.5 mm. b. sillimanite, (010) cleavage visible, with rim of spinel and plagioclase; fieldwidth 4 mm. c. newly formed corundum (heavy relief), surrounded by sanidine, in core of sillimanite; relicts of andalusite indicated by AND; fieldwidth 4 mm. d. bundles of elongated corundum crystals, which sometimes grade into green spinel of rim; fieldwidth 4 mm. e. aggregate of spinel and plagioclase, surrounded by plagioclase and biotite (upper right); fieldwidth 1.5 mm. f. elongated crystal of grandidierite associated with spinel; fieldwidth 1.3 mm.*

remaining, non-pseudomorphed andalusite is completely replaced. Sillimanite generally inherited its crystallographic orientation from andalusite. It often shows a patchy extinction in sections perpendicular to the c-axis. Continued formation of spinel + plagioclase results in type 1 pseudomorphs, but where corundum forms at the expense of sillimanite type 2 is the final pseudomorph. Pseudomorphs of type 3 are rare and consist of spinel embedded in a yellowish glassy material. The occurrence of euhedral crystals of the rare borosilicate grandidierite in type 4 has been described by van Bergen (1980). This mineral formed in the core of the pseudomorphs and replaced sillimanite relicts.

In the central parts of type 1 spinel and plagioclase usually occur in more or less equal amounts and grain sizes. The spinel is subhedral to euhedral, and the plagioclase is unzoned, limpid and devoid of inclusions. Towards the rim the grain size of the plagioclase increases, glassy inclusions appear and twinning becomes more frequent, and in the outer rim spinel rapidly decreases in grain size resulting in tiny rounded inclusions in the plagioclase.

Spinel may also occur in bunches of elongated, irregularly rounded grains, sometimes perpendicular to the outlines of the former andalusite, but also orientated randomly. Towards the centres of type 2 pseudomorphs such grains of spinel may grade into similar grains of corundum.

Sanidine as an interstitial phase in the pseudomorphs is common, especially in the centre of type 2, where it co-exists with corundum. It often separates spinel from relictic andalusite or sillimanite, and it replaces plagioclase. Biotite flakes are sometimes present within the pseudomorphs, and in a few samples cordierite was observed along the outer rim of type 2.

Microprobe analyses of spinels and plagioclases in pseudomorphs indicate that the former are rich in the hercynite component and that the latter are very rich in anorthite. Optical observations suggest this mineral chemistry to be general for all pseudomorphs.

Biotite as a major constituent of this subgroup A<sub>1</sub> shows a wide variety of appearances. Volume contents are always less than 50%, a figure for micas which Didier (1973) adopts as lower limit for the so-

called surmicaceous enclaves (Lacroix, 1893). The most frequent are anhedral to subhedral biotites of the melanocratic areas, often associated with green spinel. A preferential orientation, due to mimetic growth parallel to the schistosity or determined by a pre-existing mineral, is sometimes observed. The latter case is illustrated in some spotted hornfelses where biotites, that have replaced a mineral in the spots (possibly cordierite) together with spinel and minor sanidine, are preferentially orientated in contrast to those in the surrounding matrix. Biotites following microfolds appear to be strain-free and tend to form polygons. Elongated ilmenites, which are always parallel to the schistosity, are often rimmed by biotites with various crystallographic orientations.

Biotite, either alone or with spinel or in symplectitic intergrowth with hypersthene, may replace garnet. On the other hand indications that some of the biotite itself has been replaced are also present: some samples suggest a reaction to hypersthene, and others contain small 'droplets' included in cordierite and feldspars.

Leucocratic areas may contain relatively large anhedral grains of biotite. If glass is present the mineral may appear as perfectly euhedral crystals, elongated flakes or tiny laths.

The usual pleochroic colours vary from pale yellow to deep dark brown, and reddish colours are less frequent. Preliminary microprobe analyses indicate relatively large chemical varieties, even in one thin section, especially with respect to Fe/(Fe+Mg) ratios and TiO<sub>2</sub> contents. In a few cases chemistry strenghtens the textural evidence for the presence of different generations. Compare for example the TiO<sub>2</sub> contents of a honey-coloured 'drop' included in cordierite with a dark brown flake from the same sample, which has a relatively usual composition (analyses c and d, table 3).

Subhedral to euhedral crystals of spinel are abundant and ubiquitous except for a number of samples containing only small amounts around the relicts of aluminosilicates or garnet. The association with biotite is common and with hypersthene rare. Small rounded inclusions appear in grandidierite as well as in plagioclase in the outer rims of the pseudomorphs as mentioned before, and in rims of the rock contiguous to the

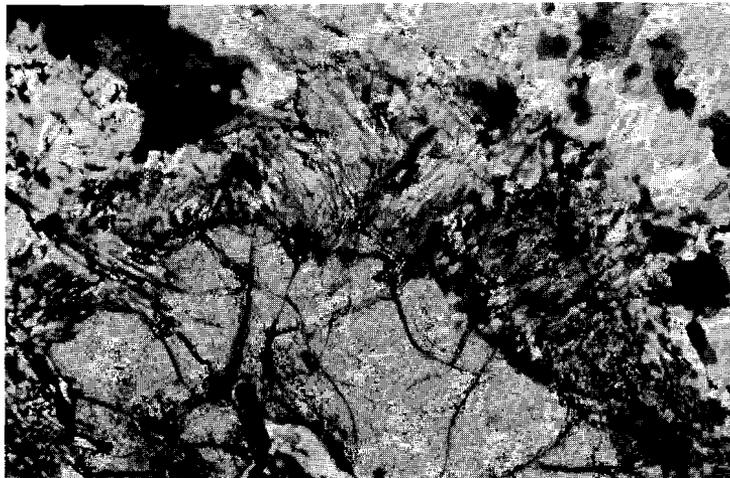
surrounding lava. Spinel may also be opacified.

The normal colour is dark green, sometimes nearly opaque, and greyish and violet varieties also occur. A number of spinels were analysed by microprobe. They are rich in hercynite with Fe/(Fe+Mg) ratios between 0.70 and 0.90 (see table 3 for example).

A subordinate number of inclusions contain cordierite or garnet, and the combination of both minerals is rare. As an exception one sample was found with cordierite and garnet virtually as the only constituents.

Garnets, reddish or colourless, are usually rounded and sometimes embayed. A few inclusions of elongated ilmenites indicate post-tectonic growth of the mineral. Corona-forming reactions and complete pseudomorphism resulted in the following breakdown products: biotite, biotite-spinel, biotite-Fe-Ti oxide, biotite-hypersthene (in symplectites, cf. Fig.3), hypersthene, cordierite (?), olivine (?). Several types of replacement may be found in one thin section and even on opposite sides of larger grains.

The garnets belong to the pyrope series and are rich in almandine. Microprobe analyses give 10-20% pyrope and low amounts of Mn and Ca (cf. table 3).



*Fig.3. Replacement of garnet by symplectitic corona of biotite, sanidine and (partially) orthopyroxene; fieldwidth 2.5 mm.*

Cordierite is easily recognized by its blue pleochroism, complex twinning or alteration into a yellowish isotropic mass. It occurs in varying quantities mainly due to different degrees of replacement. Some samples grade into subgroup A<sub>2</sub> and contain large amounts of poikiloblastic cordierite in association with andalusite. In others replacement by spinel (with or without biotite) has been more advanced, and only rounded, optically continuous relicts are present. There are also clear indications that the 'spots' of some hornfelses were originally cordierites. Glass, graphite, relict biotite and Fe-Ti-oxide may be present as inclusions. Newly formed spinel is often separated from cordierite by a small rim of glass or sanidine.

Analyses show ratios of Fe/(Fe+Mg) ranging between 0.40 and 0.75 (examples in table 3).

Limited quantities of orthopyroxene are mainly restricted to the leucocratic areas and to the outer parts of the inclusions. The pyroxene is never associated with the aluminosilicates and tends to avoid aluminium-rich areas. Textures suggest several modes of formation, for example as breakdown-product of biotite and garnet, and as product of a reaction between inclusion and magma. On the other hand it cannot be excluded that some late biotite formed at the expense of pyroxene.

The pyroxene crystals are usually anhedral except when they are surrounded by glass in leucocratic areas. Because of the negative axial angle and characteristic pleochroism (pink and green), they are considered to be hypersthene. The Fe/(Fe+Mg) ratios of orthopyroxenes analysed range between about 0.50 and 0.65. They may contain up to more than 5 weight % Al<sub>2</sub>O<sub>3</sub> (cf. table 3).

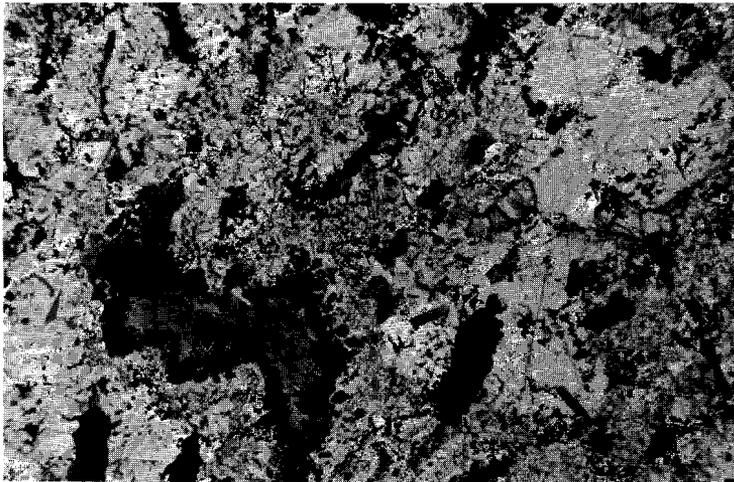
Small amounts of olivine are present in six samples. It occupies a position comparable to that of hypersthene. Anhedral greenish grains with high birefringence and refractive indices occur mainly in the sanidine-rich leucocratic areas associated with sanidine and sometimes biotite (Fig.4). Contacts with spinel are rare. In one sample olivine was found near the rim of a garnet.

According to microprobe analyses the olivines are rather rich in iron. Fe/(Fe+Mg) ratios vary between 0.63 and 0.72.

In this A<sub>1</sub> subgroup sanidine is nearly always present in excess. It

is often the interstitial phase but more frequently large crystals (in the order of several tenths of mm) make up the complete 'groundmass' of the rock, enclosing other minerals, among which plagioclase, graphite, cordierite and apatite are the most common. In melanocratic areas sanidines tend to be small and anhedral with ovoid crystals faintly orientated according to the relict foliation. In leucocratic areas and veinlets, where inclusions of other minerals are less frequent to absent, the largest dimensions are reached and straight crystal-boundaries meet in triple points. Perfectly euhedral crystals are found if sanidines are enclosed by glass. In this case bundles of a lath-like type of sanidine may have grown by epitaxy upon the margins. A few samples contain rounded microperthitic grains which are replaced by sanidines of the usual type. Axial angles of the latter are always small, and Karlsbadtwinning as well as a weak optical zoning are rare. Analysed sanidines in four samples show little chemical variation:  $Ab_{16-20}Or_{77-83}An_{1-5}$ .

Plagioclase occurs in varying and usually subordinate quantities. In many samples it is present only in rims of the inclusions or in the



*Fig.4. Grains of olivine visible in white sanidine-rich area near sillimanite-spinel pseudomorph; fieldwidth 4 mm.*

pseudomorphs after andalusite. Grainsizes, small in melanocratic areas, may reach some tenths of mms. in leucocratic areas. The crystals are usually corroded and often included in sanidine. The plagioclase itself may contain numerous small glass inclusions and other minerals such as biotite, graphite, Fe-Ti oxide and apatite. Some samples or part of them have small euhedral crystals with glassy cores, which appear to have crystallized from a melt. Polysynthetic twins are frequent, and a weak optical zoning is sometimes observed. The chemical composition is, in contrast to sanidine, inhomogeneous. Rather large differences can be measured in one sample. Plagioclase in the pseudomorphs after andalusite is the most basic with a bytownite to anorthite composition. Others are usually andesine to labradorite.

Ilmenite is a common opaque constituent with modal amounts up to one percent. The relatively large, elongated grains always follow the micro-folds. Biotites, sometimes associated with spinel, have often grown along their rims. The ilmenite may be found included in andalusite, sillimanite, garnet, biotite, cordierite. Investigations with the microprobe also showed the less widespread occurrence of a low titanium Fe-oxide, probably magnetite.

Nearly all samples contain graphite in varying, sometimes considerable amounts. The small, elongated flakes or acicular particles are oriented according to the microfolding except when included in chiastolite, biotite (in some cases) and glass. Other host minerals are sanidine, cordierite, plagioclase and garnet.

Accessory apatite is frequently found as small needles which often give the impression to be hollow. It is preferentially included in large sanidines of the leucocratic areas and also in plagioclase. Zircon, as rounded or euhedral crystals, is much less common, and rutile is rare. A few grains of clinopyroxene were found in a thin section of a sanidine-plagioclase-biotite-hypersthene rock. Leucocratic areas of some samples contain minor relictic quartz.

Silica-poor subgroup A<sub>2</sub> (cf. table 1b)

Inclusions belonging to the A<sub>2</sub> subgroup abundantly contain minerals rich in aluminium, and only subordinate feldspar and little or no bio-

tite are present. Cordierite and andalusite are nearly always dominant constituents. Large shapeless poikiloblasts of cordierite show the usual yellowish alteration colour, and andalusite occurs both as euhedral prisms, which virtually lack replacement by spinel, and as large aggregates of optically continuous rounded grains. Needles of newly formed sillimanite are sometimes associated with these aggregates and with cordierite. Subhedral to euhedral crystals of corundum may be surrounded by depletion halos of aluminium. The mineral has grain-to-grain contacts with sanidine, spinel and sillimanite, and it may contain inclusions of rutile. Spinel tends to be very dark to opaque. If included in cordierite it is often surrounded by a rim of isotropic material (glass?) or sanidine. In general sanidine is much less abundant than in A<sub>1</sub>, and it mainly occurs in rare leucocratic areas, where it replaced cordierite, and around andalusite and corundum. Opaque material indicates intense microfolding.

One aberrant specimen contains cordierite-rich domains with small euhedral garnet crystals embedded in an isotropic substance. The cordierite appears to be partially melted. Some hypersthene is present in the same thin section.

#### Silica-rich group B (cf. table 2)

The rocks of this small group, characterized by the presence of excess quartz, are fine-grained, partially due to recrystallization of this mineral. A heavy tectonization prior to the metamorphic overprint is indicated by microfolds, flattened bands, anastomosing schistosity and fracture cleavage.

The aluminous subgroup B<sub>1</sub> is a transition to group A. Textures of garnet and cordierite are basically similar. They show contacts with each other and with quartz, hypersthene and sanidine. Cordierite sometimes surrounds the thin spinel rims of andalusite.

Pyroxene crystals are always anhedral. Orthopyroxene often formed by breakdown of biotite, which is a subordinate mineral in this group. The pyroxenes analysed proved to be ferrohypersthene with only little aluminium. In the calcic subgroup B<sub>3</sub> orthopyroxene may be rimmed by or intergrown with clinopyroxene, which has an augitic composition (see

group B	quartz	k-feldspar	plagioclase	andalusite	sillimanite	cordierite	spinel	biotite	garnet	orthopyroxene	clinopyroxene
aluminous subgroup B 1											
33	x					x					?
34	x					x		x	x	x	
35	x	x	x	x	x	?	x	x	x	x	
36	x	x	(x)			x		x	x	x	
37	x	x		x		x					
38	x	x				x		x	x	x	
39	x	x		x		x	x	x	x	(x)	
siliceous (s.s.) subgroup B 2											
40	x	x	(x)					x			
41	x		x							(x)	
42	x	x	(x)					x		x	
43	x	(x)	(x)					x		x	
44	x		x					x		x	
calcic subgroup B 3											
45	x		(x)								x
46	x		(x)					x		x	x
47	x		(x)							x	x
48	x	x	(x)					x		x	x
49	x		x							x	x

Table 2. Qualitative mineral contents of the silica-rich group B. Subgroup B<sub>1</sub>: aluminous, B<sub>2</sub>: siliceous s.s., B<sub>3</sub>: calcic. Parentheses indicate minor quantities. All extremely rare.

analysis in table 3). Some cpx-crystals are twinned.

The rocks of this group are poor in feldspars. Sanidine occasionally occurs as an interstitial phase. Its composition, as determined in a sample without plagioclase, may show a high albite content:  $Ab_{32}Or_{67}An_1$ . Small rims of glass often separate quartz and other minerals. Inclusions of glass and biotite are common in quartz and cordierite as well.

#### METAMORPHIC EVENTS AND CONDITIONS

The petrographical and mineralogical data point to three subsequent metamorphic events: a regional metamorphic M<sub>0</sub>, a thermometamorphic M<sub>1</sub> and a higher grade thermometamorphic M<sub>2</sub>, accompanied by possible melting and sanidinization. The growth of minerals in each event is indicated in

	a	b	c	d	e	f	g	h	i	j	k	l	m	n
	biot.	biot.	biot.	biot.	spinel	spinel	cord.	cord.	garn.	garn.	opx.	opx.	cpx.	oliv.
SiO <sub>2</sub>	35.6	34.9	35.5	35.9	0.17	0.37	47.8	47.0	37.1	35.9	50.1	48.6	51.6	32.8
TiO <sub>2</sub>	5.0	3.8	5.8	0.30	0.22	0.00	0.00	0.02	0.06	0.09	0.11	0.08	0.18	0.04
Al <sub>2</sub> O <sub>3</sub>	16.3	17.8	17.0	19.2	58.1	61.5	31.8	31.7	21.2	20.2	0.32	5.02	0.94	0.80
FeO	22.9	18.2	18.2	16.3	34.1	30.9	9.6	14.0	35.5	38.2	33.1	30.6	16.2	48.8
MnO	0.08	0.17	0.06	0.09	0.43	0.34	0.34	0.15	1.53	1.47	0.90	0.69	0.37	1.00
MgO	7.3	11.4	10.2	13.1	6.2	8.2	7.8	4.5	4.2	2.4	14.2	15.2	10.4	15.9
CaO	0.07	0.00	0.07	0.04	-	-	-	-	1.35	0.68	1.21	0.22	19.5	0.13
Na <sub>2</sub> O	0.44	0.35	0.42	0.37	-	-	-	-	-	-	-	-	0.17	-
K <sub>2</sub> O	8.4	9.5	9.3	9.5	-	-	-	-	-	-	-	-	-	-
Total	96.09	96.12	96.55	94.80	99.22	101.31	97.34	97.37	100.94	98.94	99.94	100.41	99.36	99.47
Numbers of cations	0=22	0=22	0=22	0=22	0=32	0=32	0=18	0=18	0=12	0=12	0=6	0=6	0=6	0=4
Si	5.46	5.27	5.33	5.42	0.038	0.080	5.02	5.01	2.96	2.96	1.98	1.88	1.99	0.99
Al	2.94	3.16	3.01	3.41	15.49	15.70	3.93	3.99	2.00	1.97	0.015	0.23	0.04	0.03
Ti	0.57	0.43	0.66	0.034	0.038	0.000	0.000	0.002	0.003	0.006	0.003	0.002	0.005	0.001
Fe <sup>1)</sup>	2.93	2.30	2.28	2.05	6.45	5.59	0.84	1.25	2.37	2.64	1.09	0.99	0.52	1.23
Mn	0.010	0.022	0.008	0.012	0.082	0.063	0.030	0.014	0.10	0.10	0.030	0.023	0.012	0.026
Mg	1.67	2.57	2.28	2.95	2.08	2.64	1.22	0.71	0.50	0.30	0.84	0.87	0.60	0.71
Ca	0.011	0.000	0.011	0.007	-	-	-	-	0.12	0.06	0.05	0.009	0.81	0.004
Na	0.13	0.10	0.12	0.11	-	-	-	-	-	-	-	-	0.013	-
K	1.64	1.82	1.79	1.82	-	-	-	-	-	-	-	-	-	-
Fe/(Fe+Mg)	0.637	0.472	0.500	0.410	0.756	0.679	0.408	0.638	0.826	0.898	0.565	0.532	0.464	0.634

Table 3. Selection of representative microprobe analyses. a, h, j: from one sample of the silica-rich group B; m: other sample of group B; others: various samples of the silica-poor group A, biotites c and d from the same sample. The analyses were made with a manual wavelength-dispersive TPD-microprobe using natural minerals and pure elements as standards. Corrections for dead-time, background, atomic number, absorption and fluorescence were applied. <sup>1)</sup> all iron as FeO or Fe<sup>2+</sup>.

table 4. The formation of minerals under volcanic conditions, mainly by quenching, is also given. As some of the minerals have originated by several different mechanisms under physical and chemical conditions which were not always constant, and as the observed textures do not provide conclusive evidence in every case, this table can only be schematic.

#### Regional metamorphism - $M_0$

The only residual minerals representing this event, besides ilmenite and graphite, are quartz and biotite, which have grown pre- or syntectonically. The biotite indicates a medium grade metamorphism of at least part of the original rocks. Possible additional phases were plagioclase, garnet and, for chemical reasons, muscovite. Evidence for a regional metamorphism is also provided by rare 'ghosts' of unknown minerals (cf. Fig.5c). It should be noted that regional metamorphism of the Tuscan basement is polyphase (see discussion), but relicts are too scanty to trace this in the inclusions.

#### Thermometamorphism - $M_1$

The post-tectonic assemblages of  $M_1$  correspond best with those of the pyroxene hornfels facies (Turner, 1968).  $Al_2O_3$ -CaO-(Mg,Fe)O and (Mg,Fe)O- $Al_2O_3$ - $SiO_2$  triangles representative for silica-rich and silica-poor rocks, and based on the classic studies of contact aureoles by Goldschmidt (1911) and Tilley (1924) respectively, are given in Fig.6.

Assemblages 1-6 (Fig.6) are equivalent to those of the silica-rich group, and 11-15 to those of the silica-poor group. The crossing of tie-lines and the introduction of garnet and olivine are explained by variable Fe/(Fe+Mg) ratios in the minerals and by the prevailing Fe-rich character of the inclusions, as indicated by the available microprobe analyses and by some preliminary total-rock analyses.

The tie-line connecting andalusite and spinel is based on observations in subgroup  $A_2$ . Although spinel partly originated by the breakdown of andalusite and probably of cordierite during  $M_2$ , textures suggest a  $M_1$ -assemblage of corundum + andalusite + cordierite + spinel in some cases. From experimental work on the pure Mg-system the tie-line cordierite-corundum appears to be stable at low pressures and temperatures up to

	REGIONAL METAMORPHIC M <sub>0</sub>	THERMOMETAMORPHIC			VOLCANIC (quench)
		M <sub>1</sub>	partial melting	M <sub>2</sub> sanidin- ization	
quartz	B, A <sub>1</sub> (?)	B			
k-feldspar					
plagioclase			→ % An		
andalusite		A, B <sub>1</sub>			
sillimanite				A, B <sub>1</sub>	
corundum		A <sub>2</sub>		A <sub>1</sub>	
cordierite		A, B <sub>1</sub>			
spinel		A <sub>2</sub>		A <sub>1</sub>	
biotite		A <sub>1</sub> , B			
garnet	(?)	A <sub>1</sub> , B <sub>1</sub>			
orthopyroxene			A <sub>1</sub> , B <sub>2</sub> , B <sub>3</sub>		
clinopyroxene			B <sub>3</sub>		
olivine			A <sub>1</sub>		
grandierite				A <sub>1</sub>	

time →

Table 4. Growth of minerals during three subsequent metamorphic events (M<sub>0</sub>, M<sub>1</sub>, M<sub>2</sub>) and the final "volcanic" (quench) event in the metamorphic inclusions of Mt. Amiata. Letters refer to the distinct (sub)groups.

800°C, but the introduction of FeO would produce the assemblage cordierite + spinel + corundum + Al<sub>2</sub>SiO<sub>5</sub> and eventually spinel + Al<sub>2</sub>SiO<sub>5</sub> (+corundum) (Seifert, 1973).

Another complication involves the presence of garnet in both the silica-rich and silica-poor groups. As some of the observed breakdown products are characteristic not only for M<sub>2</sub>, but also M<sub>1</sub>, a regional metamorphic origin must be taken into account. However, textures in the garnet-bearing inclusions do not suggest a pre- or syntectonic growth, and therefore the garnet is considered to belong to M<sub>1</sub>, forming assemblages with cordierite, andalusite and quartz. Almandine-rich garnet is occasionally reported from thermometamorphic rocks (e.g. Chinner, 1962; Propach, 1968; Okrusch, 1971), where its presence is ascribed to relatively high pressures and/or restricted (Fe-rich) chemical environments. Although a M<sub>1</sub>-origin of the almandine-rich garnets in the inclusions is feasible, the textural evidence is not always conclusive, and a pre-thermometamorphic origin of (some of) the garnet cannot be excluded<sup>1)</sup>.

The introduction of olivine in Fig.6 needs some explanation as well. There are few records of this mineral occurring in thermometamorphic

sediments, nearly always concerning fayalitic varieties in high-grade Fe-rich rocks (e.g. Sadashivaiah, 1950; Bonnicksen, 1969; Abraham & Schreyer, 1973). In experiments Smith (1971) has shown that at relatively low pressures and temperatures between 600 and 1000°C the reaction orthopyroxene = olivine + quartz proceeds to the right in systems with high Fe/(Fe+Mg) ratios. An investigation at 780°C of the reaction spinel + orthopyroxene = olivine + cordierite by Lal & Seifert (1979) demonstrated that, if the Fe/(Fe+Mg) ratio is high, the formation of olivine is favoured by low pressures and low oxygen fugacities. From this evidence it can be concluded that olivine is stable in the (high) pyroxene hornfels facies at certain unusual conditions which might account for its rarity. The present data on the olivine-bearing inclusions clearly indicate a thermometamorphic origin of the mineral (being rich in Fe) probably during M<sub>1</sub>. In one thin section its presence near the rim of a garnet could suggest a M<sub>2</sub> origin if the latter grew during M<sub>1</sub>.

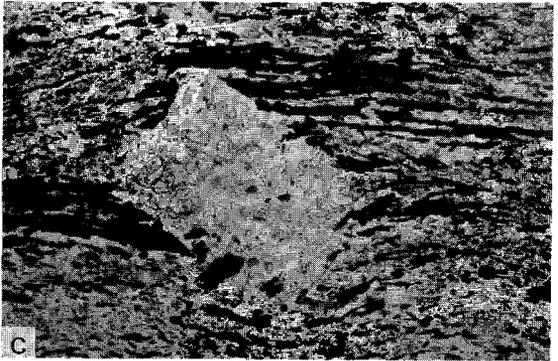
Thermometamorphism - M<sub>2</sub> (partial melting, sanidinization)

During this event temperatures reached such high values that partial melting could occur. The metamorphic conditions are considered to represent those of the sanidinite facies, based on similarities with assemblages reported by Brauns (1911), Thomas (1922) and Agrell & Langley (1958), that are often taken as examples of this facies (e.g. Turner, 1968). It should be noted that for pelitic and psammitic rocks the sanidinite facies is poorly defined with respect to the pyroxene hornfels facies (Miyashiro, 1973). Mineral assemblages are rather similar (one of the main features being the instability of garnet in the former facies), and the value of sanidine as a diagnostic mineral has been doubted.

In the inclusions some assemblages, formed during M<sub>1</sub>, appear to remain stable during M<sub>2</sub>, and the petrographical data do not allow to make

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1) Some regional metamorphic garnets found in Tuscan boreholes have appreciably higher Ca and Mn contents (Puxeddu, 1980, pers.comm.) than the garnets from the xenoliths, but no conclusions can be drawn from this fact.



*Fig.5. Aspects of microtectonics. a. multiple folding in graphite-rich xenolith; note tiny squares of andalusite; fieldwidth 2 cm. b. fracturing and offsetting of leucocratic areas; all white areas, including fractures, consist of sanidine; fieldwidth 2 cm. c. ghost of pre- or syntectonically grown mineral; black trails mainly graphites; fieldwidth 2.5 mm.*

a strict distinction between both events. The most indicative features for  $M_2$  are the presence of glass and the breakdown to andalusite and garnet, while corundum, spinel and grandidierite (applying to  $A_1$  only), anorthite-rich plagioclase and sillimanite were typically new minerals. Hence,  $M_1$  and  $M_2$  can be distinguished best in inclusions from group A and subgroup  $B_1$ .

Direct and indirect evidence of partial melting can be found especially in subgroup  $A_1$ . Glass is present in leucocratic areas (brownish-coloured in contrast to rarely occurring colourless glass of infiltrated magma, Fig.7a), as inclusions in minerals and along grain boundaries. Graphite-flakes and other small particles are enclosed in sanidine if this mineral grew by solid-solid replacement, and they were pushed aside if the sanidine crystallized in contact with a melt. The acicular shape of apatites, enclosed by sanidine, could also be indicative for melting (Wyllie et al., 1962).

Quartz, feldspar and biotite were probably the most important melt-producing phases, but other minerals, such as cordierite and andalusite/sillimanite may also have been involved. The formation of coronas and pseudomorphs at the cost of andalusite required addition of Fe, Mg and

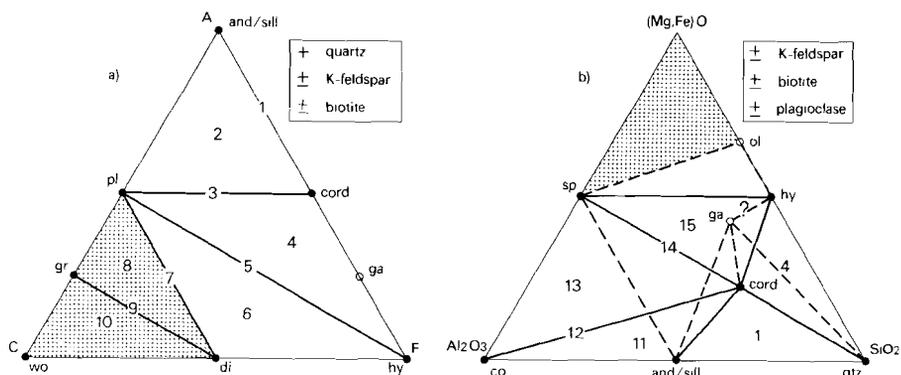
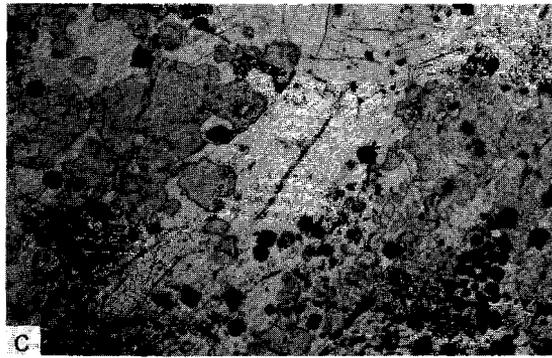
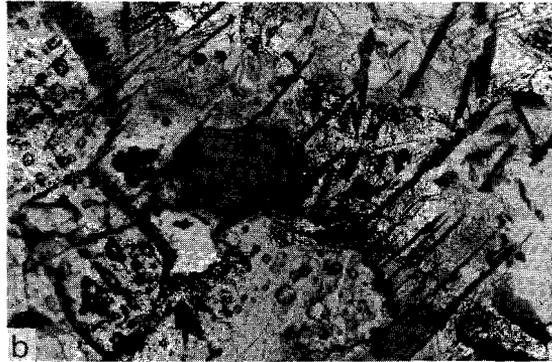
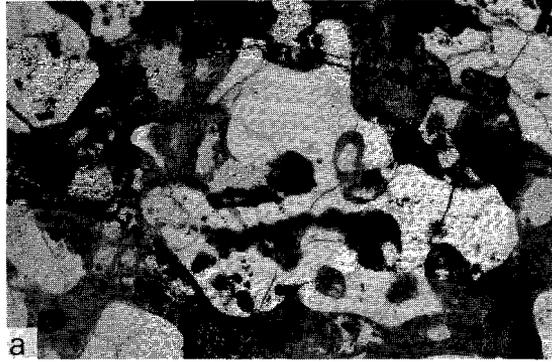


Fig.6. ACF and  $Al_2O_3$ -(Mg,Fe)O- $SiO_2$  diagrams representing  $M_1$ -assemblages. Numbers and solid tie-lines refer to Turners pyroxene hornfels facies. Additional assemblages applying to the inclusions are shown by broken tie-lines. and=andalusite, co=corundum, cord=cordierite, di=diopside, ga=pyralpsite garnet, gr=grossular, hy=hypersthene, ol=olivine, pl=plagioclase, sill=sillimanite, sp=spinel, wo=wollastonite. Dotted fields not represented.



*Fig.7. Partial melting and sanidinization. a. relict of quartz, surrounded by brownish glass containing graphite, orthopyroxene and vesicles, in a sanidine-rich area; fieldwidth 2.5 mm. b. glassy area (upper right) with quenched feldspars and biotite; the latter shows a preferent orientation controlled by large orthopyroxene (lower left), containing numerous glassy inclusions; fieldwidth 1 mm. c. sanidine (white) replacing cordierite (grey), associated with green spinel (black); fieldwidth 2.5 mm.*

Ca, and removal of Si. There is no textural evidence that reaction with nearby minerals was responsible for this chemical exchange, and it is therefore reasonable to suppose that an interstitial melt was involved. 'Phenocrysts' of orthopyroxene possibly formed by a melt-producing reaction of biotite, and in other cases patterns of glassy inclusions in pyroxene suggest crystallization from the melt (cf. Fig.7b). Sometimes large biotites were obviously stable in the melt, but rarely in combination with orthopyroxene.

Melting probably took place to a greater extent than is visible now because the extensive late crystallization of sanidine thoroughly changed the textural aspects, again mostly in subgroup A<sub>1</sub>. This sanidinitization could explain the origin of the leucocratic areas, but the presence of relictic quartz and residual glass suggests that in many cases the areas existed before potassium was mobilized. An illustrative example is a sample which shows faulting and offsetting of melanocratic and leucocratic areas (Fig.5b). Undeformed sanidine is the only constituent of the leucocratic areas, but also of the borders along the fault-planes. This suggests that the sanidine preferentially replaced areas originally rich in felsic minerals.

Although the redistribution of potassium was probably facilitated by the presence of melt, non-melted areas, such as melanocratic areas containing cordierite or other minerals, could also be saniditized (cf. Fig.7c).

The origin of potassium could be sought in the breakdown of potassic minerals like muscovite and biotite. To account for the vast amount of potassium, it would imply rather unusual bulk-rock compositions. Therefore supply from the host magma, that contains about 5-6 weight % K<sub>2</sub>O (Mazzuoli & Pratesi, 1963) is another reasonable explanation, considering that a metasomatic influx of alkalis in the wall-rocks of granitic intrusions is a well-known phenomenon (e.g. Mehnert, 1968).

The effect of partial melting and sanidinitization can be considered as an assimilation process. Many samples of the large A<sub>1</sub>-subgroup have a qualitative mineral content which differs from that of the lava only in the presence of graphite and spinel. A direct form of assimilation occurred at the contacts of these inclusions and the magma, where reaction

produced rims of hypersthene and abundant An-rich plagioclase which incorporated most of the aluminium mainly at the cost of spinel. In the quartz-rich group these rims are absent.

#### Causes of the events

The  $M_1$  and  $M_2$  metamorphic events obviously resulted from the heat effect of the magma, and they are considered as two subsequent overprints on the regional metamorphic  $M_0$  before and after incorporation of the inclusions. The relicts of a well developed contact-metamorphic assemblage suggest the presence of a contact aureole at a certain depth. From this aureole fragments were disrupted and metamorphosed (metasomatized) in the melt, resulting in the higher grade  $M_2$  assemblage<sup>2)</sup>. A contact- and a pyrometamorphic event were similarly recognized by Rodolico (1935), and a comparable succession was described for xenoliths within the Laacher See volcanics by Brauns (1911). It is of interest to note that many aspects of  $M_2$  resemble those observed in metasedimentary xenoliths from acid volcanics in the French Central Massif (Maury et al., 1978).

The absence of  $M_1$  relicts in a number of samples is likely due to a long residence time in the magma, or, possibly in some cases, to an original position at larger distances from the chamber. The fragments derived from the wall-rock in an early stage prior to eruption were completely transformed into the  $M_2$  assemblage, while some of those, detached during eruption, might originate from shallower levels outside the aureole. That there was sufficient time between disruption and final atmospheric cooling is also suggested by the absence of hornfels relicts belonging to a lower facies than the pyroxene hornfels facies.

#### P-T conditions

The mineral assemblages allow some estimates on the PT-conditions of

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<sup>2)</sup> The microgranitic inclusions found in QLA and QLB, and consisting of quartz, plagioclase, sanidine, biotite, orthopyroxene, + cordierite, are interpreted as early crystallizates of the host-magma. They formed by rapid crystallization at contacts with the relatively cool wall-rock, and subsequently they underwent a similar development as most of the metamorphic xenoliths, viz. disruption and incorporation in the magma, partial re-melting and possible metasomatism. This origin implies that the fragments be called cognate inclusions rather than xenoliths.

M<sub>1</sub> and M<sub>2</sub>. As already mentioned the regional metamorphism (M<sub>0</sub>) could have been above the biotite isograd at least for part of the xenoliths.

The pyroxene hornfels assemblages indicate maximum temperatures during M<sub>1</sub> higher than 600°C (Turner, 1968). Crystallization occurred mainly within the andalusite field, which points to pressures less than 5.5 Kb (Richardson et al., 1969). By intersection of dehydration-curves of muscovite (e.g. Evans, 1965) with the andalusite-sillimanite boundary (Richardson et al., op.cit.) it can be inferred that pressures must have been less than 3.5 Kb. Considering the pressure effect on the stability of garnet and cordierite (e.g. Hensen & Green, 1971) the maximum pressure could have been 3 Kb if the conclusion is correct that (some of) the almandine-rich garnet originated by contactmetamorphism.

Temperatures during M<sub>2</sub> were distinctly higher than those indicated by the curve for the beginning of melting of granite (Tuttle & Bowen, 1958) and crystallization occurred within the sillimanite field, which points to temperatures higher than 750°C at an assumed pressure of 2 Kb. The high temperature breakdown of garnet strongly depends on composition and on oxygen-fugacity (Hsu, 1968). At relatively reducing conditions, which in the case of the xenoliths are suggested by the abundance of graphite, almandine by itself breaks down above about 800°C. Preliminary results of two-pyroxene thermometry (van Bergen, in prep.) give temperatures slightly higher than 800°C.

These values for M<sub>2</sub> are compatible with the maximum temperatures of the host magma, which, at its origin, must have been in the order of 850 to 880°C according to estimates for the chemically quite analogous volcanics of Mt.Cimino (Puxeddu, 1971).

#### DISCUSSION ON ORIGIN AND CONCLUSIONS

Using the complex metamorphic history discussed previously, in combination with the lithological and microstructural aspects, an attempt can be made to interpret the origin of the xenoliths in relation to the subsurface geology of Mt.Amiata area.

The indications that the formation of M<sub>1</sub>-assemblages could take place at pressures up to about 3 Kb suggest that the magma causing contact metamorphism in regional metamorphic rocks possibly intruded at a fairly

large depth. Detailed subsurface data presently available from drilling and geophysical surveys have been gathered from levels not deeper than 3000 m. The rocks directly underlying the Amiata volcanics are predominantly shaly sediments of the Alberese-Pietraforte Group, which tectonically cover the autochthonous Tuscanids represented by the Upper Triassic Anhydrite Formation (Calamai et al., 1970). The total thickness of this pile largely varies between 500 and 1000 meters. In Tuscany the Anhydrite Formation generally lies on top of a clastic sequence deposited transgressively on Paleozoic rocks which were folded during the Hercynian orogenesis (e.g. Giannini et al., 1971). Recent drilling near Mt. Amiata shows the presence, down to 3000 m. of rocks resembling Carboniferous rocks known from other places in Tuscany (Bagnoli et al., 1981). They are low-grade regional metamorphic and provide no evidence of a thermo-metamorphic overprint, which is in accordance with a non-shallow position of the contact aureole.

The stratigraphy of the Tuscan Paleozoic, deduced from sporadic outcrops, data from deep drilling and comparison with nearby regions, is complicated by lateral facies variations and Hercynian and/or Alpine tectonics (Bagnoli et al., 1979). These authors proposed a subdivision into two Supergroups: A) the Tuscan Permo-Carboniferous and B) the Tuscan Crystalline. In both Supergroups rocks of clastic origin are dominant. Further general characteristics (Puxeddu et al., 1977; Bagnoli et al., 1979), relevant for the origin of the inclusions, are: weak recrystallization, very low grade metamorphism, weak foliation and presence of organic material in A; good to complete recrystallization, low to medium grade metamorphism, strong deformation with two or more foliation planes, relicts of pre-alpine foliation and presence of organic matter in B. Considering the characteristics of the xenoliths (lithology, the often observed strong deformation with one or more foliations, biotite as pre-thermometamorphic relict and graphite-content) the Tuscan Permo-Carboniferous as their origin is most unlikely.

Of special interest is the so-called Micaschist Group, being the oldest unit of the Tuscan Crystalline and occurring in scattered outcrops and deep boreholes (Gianelli et al., 1978; Gianelli & Puxeddu, 1979; Bagnoli et al., 1979). Besides subordinate quartzite and amphibolite,

this group consists of polymetamorphic micaschists containing acidic plagioclase and rotated garnet in addition to quartz, muscovite and chlorite, which are the main components. Chemically the micaschists have high aluminium and iron contents (Gianelli & Puxeddu, 1979), and they are in this respect similar to many of the inclusions according to mineralogy and preliminary total rock analyses of the latter. Furthermore, a number of inclusions show some similarities to the basal muscovite-biotite schists of the Capo Calamita Complex of Elba (Barberi et al., 1967), which may be correlated with the Micaschist Group (Bagnoli et al., 1979): intensive folding, graphitic levels and post-tectonic andalusite.

In the Larderello-Travale geothermal area, situated approximately 50 km NW of Mt. Amiata, the Micaschist Group is found in boreholes at a depth of about 2-3 km. Tightly related gneisses containing quartz, K-feldspar, plagioclase, biotite, cordierite, sillimanite + andalusite, ± muscovite are present in the deepest levels (3.5 to more than 4 km) (Gianelli et al., 1978). A deep seismic reflecting horizon, detected at depths between 4 and 7 km, suggests a sudden lithological change tentatively interpreted as the regional basement (Calore et al., 1979; Batini et al., 1978), which is thought to consist of a granito-gneissic Hercynian complex (Bertini et al., 1980).

The relatively shallow level of the Micaschist Group in the Larderello-Travale area, in contrast to the deeper position supposed for the Amiata contact aureole, seems to exclude this Group as main source of the inclusions. A mere extrapolation of depth relations is, however, not allowed. Tectonic doubling of paleozoic rocks (Bagnoli et al., 1979) and/or thicker development of certain formations (e.g. the Carboniferous rocks mentioned above), both also suggested by varying crustal thicknesses in the Tuscan-Latium region (Nicolich & Pellis, 1979; Giese et al., 1978), makes a rather deep level for the Micaschists below Mt. Amiata possible. There is no record of a seismic horizon analogous to that of Larderello-Travale area.

The conclusion that the metasedimentary inclusions, before being strongly transformed by incorporation in the magma, are fragments of a contact aureole, implies the presence of a reservoir where the Mt. Amiata

magma accumulated before eruption, and it strongly supports the view (Marinelli, 1963, 1967) that a cooling intrusion related to the volcanism is responsible for the actual high geothermal activity in the area. The aureole formed in pre-mesozoic strongly folded regionally metamorphic sediments, probably schists, gneisses and subordinate quartzites from the Tuscan Crystalline. The present data do not allow to precisely estimate the depth of the intrusion, but the possible pressure conditions during contact metamorphism, the recent results from drilling and a cooling period as long as the age of the volcano are all compatible with a non-superficial intrusion.

In consequence of this study further detailed petrological and mineralogical work is recommended in order to explore the potential of metamorphic xenoliths in volcanic rocks, associated with geothermal activity, to provide accurate information on the heat-source.

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## CHAPTER III

### COMPLEX INTERACTION OF ALUMINOUS METASEDIMENTARY XENOLITHS AND SILICEOUS MAGMA; AN EXAMPLE FROM MT. AMIATA (CENTRAL ITALY)

Manfred J. van Bergen and Michael Barton

*submitted to Contributions to Mineralogy and Petrology*

#### ABSTRACT

Aluminous, silica-deficient metasedimentary xenoliths in siliceous lavas of Mt. Amiata (Central Italy) have preserved composite zoning-patterns indicative for complex processes of magma-rock interaction. Petrographical observations and small-scale mineralogical and chemical differences between up to five distinct zones (including the core and envelope of lava) provide evidence that

1. partial melt formed in and extracted from the xenoliths was more mafic than the host magma and had a Mg/Fe ratio higher than that of the restite, at least during the peak of thermometamorphism.
2. liquid-state interdiffusion occurred at the interface of partial melt and the enclosing magma.
3. certain mineral phases in the restite (notably Al-spinel) became unstable in the presence of a siliceous liquid.

Quartz-poor muscovite-biotite schists are considered to be the most likely parent-rocks and it is believed that release of volatiles from decomposing micas played a significant role in the high-temperature metamorphic evolution of the xenoliths and their interaction with the magma.

The conditions favourable for assimilation were enhanced by injection of mafic magma into the magmachamber. Although this concurrent operation of magma mixing precludes a quantitative estimate of contamination from the wall-rocks (which was probably of minor importance), the present example indicates that dry acid magma may potentially become more mafic by interaction with partially melted hydrous rocks.

#### INTRODUCTION

Accidental xenoliths in lavas potentially yield information about the mechanisms and extent of contamination experienced by magmas as they

traverse the earth's crust. They may provide an opportunity to examine the effects of chemical interaction that was suddenly interrupted by eruption and was therefore not obliterated by subsequent slow cooling, as might occur in plutonic rocks. Most recent studies have focused on interaction between crustal xenoliths and relatively mafic magmas (e.g., Sigurdsson, 1968; Leyreloup, 1973; Le Maitre, 1974; Maury and Bizouard, 1974; Maury et al., 1978; Harris and Bell, 1982; Woerner et al., 1982), whereas interaction between crustal xenoliths and more siliceous magmas has received less attention (e.g. Maury et al., 1974; Sigurdsson and Sparks, 1981), possibly because such xenoliths are less common in acid lavas.

Metasedimentary xenoliths are abundant in the siliceous lavas of Mt. Amiata, a Pleistocene volcanic complex situated in Southern Tuscany, Italy. Early descriptions of these xenoliths are to be found in the classic work of Lacroix (1893) and also in the study of Rodolico (1935). Among the various types present, aluminous varieties predominate, and quartzitic xenoliths are relatively rare. Textural evidence for several superimposed metamorphic assemblages together with geological considerations suggest that the xenoliths represent fragments of regionally metamorphosed pelitic schists, gneisses and quartzites of the pre-Mesozoic basement and that they underwent progressive thermometamorphism initially in a contact aureole and subsequently during their residence in the magma (Van Bergen, 1983).

In this paper the interaction between the silicious magma and the aluminous xenoliths is described in detail, and the results are used to demonstrate the complexity of the assimilation process that took place in the magma-chamber of Mt. Amiata.

## PETROGRAPHY

### Xenoliths

Detailed petrographic descriptions of the metasedimentary xenoliths of Mt. Amiata have been presented elsewhere (Van Bergen, 1983) and only a brief summary of the petrography of the aluminous xenoliths will be

given here. These are fine-grained, foliated or hornfelsic fragments with rounded outlines and maximum dimensions of a few decimeters. The main constituents are sanidine, spinel, biotite and plagioclase. If present, andalusite, cordierite and possibly garnet are considered to represent contact-metamorphic assemblages formed prior to engulfment by the magma. The andalusite is mostly pseudomorphed by combinations of sillimanite, corundum, spinel, An-rich plagioclase and (in one case) the borosilicate grandidierite (see Van Bergen, 1980). Irregularly shaped leucocratic areas frequently dissect the xenoliths and predominantly consist of sanidine together with some plagioclase, biotite or orthopyroxene, whereas in several samples a rather Fe-rich olivine appears instead of the latter. These areas provide irrefutable evidence for partial melting as they may contain patches of vesicular brown glass in which biotite or orthopyroxene, opaques and sometimes heavily resorbed relicts of quartz may be present. Melting has probably been more widespread than suggested by the limited amounts of glass, because extensive late-stage crystallization of sanidine, which often encloses the other minerals poikilistically and shows straight crystal faces when in contact with the brown glass, has caused a marked textural overprint. Ilmenite is a common opaque constituent and is orientated according to the microfoliation, which suggests a pre-thermometamorphic origin. Magnetite and hematite may also occur and probably formed later than ilmenite. Preferred orientation is often also shown by flakes of graphite, but in some cases the graphite gives the impression of 'floating' in the glass. Apatite, zircon and Fe-sulfide are accessory phases.

#### Enclosing lavas

The enclosing lavas are K-rich rhyodacites<sup>\*</sup>) that contain phenocrysts of plagioclase (with a complex zoning including An-rich cores), sanidine, biotite, pyroxene and ilmenite. From available mineralogical data (Van Bergen et al., 1983) it appears that the equilibrium plagioclase is

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<sup>\*</sup>) The term 'rhyodacite' is used here for potassium-rich, often peraluminous lavas (62-67 wt.% SiO<sub>2</sub>, 5-6% K<sub>2</sub>O, K<sub>2</sub>O/Na<sub>2</sub>O=2-3) that are also known as quartz-latites or trachytes.

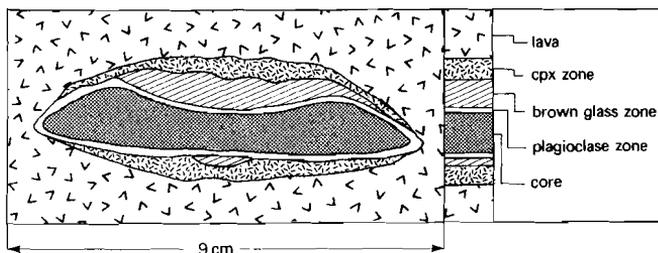
An<sub>47-62</sub> and that sanidine is around Or<sub>79-84</sub>. Biotite is rich in TiO<sub>2</sub> (5-8 wt.%) and has Mg-numbers (Mg/(Mg+Fe<sup>tot</sup>)) between 0.50 and 0.60. Orthopyroxene (En<sub>40-55</sub>) and two types of clinopyroxene are also present. One type is diopsidic and occurs mainly as microphenocrysts, whereas the other type is augitic and is mostly found in certain crystal-aggregates that may further be composed of plagioclase (up to An<sub>90</sub>), orthopyroxene, biotite and an Fe-rich olivine. Although these mineralogical data are based on a limited number of samples, which could imply that the reported compositional ranges are slightly too narrow, the phenocryst compositions are considered to be adequately characterized in view of the relatively uniform petrography and chemistry of the lavas.

The groundmass is generally glassy (with perlitic cracks and, sometimes, spherulitic textures) or microcrystalline. There are several accessory phases: apatite, zircon, Fe-sulfide and the REE-Ti silicate perrierite (Van Bergen, 1984). Rare, embayed crystals of quartz also occur.

#### Zoning of xenoliths

Along their margins many xenoliths show a concentric mineralogical/textural zoning from the core towards the enclosing lava. Examination of lava-xenolith contacts in thin sections from some 20 samples revealed several sequences of zones, from which the following complete sequence has been compiled:

- 1) Core of xenoliths, essentially composed of sanidine, biotite, spinel, plagioclase, andalusite/sillimanite/corundum, Fe-Ti oxides and graphite (see general description above).
- 2) Plagioclase zone (very common), consisting of plagioclase and subordinate biotite or orthopyroxene, as well as relicts of spinel. Glass may be present along grain boundaries.
- 3) Brown glass zone, which is absent in many samples and is only locally developed in others. In a few specimens it has been found as a distinct zone intermediate between the xenolith and lava. Brownish coloured glass and 'phenocrysts' of biotite and/or plagioclase and/or orthopyroxene are the main constituents. The glass is often extremely vesicular.



*Fig.1. Cross-section of xenolith MA15.14 showing its complex zoning pattern. Note that the thin plagioclase zone circumvents the entire core and that the brown glass zone is well developed on only one side.*

4) Clinopyroxene zone (also rare), characterized by phenocrysts that are identical in type and appearance to those in the lava and are embedded in a vesicular groundmass of fine-grained clinopyroxene, sanidine, biotite and minor colourless glass.

5) Unmodified lava (see description above).

The thickness of the plagioclase, brown glass and cpx zones are variable with a maximum of a few millimeters. Sometimes the first two zones are apparently condensed into one, for example in those cases that orthopyroxene, being typical for the outer part of brown the glass zone, is present in the plagioclase zone. Although contacts can be gradual (especially along the plagioclase zone), they are generally easy to define optically.

#### Xenolith MA 15.14

Specimen MA 15.14 was selected for detailed analytical work as in this rock the five distinct zones are best developed and, except for the very thin plagioclase zone, are sufficiently voluminous for bulk chemical analysis. It is a relatively small lenticular xenolith with a maximum diameter less than 1 dm, which was found in a typical perlitic lava. As shown by the schematic cross-section in fig. 1, the plagioclase zone circumvents the whole xenolith, whereas the other zones are not continuous and pinch out laterally. The brown glass zone is present mainly on one side of the xenolith.

The petrography is in agreement with the general scheme outlined above. In the core sanidine and spinel are particularly abundant

(together some 60 modal %), while biotite and plagioclase are the other major constituents, and opaques (ilmenite and graphite) also occur. A few grains of corundum as well as accessory apatite are present. Some relictic intergrowths of spinel and plagioclase are reminiscent of the pseudomorphs after andalusite in other samples, but more commonly the spinel is associated with biotite.

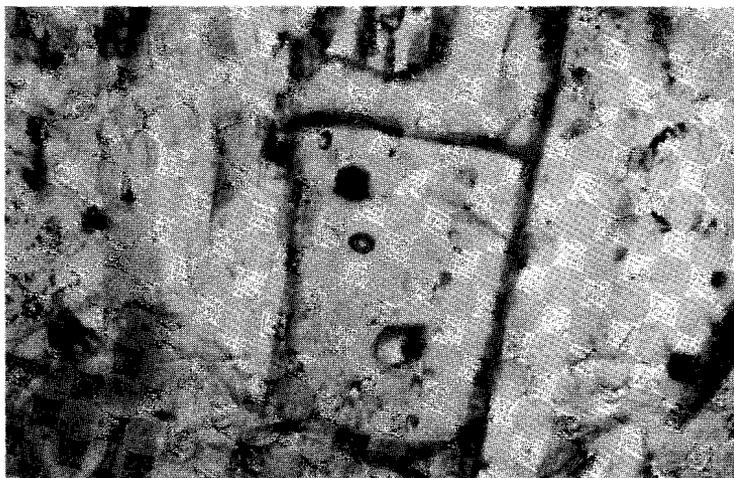
The plagioclase zone consists of more than 90% plagioclase with subordinate biotite, relicts of spinel, ilmenite and some graphite. Minor amounts of glass are present along grain boundaries and as inclusions in plagioclase that often surround corroded spinels.

Plagioclase is also dominant in the brown glass zone, which further contains orthopyroxene and biotite. These 'phenocrysts' form sub- to euhedral crystals. Plagioclases sometimes show a continuous optical zoning, while those occurring near the plagioclase zone contain relicts of spinel. The brown glass is slightly birefringent, partly devitrified and may exhibit a radial texture reminiscent of spherulites. There are numerous vesicles. Elongate crystals of biotite, orthopyroxene, sanidine (also as hopper crystals and frequently as rims around plagioclase) and trace amounts of Fe-Ti oxide occur as quench phases. In a region containing abundant graphite, a few practically opaque grains of fayalite were found, which are partly replaced by Ti-poor magnetite. Where the brown glass zone is thickest, biotite tends to be concentrated towards the plagioclase zone and orthopyroxene towards the cpx zone, but occasional intergrowths also suggest that one mineral may replace the other. Apatite occurs as relatively large prismatic crystals, and some 'drops' of Fe-sulfide are present as inclusions in biotite.

The cpx zone is porphyritic with phenocrysts that are somewhat smaller and less abundant than those in the lava. These are set in a fine-grained vesicular groundmass that consists of sanidine, clinopyroxene, biotite, Fe-Ti oxide and minor interstitial colourless glass, that is concentrated mainly along the vesicles. Plagioclase phenocrysts are rounded in contrast to those in the lava, and they may have a small rim of sanidine. Orthopyroxenes are rimmed by clinopyroxene. Biotite and ilmenite are uncommon, and phenocrysts of sanidine were not found in the thin sections available.

One resorbed grain of quartz was observed. Vesicles are exceptionally numerous at contacts with the plagioclase zone.

Newly-formed minerals, particularly the plagioclase and orthopyroxene in the plagioclase and brown glass zones, contain well-developed, primary fluid inclusions with gas-bubbles (fig. 2). Rough determinations of homogenization temperatures ( $\pm 30^{\circ}\text{C}$ ) and the critical homogenization indicate that the fluid is pure  $\text{CO}_2$ , close to critical density, which suggests low pressures during entrapment and is in agreement with the LP-HT assemblages in the xenoliths. Based on the presence of rare almandine-rich garnet as a possible contact-metamorphic mineral, it was suggested (Van Bergen, 1983) that pressures up to some 3 kbar should be reckoned with. Further detailed work on these fluid inclusions will be carried out, which may yield more precise constraints on the pressure conditions and thus on the depth of the magmachamber. There is little doubt that the  $\text{CO}_2$  was produced by oxidation of graphite, as its abundance is strongly reduced in areas where the inclusions occur, notably along the margins of the xenolith.



*Fig.2. 'Phenocryst' of orthopyroxene in the brown glass zone of MA15.14 containing inclusions of glass and of  $\text{CO}_2$  (e.g., near the centre of the crystal). Long dimension approx. 0.3 mm.*

## ANALYTICAL PROCEDURE

Some 500 microprobe analyses were performed on polished thin sections covering the zones on both sides of the xenolith. The majority of the data were obtained at the Vening Meinesz Laboratory, Utrecht using a TPD-microprobe, and additional analyses were carried out at the University of Manchester using a Cambridge Geoscan microprobe. Energy-dispersive techniques were applied, with operating conditions of 15 kV accelerating voltage and about 16 and 3 nA sample current respectively. On-line data reduction included corrections for deadtime, background, atomic number, absorption and fluorescence. Glasses were analysed with a broad beam (20-40  $\mu\text{m}$ ) in order to minimize loss of alkalis. For whole-rock analyses, samples of the core, brown glass zone, cpx zone and adjacent lava of specimen MA 15.14 were obtained by slicing the rock with the use of a micro-saw. These samples were purified by removal of all visible contamination before crushing. Major elements were determined by standard wet-chemical methods and trace elements of three zones (because of insufficient material from the cpx zone) by XRF.

## MINERAL AND GLASS CHEMISTRY

Representative microprobe analyses of the major mineral phases and glasses are given in tables 1-4. Figures 3-5 illustrate the existence of small but nevertheless consistent variations in the chemistry of biotites, pyroxenes and feldspars in the individual zones, and these are discussed in some detail.

The biotites in the core are richest in Fe (Mg-number=42-46) and have sufficient Al to fill Si-deficiencies in the tetrahedral sites. The large biotites in the other zones are indistinguishable in terms of Mg-number (51-54) but have insufficient Al to fill the tetrahedral sites. Although they are all characterized by high Ti contents, the biotites in the brown glass and plagioclase zones contain slightly more Ti than those in the other zones (0.83-0.98 a.f.u., compared with 0.63-0.83 in the core, and 0.60-0.80 in the lava, based on 22 oxygens). Surprisingly, two analysed biotites in the cpx zone (one of which occurs in an aggregate with orthopyroxene, plagioclase and ilmenite) are also among the highest in Ti and

## BIOTITE

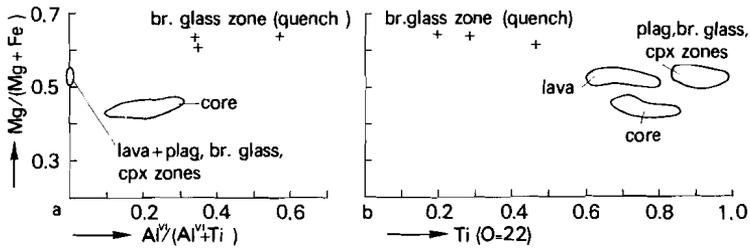


Fig. 3.  $Mg/(Mg+Fe)$  vs.  $Al^{VI}/(Al^{VI}+Ti)$  and vs.  $Ti$  for biotites of xenolith MA15.14. Each area represents at least 10 analyses.

do not plot in the field of biotites from the lava for this particular sample, but it should be noted that such compositions have been found in other lava samples.

Analyses of three quench biotites in the brown glass zone show that they are compositionally quite different from the other biotites in this zone inasmuch as they have high Mg-numbers (60-64), contain octahedral Al and are relatively poor in Ti (0.20-0.47 a.f.u.). These results contrast with experimental results reported by Edgar et al. (1976), who found that quench phlogopites are richer in Fe and Ti than primary phlogopites. Unfortunately biotites in the groundmass of the cpx zone were too small to analyse.

In comparison with the orthopyroxenes in the cpx zone, those in the brown glass zone are markedly richer in Mg ( $En_{49-53}$ ), and their Mg-numbers are close to those of the biotites in the same zone. Compositions of orthopyroxenes in the cpx zone commonly fall within the range for those in the lava ( $En_{42-47}$ ), which is typical for the rhyodacites, although pyroxenes somewhat richer in Mg are known to occur also. Similarly more magnesian compositions (up to  $En_{56}$ ) were measured in a single pyroxene-plagioclase aggregate in the cpx zone (e.g., opx b, table 2, not shown in fig. 4).

Two types of clinopyroxenes are present in the cpx zone and the lava envelope. Those with augitic compositions (e.g., cpx d and f, table 2) are relatively large grains in association with the other aggregate minerals such as frequently found in the lavas. They are much richer in

biotites						
	core	plag zone	brown glass zone		cpx zone	lava
			a	b		
SiO <sub>2</sub>	35.2	36.4	36.1	38.4	37.1	37.5
Al <sub>2</sub> O <sub>3</sub>	16.2	13.1	12.4	12.7	12.9	12.2
TiO <sub>2</sub>	6.1	7.3	7.7	2.5	8.1	5.8
FeO	20.1	17.6	18.1	15.2	17.6	18.7
MnO	n.d.	0.3	n.d.	0.2	n.d.	n.d.
MgO	8.8	10.8	11.1	14.7	11.7	11.4
CaO	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Na <sub>2</sub> O	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
K <sub>2</sub> O	9.6	9.6	9.6	9.8	9.5	9.4
total	96.0	95.1	95.0	93.5	96.9	95.0
Si	5.36	5.56	5.54	5.87	5.54	5.74
Al <sup>IV</sup>	2.64	2.35	2.25	2.13	2.27	2.20
Al <sup>VI</sup>	0.27	-	-	0.15	-	-
Ti	0.70	0.84	0.88	0.29	0.91	0.66
Fe	2.56	2.25	2.32	1.94	2.20	2.39
Mn	-	0.04	-	0.03	-	-
Mg	2.01	2.46	2.53	3.34	2.60	2.59
Ca	-	-	-	-	-	-
Na	-	-	-	-	-	-
K	1.87	1.86	1.87	1.91	1.80	1.83
Z	8.00	7.91	7.79	8.00	7.81	7.94
XY	5.54	5.59	5.73	5.75	5.71	5.64
W	1.87	1.86	1.87	1.91	1.80	1.83
Mgno	44.0	52.2	52.2	63.3	54.2	52.0

Table 1. Representative compositions of biotites in the core, plagioclase zone, brown glass zone, clinopyroxene zone and lava-envelope of xenolith MA15.14. All iron is taken as FeO or Fe<sup>2+</sup>. Cations are based on 22 oxygens. a: large crystal, b: quench crystal, n.d.: not detected, Mgno = Mg/(Mg+ΣFe<sup>2+</sup>)

Fe than the microphenocrysts and groundmass crystals which plot near the diopside-salite join. Although there is a considerable overlap, the clinopyroxenes in the cpx zone tend to be richer in Ca than those in the lava envelope.

Plagioclases exhibit the most pronounced chemical variation (fig. 5). Plagioclases in the core of the xenolith are relatively poor in anorthite (An<sub>53-67</sub>) and their compositions are apparently dependent on position, as An-contents gradually increase from the centre of the core outwards. Those in the plagioclase and brown glass zones vary between An<sub>65</sub> and

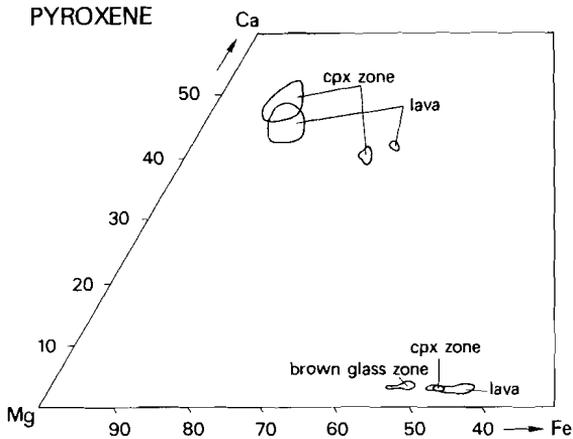


Fig.4. Pyroxene compositions plotted in a Ca-Mg-Fe diagram. Each area represents 5-15 analyses, except for the augites which are from a few crystal-aggregates (see text). Some relatively magnesian orthopyroxenes from an aggregate in the clinopyroxene zone are omitted for clarity.

$An_{88}$  with highest values predominantly in the former zone. Core-rim zoning in single crystals is usually normal, but reversed grains were also found. Equilibrium phenocrysts in the lava zone and rounded equivalents in the cpx zone are lowest in anorthite ( $An_{44-58}$ ). Much higher An-contents are characteristic for non-equilibrium resorbed cores of phenocrysts and plagioclases in the aggregates. For the sake of clarity these have been omitted in fig. 5, because they would coincide with the plagioclases in the plagioclase and brown glass zones. The observed systematic variations are illustrated in fig. 6 which is an example of the results obtained by measuring cores of grains at more or less regular intervals along several paths across the xenolith.

A limited compositional range was found for the sanidines. Large sanidines in the core approach values of  $Or_{86}$ , while analysed rims on plagioclase in the brown glass zone are close to  $Or_{80}$ . Phenocrysts in the lava are also around  $Or_{80}$ , whereas groundmass crystals as well as small sanidines in the cpx zone tend to be richer in Na and Ca (fig. 5).

Ilmenites are chemically uniform in all zones as are the spinels in the core and their relicts in the plagioclase and brown glass zones. The small deviations from ideal stoichiometry in the microprobe analyses suggest the presence of only minor hematite or magnetite in solid solution.

	opx				cpx			
	br. gl. zone	cpx zone		lava	cpx zone		lava	
		a	b		c	d	e	f
SiO <sub>2</sub>	50.7	50.6	50.2	51.1	50.6	51.1	51.0	51.5
Al <sub>2</sub> O <sub>3</sub>	0.3	0.0	0.7	0.0	4.9	1.2	4.4	0.9
Cr <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	n.a.	n.a.	0.1	0.1	0.2	0.2
TiO <sub>2</sub>	0.3	0.0	0.5	0.0	1.0	0.4	0.8	0.2
FeO	29.1	32.5	27.7	33.8	6.5	15.5	6.7	16.2
MnO	0.5	0.9	0.5	0.7	0.2	0.3	n.d.	0.4
MgO	16.7	15.1	17.3	14.1	14.2	12.0	15.3	10.4
CaO	1.6	1.3	1.6	1.1	22.6	19.1	21.3	20.0
Na <sub>2</sub> O	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	0.5	0.2
total	99.2	100.4	98.5	100.8	100.4	99.7	100.2	100.0
Si	1.98	1.99	1.96	2.00	1.87	1.96	1.88	1.98
Al <sup>IV</sup>	0.01	-	0.03	-	0.13	0.04	0.12	0.02
Al <sup>VI</sup>	-	-	-	-	0.08	0.02	0.07	0.02
Cr	-	-	-	-	0.004	0.004	0.01	0.005
Ti	0.01	-	0.01	-	0.03	0.01	0.02	0.01
Fe	0.95	1.06	0.91	1.10	0.20	0.50	0.21	0.52
Mn	0.02	0.03	0.02	0.02	0.01	0.01	-	0.01
Mg	0.97	0.88	1.01	0.82	0.78	0.68	0.84	0.60
Ca	0.07	0.06	0.07	0.05	0.89	0.78	0.84	0.82
Na	-	-	-	-	0.02	-	0.03	0.02
Σ	4.01	4.02	4.01	3.99	4.014	4.004	4.02	4.005
Mgno	50.5	45.4	52.6	42.7	79.6	57.6	80.0	53.6

Table 2. Representative compositions of pyroxenes in the brown glass zone, clinopyroxene zone and lava-envelope of xenolith MA15.14. All iron is taken as FeO or Fe<sup>2+</sup>. Cations are based on 6 oxygens. a, c and e: normal (micro)phenocrysts, b, d and f: grains in crystal aggregates (see text), n.a.: not analysed, n.d.: not detected, Mgno = Mg/(Mg+ΣFe<sup>2+</sup>)

Mg-numbers of spinels range between 22 and 25. The tiny opaque grains in the cpx zone are probably titaniferous magnetites.

Average results of multiple spot analyses of glasses are given in table 4. Some small variations between individual spots of the brown glass (note 2σ-values) may reflect true chemical variations, or be due to the presence of microliths that could not always be avoided. In any case, compositions did not vary systematically from the plagioclase zone to the cpx zone. Therefore, the results were averaged, with omission of a few that were obviously contaminated by microliths. For comparison a brown glass occurring in the core of another xenolith (AM 4.13) was analysed. This glass (with only biotites as 'phenocrysts' and quenched crystals) has a composition fairly similar to that of the brown glass zone. The

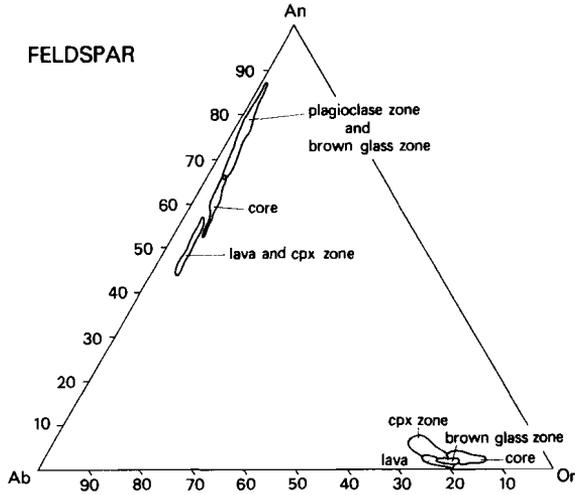


Fig. 5. Feldspar compositions plotted in an Ab-An-Or diagram. Areas for plagioclases represent 15-50 analyses, those for sanidines 5-12 analyses. An-rich disequilibrium compositions of plagioclase cores and of plagioclases in crystal-aggregates from the lava and clinopyroxene zone are omitted for clarity.

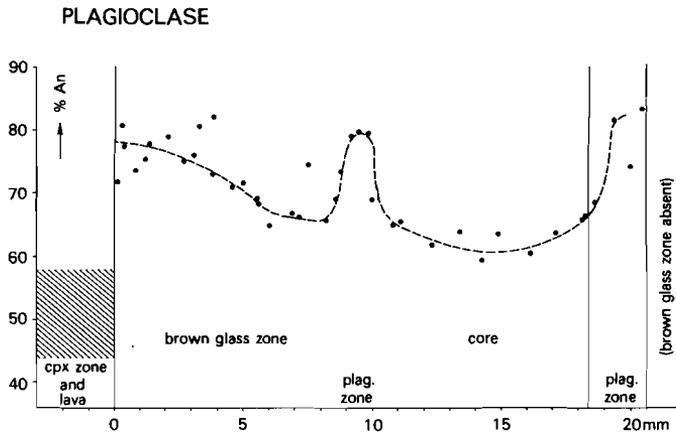


Fig. 6. Anorthite-content of plagioclase cores vs. distance in a representative section across xenolith MA15.14. Hatched area indicates compositions of equilibrium phenocrysts from the lava and clinopyroxene zone.

	ilmenites					spinel	magn.	olivine
	core	plag zone	br.gl. zone	cpx zone	lava			
SiO <sub>2</sub>	0.3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	29.4
Al <sub>2</sub> O <sub>3</sub>	0.3	0.2	0.1	0.2	0.3	56.5	1.9	0.2
Cr <sub>2</sub> O <sub>3</sub>	n.a.	n.a.	n.a.	n.a.	n.a.	0.3	n.a.	n.a.
TiO <sub>2</sub>	53.0	52.9	51.9	52.2	53.0	0.4	14.9	0.0
FeO	42.5	43.1	44.8	46.1	45.8	36.1	74.7	69.4
MnO	0.6	0.4	0.7	0.6	0.6	0.6	0.5	0.5
MgO	2.5	2.6	1.6	1.8	1.8	6.0	0.4	0.2
total	99.2	99.2	99.1	101.9	101.5	99.9	92.4	99.7
Si	0.03	-	-	-	-	-	-	1.00
Al	0.03	0.03	0.01	0.02	0.04	1.90	0.30	0.01
Cr	-	-	-	-	-	0.01	-	-
Ti	3.97	3.97	3.95	3.91	3.92	0.01	1.50	-
Fe	3.54	3.60	3.79	3.84	3.78	0.86	8.40	1.97
Mn	0.06	0.03	0.06	0.05	0.05	0.015	0.05	0.01
Mg	0.38	0.39	0.24	0.27	0.27	0.25	0.09	0.01
Σ	8.01	8.02	8.05	8.09	8.06	3.045	10.34	3.00
Mgno						22.5		

Table 3. Representative compositions of ilmenites, green spinels, Ti-magnetites and olivine in the core, plagioclase zone, brown glass zone, clinopyroxene zone and lava-envelope of xenolith MA15.14. All iron is taken as FeO or Fe<sup>2+</sup>. Cations are based on 12, 4, 12 and 4 oxygens respectively. n.a.: not analysed, Mgno = Mg/(Mg+ΣFe<sup>2+</sup>)

	glasses					
	lava		brown glass zone		AM 4.13	
	x	2σ	x	2σ	x	2σ
SiO <sub>2</sub>	75.8	1.2	69.8	1.2	71.2	1.2
Al <sub>2</sub> O <sub>3</sub>	12.6	0.6	15.8	0.8	15.1	0.8
TiO <sub>2</sub>	n.d.	-	0.5	0.1	0.4	0.2
FeO	1.1	0.6	1.3	0.8	1.25	0.4
CaO	0.9	0.4	2.2	0.4	1.9	0.6
Na <sub>2</sub> O	2.2	0.5	2.5	0.6	2.7	0.4
K <sub>2</sub> O	6.5	0.4	7.3	0.6	6.6	1.1
total	99.1		99.4		99.15	
n	10		8		9	

Table 4. Average compositions of glasses in the lava-envelope and brown glass zone of xenolith MA15.14 and in a biotite-bearing melt-patch of AM4.13. n.d.: not detected.

analysis of the glass in the lava is in agreement with wet chemical analyses of separated glasses from Mt. Amiata rhyodacites reported by Mazzuoli and Pratesi (1963) and Dupuy (1970), which indicates that the microprobe results are satisfactory. It thus appears that the brown glass is poorer in  $\text{SiO}_2$  and richer in practically all other major elements (notably  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ ) than the lava glass. The colourless glass in the cpx zone could not be analysed with a broadened beam, but semiquantitative results using a normal beam, together with its colourless appearance suggest that its composition is similar to that of the lava glass.

#### WHOLE ROCK CHEMISTRY

Chemical analyses are listed in table 5. In order to obtain a complete view of the chemical variations across the lava-xenolith contact, the composition of the unanalysed plagioclase zone has been calculated from modal amounts (90% plagioclase, 6% biotite, 3% spinel, 1% ilmenite, other phases negligible) and analytical data for individual minerals. This result has been used in fig. 7 which is a variation diagram of major oxides against  $\text{SiO}_2$ . The xenolith core is poorest in  $\text{SiO}_2$  and its composition resembles that of aluminous silica-deficient hornfelsic inclusions and contact-metamorphic rocks such as those described by Leake and Skirrow (1960) and Barker (1964), but it is unusually rich in  $\text{K}_2\text{O}$ . The enclosing lava zone has the highest content of  $\text{SiO}_2$  and its composition is similar to typical siliceous lavas from Mt. Amiata that are characterized by relatively high  $\text{K}_2\text{O}$  contents (Mazzuoli and Pratesi, 1963; Van Bergen et al., 1983). As can be seen in fig. 7, the trends of most oxides are inconsistent with a gradual transition from the xenolith core to the lava. Although  $\text{SiO}_2$  increases in this direction, most major oxides show marked deviations relative to straight-line trends, the most striking anomalies being the enrichment in  $\text{CaO}$ ,  $\text{FeO}$  and  $\text{MgO}$  and impoverishment in  $\text{K}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  in the brown glass zone. The Mg-number is distinctly low in the core compared to the other zones, while the oxidation ratio ( $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) decreases from the core to the lava.

Of the trace elements analysed, Ba, Rb and Zr behave like K inasmuch as they are relatively low in the brown glass zone. It should, however, be noted that Ba in the lava is anomalously high in comparison with

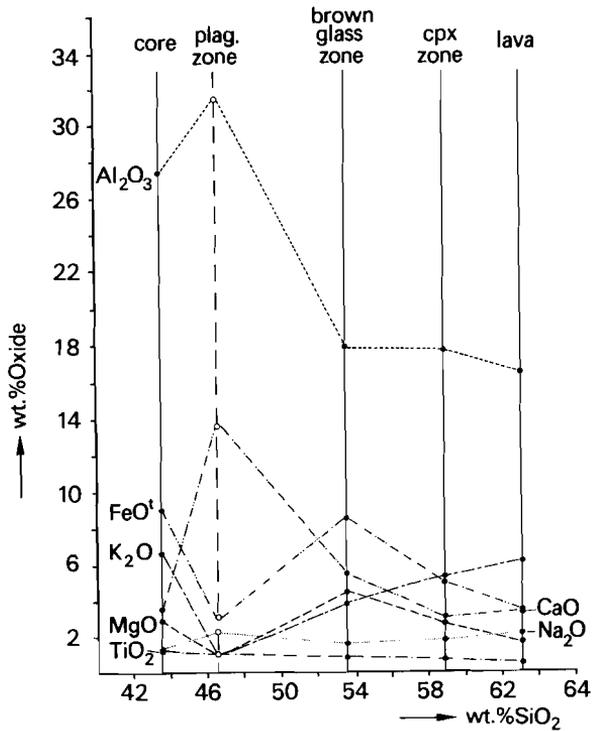


Fig.7. Variations of major oxides ('whole-rock') as a function of  $SiO_2$  from core to lava-envelope of xenolith MA15.14. The composition of the plagioclase zone was calculated from modal abundances.

other rhyodacites from Mt. Amiata (cf. Van Bergen et al., 1983). Surprisingly, Sr does not follow Ca, because it has its maximum in the core, as has Zn. While Sr is probably retained in feldspars, Zn is undoubtedly held in spinel.

#### DISCUSSION

Interaction at the interface of magma and solid rock is bound to be complex given the diversity of processes that may be involved successively or even simultaneously. Reaction between melt and unstable minerals, solution of minerals into the melt and mixing of magma and (partial) melt extracted from the contact-rock are mechanisms long ago identified and discussed by Bowen (1928). Additional processes that

	chemical analyses				CIPW-norm				
	core	br.gl. zone	cpx zone	lava	core	br.gl. zone	cpx zone	lava	
SiO <sub>2</sub>	43.51	53.64	58.93	63.10	qtz	-	7.9	15.8	15.3
Al <sub>2</sub> O <sub>3</sub>	27.42	17.80	17.69	16.43	co	11.8	2.1	4.2	0.5
TiO <sub>2</sub>	1.29	0.93	0.75	0.49	or	40.6	22.5	31.8	36.0
Fe <sub>2</sub> O <sub>3</sub>	3.77	1.54	0.91	0.04	ab	9.1	13.2	15.7	18.5
FeO	5.80	7.22	4.08	3.45	an	16.4	24.8	13.1	15.6
MnO	0.12	0.15	0.11	0.07	ne	1.6	-	-	-
MgO	2.93	4.39	2.67	1.70	en	-	11.0	6.7	4.2
CaO	3.39	5.38	3.00	3.45	fs	-	10.8	5.8	5.6
Na <sub>2</sub> O	1.41	1.56	1.84	2.18	fo	5.2	-	-	-
K <sub>2</sub> O	6.83	3.80	5.33	6.09	fa	4.4	-	-	-
P <sub>2</sub> O <sub>5</sub>	0.08	0.30	0.29	0.23	mt	5.5	2.2	1.3	0.1
L.O.I.	2.77	3.14	3.43	2.74	il	2.5	1.8	1.4	0.9
					ap	0.2	0.7	0.7	0.6
total	99.32	99.85	99.03	99.97					
Mgno*	21.0	29.9	31.4	29.1					
trace elements (ppm):									
Ba	1060	710	-	835					
Sr	590	530	-	490					
Rb	290	255	-	385					
Zr	210	165	-	205					
Zn	275	85	-	35					

Table 5. 'Whole-rock' compositions and CIPW-norms of the core, brown glass zone, clinopyroxene zone and lava-envelope of xenolith MA15.14. Mgno =  $Mg/(Mg+\Sigma Fe^{2+})$

potentially play a role are elemental interdiffusion between coexisting melts, vapour phase transport (e.g., Maury and Bizouard, 1974) and 'flash' melting by decompression during the ascent (Irving and Mathez, 1982). The development of composite reaction zones of the type described above suggests that more than one process was active at the interface of the aluminous xenoliths and the Mt.Amiata magma.

#### Extraction of partial melt

Spinel-rich assemblages are typical for high-grade, silica-deficient aluminous hornfelses (e.g., Turner, 1968) and have been frequently reported to result from the thermometamorphism of pelitic metasediments by mafic and ultramafic intrusions (Thomas, 1922; Read, 1931, 1935; Leake and Skirrow, 1960; Barker, 1964; Evans, 1964; Gribble and O'Hara,

1967; Gribble, 1968; Propach, 1968; Smith, 1969). Non-isochemical modifications of the original rocks are generally considered to be responsible for the observed enrichment in Al along with elements such as Fe, Mg, Ti and Ca, and impoverishment in Si, K and Na in the metamorphosed equivalents. The more recent studies among those cited have provided convincing arguments for segregation of partial melts as a major control. Suites of glass-bearing granitic and metapelitic xenoliths from volcanics provide unequivocal evidence for partial fusion, and their chemical variation sometimes also indicates progressive removal of the melt (Sigurdsson, 1968; Maury et al., 1978; Woerner et al., 1982).

Regarding the evolution towards silica-deficient aluminous assemblages as well as the presence of glass, there is little doubt that the mineralogy and chemistry of the Mt. Amiata xenoliths is largely the result of extraction of a melt from metasedimentary parent rock. Consequently, the brown glass zone in sample MA 15.14 is likely to represent such a melt, in view of its specific chemistry and mineralogy and its particular position around the xenolith. Furthermore, because textural evidence suggests that the minerals in this zone crystallized from a liquid, it is reasonable to suppose that the total composition of the zone (table 5) approaches that of the removed melt. A quantitative treatment of the extraction process is, however, impracticable because interaction with the surrounding lava probably modified this composition to a certain extent (see below) and because of the absence of data on the original country rocks. Uncertainties as these make it difficult, for example, to evaluate the significance of the compositional difference that exists between the brown glass zone and the melted area in AM 4.13 (as can be inferred from the presence of only biotite together with brown glass in this area). Nevertheless, several interesting points relevant to the evolution of the aluminous xenoliths are worth noting:

1. The removed melt is surprisingly poor in  $\text{SiO}_2$  and is compositionally comparable to a mafic latite. It clearly does not coincide with experimentally determined melt compositions in granitic and related systems (cf. Brown and Fyfe, 1970; Winkler, 1974). The relatively high contents of  $\text{FeO}^{\text{tot}}$ , MgO and CaO indicate a substantial contribution of ferromagnesian minerals and the anorthite component of plagioclase to the

melt. In fact, the melt could have originally been even more mafic, in view of the presence of relicts of early-formed fayalite. Interestingly, the occurrence of olivine or its alteration products in partially fused xenoliths is not uncommon even if these are dominated by felsic minerals (Le Maitre, 1974; Maury and Bizouard, 1974; Harris and Bell, 1982).

2. The melt must have been hydrous, given the numerous vesicles and the fact that it could be generated by the heat supplied by a much more acid magma. Decomposition of micas probably supplied  $H_2O$  and other volatiles necessary to lower the solidus (cf., Manning, 1981). Muscovite must have been an important source of volatiles (see below and cf. Leyreloup, 1973) in addition to part of the biotite, the melting of which is often thought to be responsible for the brown colour of glasses in partially fused rocks (cf. Lacroix, 1893; Sigurdsson, 1968; Le Maitre, 1974; Maury and Bizouard, 1974).

3. The Mg-number of the melt is higher than that of the restitic core. This is readily explained by the dominance of spinel among the residual ferromagnesian minerals. Mineral analyses in several other xenoliths revealed the following general sequence:

$$X_{Mg}^{spinel} < X_{Mg}^{opx} \leq X_{Mg}^{biotite} < X_{Mg}^{cord} ,$$

sometimes with biotites showing large ranges. The residual biotites were probably stabilized by incorporation of Ti, and differ in composition from sporadic relicts of pre-thermometamorphic biotites found in some other samples. The latter are significantly poorer in Ti and also have higher Mg-numbers (Van Bergen, 1983). This concomitant increase of Ti and Fe with temperature is also observed in pelitic schists (e.g., Guidotti et al., 1977) and is qualitatively consistent with experimental work on phlogopites (Robert, 1976; Edgar et al., 1976) and with thermodynamic considerations (Ohmoto and Kerrick, 1977) which predict increasing Fe-contents with increasing temperature in graphitic metapelites. Breakdown of cordierite and relatively Mg-rich biotite and formation of spinel and relatively Fe-rich biotite by reactions that may involve melting will thus give rise to a decrease of Mg-number in the restite and a corresponding liquid with a higher Mg-number. A similar mineralogical control on the composition of extracted melt is well illustrated by the progressive fractional melting of pelitic hornfelses around the

Cashel-Lough Wheelaun intrusion, where initial removal of melt led to a relative enrichment in Mg and to cordierite-rich rocks, whereas spinel appears in the higher grade rocks that show a decrease in Mg-numbers (Leake and Skirrow, 1960; Evans, 1964).

The high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio in the core of MA 15.14 in conjunction with the low contents of calculated  $\text{Fe}^{3+}$  in the associated spinels and ilmenites suggests that part of the iron in biotites is in the trivalent state. Whether this is due to oxidation of ferrous iron, which may accompany thermometamorphism (e.g., Evans, 1964), is questionable. The occasional occurrence of magnetite and possibly also hematite in other xenoliths from Mt. Amiata could be indicative, but it seems difficult to reconcile oxidation with the presence of graphite, which may be expected to largely buffer the oxygen fugacity (Frost, 1979). Oxidizing conditions have undoubtedly reigned in the cpx zone, given the influx of  $\text{H}_2\text{O}$  (see below) and the presence of Ti-magnetite (in contrast to its absence in the lava), which explains the anomalously magnesian clinopyroxenes in this zone (Carmichael, 1963).

4. The negative anomaly of potassium in the plagioclase and brown glass zones mitigates against the influx of this element from the magma into the xenolith as an explanation for the abundance of sanidine in the core. On the contrary, it suggests that sanidine can be considered as another residual mineral that was presumably present in excess of other granitic components, assuming that initial melting was of the eutectic type. Nevertheless, potassium must have been mobile during the peak of metamorphism in view of the textural evidence for extensive late (re) crystallization of the sanidine at the cost of various other minerals in pelitic xenoliths from Mt. Amiata (cf. Van Bergen, 1983). Although microperthitic K-feldspars are seen to have been replaced in some samples by unexsolved sanidine, it is probable that muscovite was a major constituent of the parent rock and was thus largely responsible for the general K- and Al-rich chemistry of the xenoliths. Sanidine-rich aluminous xenoliths which occur in phonolitic to trachytic rocks from the Wehr volcano, East Eifel, show comparable characteristics and are likewise thought to originate from muscovite-bearing basement rock (Woerner et al., 1982).

The above points indicate an advanced stage of metamorphic evolution for sample MA 15.14 and for the majority of aluminous xenoliths of Mt. Amiata in general. On the other hand there is little evidence as to the average bulk composition of the total partial melt. Two extreme situations may be envisaged. First, the brown glass zone represents all extracted melt, and second, it is only the final most mafic melt following removal of previous more acid batches that were formed in the contact aureole and during the early stages of subsequent residence in the magma. The former alternative would imply a relatively low degree of melting (note the small proportion of brown glass zone) and consequently only a minor chemical modification of the parent rock. This could have had an approximate composition somewhere between that of the core (plus some Ca to account for the plagioclase zone) and that of the brown glass zone (cf. table 5), which is not dissimilar to certain mafic metapelites (cf. Leake and Skirrow, 1960; Barker, 1964).

If the second alternative is correct, the parent rock had a composition more closely approaching that of average metapelites (cf. Mehnert, 1969). Initial melting of such rocks should yield a liquid with composition close to granitic minimum melts (Winkler, 1974) until one of the original mineral components disappears. In the case of the xenoliths this stage may have been reached early, probably already in the contact aureole prior to its disruption. Quartz consuming reactions that are common during high-grade progressive metamorphism of pelites would have undoubtedly diminished or even exhausted the amount of free quartz. These reactions cannot be evaluated in detail, but an important one must have been muscovite + quartz =  $\text{Al}_2\text{SiO}_5$  + K-feldspar, or related more complex reactions eventually including some that produce a liquid (cf. Thompson, 1983). Subsequent stages, governed by melt-forming reactions involving biotite, cordierite, sillimanite, plagioclase, etc., then resulted in the evolution of the liquid composition towards that of the brown glass zone. This second possibility thus implies progressive changes of liquid composition, and it is interesting to note that Woerner et al. (1982) on the basis of whole rock chemical data suggest a similar mechanism for the suite of aluminous xenoliths from the Wehr volcanics.

From mass-balance model calculations by MacRae and Nesbitt (1980) it appears that even after extraction of some 40% melt from an average shale, quartz will be the major normative component in the restite. Although their approach is not strictly applicable to the problem at hand, as they consider liquids with granitic minimum melt compositions, it serves to emphasize that extensive melting of an average metapelite would be required to produce strongly silica-undersaturated restite compositions comparable to those of the xenoliths. In fact, if more mafic liquids are taken into account, melting should have occurred in quantities that are felt to be unrealistic, particularly as textural data provide no evidence for such extensive melting. For example, in many spinel-rich xenoliths microfolds, indicated by graphite flakes, are preserved although they may be less distinct in the most transformed samples. These structures are seen to be readily disturbed in the presence of liquid.

From these considerations we favour the conclusion that the spinel-rich xenoliths were derived from parental rocks that were less siliceous than average pelites and likely represent predominantly quartz-poor plagioclase bearing muscovite-biotite mica-schists. As suggested elsewhere (Van Bergen, 1983), the so-called Tuscan Crystalline is a plausible source. This pre-Mesozoic Supergroup, known mainly from deep-drilling in Tuscany consists of regionally metamorphosed sedimentary rocks of which mica-schists form a substantial part (Bagnoli et al., 1979).

#### Mineral-liquid disequilibrium

Perhaps the best example of incompatibility of certain restite minerals in the xenoliths with surrounding liquid is illustrated by the formation of An-rich plagioclase at the cost of spinel. The development of plagioclase zones is obviously due to the instability of spinel in presence of the siliceous rhyodacite liquid and, because a plagioclase zone partially separated the core from the brown glass zone in MA 15.14, spinel is apparently also incompatible with the residual liquid in the latter zone. It was probably stable in presence of the original partial melt, as plagioclase did not act as a barrier against extraction of the

melt. The relatively low An-content of plagioclase in the core and its increase towards the plagioclase zone thus resulted from the availability of Al rather than from an increasing degree of partial fusion. The replacement of spinel by plagioclase also occurred along the margins of spinel-plagioclase pseudomorphs after andalusite, as observed in the cores of many other xenoliths.

#### Diffusive interaction with the magma

Experimental studies have demonstrated that diffusion of elements across the interface of two chemically contrasting liquids is an effective process to produce compositional modifications on either side (Yoder, 1973; Sato, 1974; Alibert and Carron, 1980; Watson, 1982). Given enough time, it is to be expected that diffusion in the liquid state plays a role during interaction of xenoliths/wall-rock and magma (especially basaltic magma that has sufficient heat to induce partial melting), but there are only a few papers (e.g. Sato, 1974; Maury and Bizouard, 1974) that describe natural examples of this kind of interaction on a detailed scale. Our observations of sample MA 15.14 suggest that interdiffusion to a certain extent affected the directly adjacent siliceous liquid, as well as the melt formed in and extracted from the xenolith.

The mineralogy of the phenocrysts and the assumed composition of the colourless glass in the cpx zone indicate that it represents a thin envelope of lava, which must have been contaminated in view of the compositional difference with the enclosing rhyodacite. From the fact that the phenocrysts in this zone are less developed than those in the adjacent lava, it may be deduced that contamination started at an intermediate stage of evolution and that it imposed conditions that caused interruption and suppression of crystallization. Influx of water was most likely responsible, because evidence for originally high volatile contents is provided by the abundance of vesicles in this zone, whereas the normal rhyodacite is virtually vesicle-free and was probably under-saturated with H<sub>2</sub>O. It was thus capable of absorbing water supplied by external sources. This lowering of the liquidus temperature allowed the envelope to become relatively impoverished in Si, Na and K, and enriched

in Fe, Mg and Ti. The delay of crystallization and the chemical modification of the liquid resulted in the late-stage assemblage of abundant, fine-grained clinopyroxene, biotite, sanidine and also Fe-Ti oxide, maybe partly during quenching. Because neither the texturally well-defined boundary between the cpx and brown glass zone, nor the chemical trends shown in fig. 7 support mechanical mixing, we conclude that the lava was selectively contaminated by diffusive exchange where it was in immediate contact with partial melt from the xenolith. The amount of time required for this slow process to become effective was at least that required for the phenocrysts in the magmachamber to reach their ultimate dimensions. That the inferred liquids could coexist during this period was probably due to major differences in viscosity and density rather than chemical immiscibility as postulated for acid xenoliths in alkali basalt from the Massif Central (Maury et al., 1978).

If interdiffusion was important then, by implication, chemical gradients should exist in the brown glass zone. However, no systematic variations in glass compositions were found along microprobe traverses from the cpx zone inward. This suggests that any gradients were obliterated by the crystallization of orthopyroxene, biotite and plagioclase and is in agreement with the assumption that these phases formed as 'phenocrysts'. In fact, the spatial distribution of biotites (concentrated more towards the plagioclase zone) and pyroxene (more towards the cpx zone) may reflect original gradients in Al/Si ratio and/or volatile content, while the occasionally apparent reaction relation of these minerals suggests a gradual change in chemical conditions. On the other hand, the slightly decreasing An-content of plagioclase towards the plagioclase zone does not correspond with such a gradient in Al/Si ratio and probably reflects a depletion of the liquid in Ca, because this element was required to form the An-rich plagioclase in that zone.

#### Possible evidence for contamination

The development and preservation of reaction zones as described here, required sufficient time for extensive interaction between lava and xenolith and no disturbing differential movements along the contacts

until eruption and cooling. That such conditions are only rarely met in a convecting and erupting magma may explain the absence of the brown glass and cpx zone around many of the Mt. Amiata xenoliths and the lack of comparable examples in the literature. Maury and co-workers (1974, 1978), for example, give a detailed description of magma-xenolith relationships from various rock-types which display several features compatible with our observations, but they also noted the absence of reactions around aluminous xenoliths in siliceous lavas, which are, however, considered to be restites of partial fusion. Although, as their work suggests, liquid immiscibility could be a control in the formation of reaction zones, it should be borne in mind that the preservation of such zones requires seemingly rare conditions. In any case, information about the nature of contamination processes can probably be rarely obtained from observations of small-scale lava/xenolith interaction. Given the results of the present study, possible evidence for contamination of the Mt. Amiata lavas, which should be consistent with the evolution of the xenoliths, is briefly examined.

The Mt. Amiata rhyodacites are the products of crustal anatexis (e.g., Dupuy, 1970), and hence subsequent interaction with melts that are close to granitic minimum melt compositions would hardly influence the major element chemistry. If more mafic material was added, such as that produced by partial fusion of the aluminous xenoliths, contamination may become detectible in the major element chemistry. In order to evaluate the possible extent of contamination, the chemical characteristics of the lavas that contain metasedimentary xenoliths may be compared with those that are virtually devoid of these fragments. Indeed, small but consistent compositional differences indicate that the former are, on average, slightly poorer in Si and richer in Mg, Fe and Ca (cf. Mazzuoli and Pratesi, 1963; Dupuy, 1970; Van Bergen et al., 1983), which would support a model of contamination by incorporation of a less siliceous melt from the aluminous xenoliths. However, the same lavas in which these xenoliths occur also contain a suite of igneous inclusions that were produced by injection of mafic magma into the magmachamber (Van Bergen et al., 1983). As the composition of these lavas fits in a mixing trend defined by the most mafic inclusions and the most acid

rhyodacites, magma mixing may have been more important in producing the chemical differences noted above than assimilation. Other possible lines of evidence for contamination are also equivocal. Clinopyroxene microphenocrysts, which are too magnesian to be in equilibrium with the orthopyroxene phenocrysts in the lavas may have formed in cpx-rich reaction zones around the metasedimentary xenoliths, which were subsequently disrupted, but magma mixing as mode of origin is also feasible. The similarity of certain mineral aggregates to the assemblages occurring in the brown glass zone of MA 15.14 and in other samples is not sufficient proof that they originated from the break-up of metasedimentary xenoliths and their coronas (see Flood et al., 1977, for other possible interpretations). Present data thus indicate that both assimilation and magma mixing played a role in the evolution of Mt. Amiata lavas, but obviously further detailed study is required to fully evaluate the relative importance of each process. It is, nevertheless, clear that special volcanological conditions were highly favourable for assimilation. The abundance of metasedimentary xenoliths and their association with hybrid igneous inclusions indicate that an invasion of hot mafic magma into the magmachamber triggered or intensified convection which led to disruption of the contact aureole, and provided additional heat to facilitate assimilation. The case of Mt. Amiata thus illustrates that assimilation may be most effective when occurring in combination with magma mixing.

#### CONCLUSIONS

Aluminous xenoliths, probably originating from quartz-poor micaceous parent rocks, sometimes show complex concentric zoning patterns resulting from reaction with the enclosing siliceous magma of Mt. Amiata. The specific mineralogy and chemistry of these zones are inconsistent with a gradual chemical transition between lava and xenolith core and reflect the operation of several processes during interaction. With advanced partial melting of the xenoliths, liquids less acid than that of the magma formed, probably because the solidus was lowered by release of volatiles from hydrous minerals. Separation of the melt caused enrich-

ment of the restite in Al, Fe and K, while residual ferromagnesian minerals (spinel, Fe- and Ti-rich biotite, sometimes orthopyroxene or olivine) and those that were involved in melting (more magnesian biotite, eventually cordierite) are compatible with the melt having a higher Mg-number than the restite. In those cases where the melt was not removed from the xenolith or accumulated around it, diffusion gradients were set up at the contacts with the adjacent envelope of 'rhydoacite' liquid, which led to impoverishment of the latter in Si, Na and K and enrichment in H<sub>2</sub>O (and possibly other volatiles), Fe, Mg and Ti. The instability of spinel in the presence of a siliceous liquid resulted in crystallization of An-rich plagioclase and a concomitant positive anomaly of Ca along the magma-xenolith contacts. Fluid inclusions of CO<sub>2</sub> that was produced by oxidation of graphite, were trapped in this plagioclase and in 'phenocrysts' crystallizing from the chemically modified partial melts, probably during cooling.

Although the present data are inadequate to quantitatively estimate the amount of contamination, due to the simultaneous operation of magma mixing, it was probably small, at least with respect to major elements. This example from Mt. Amiata suggests, however, that relatively dry acid magma may potentially become more mafic by interaction with partially melted hydrous country rocks, and it also shows that, unless assimilation is complete, interaction will lead to selective contamination (cf. Watson, 1982). Injection of mafic magma into evolving magmachambers may provide mechanical and thermal conditions favourable for assimilation processes.

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## CHAPTER IV

### MINETTE INCLUSIONS IN THE RHYODACITIC LAVAS OF MT. AMIATA (CENTRAL ITALY): MINERALOGICAL AND CHEMICAL EVIDENCE OF MIXING BETWEEN TUSCAN AND ROMAN TYPE MAGMAS

Manfred J. van Bergen, Claudio Ghezzo and Carlo Alberto Ricci

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#### ABSTRACT

Major-element, trace-element and mineralogical data are reported for a series of mafic inclusions occurring in the rhyodacitic lavas of Mt. Amiata (southern Tuscany, Italy), a volcanic complex belonging to the Tuscan Magmatic Province. The inclusions form, together with some subordinate mafic latitic lavas and the host rock rhyodacites, a continuous series, which varies from olivine and minor nepheline normative to quartz, hypersthene and corundum normative rock-types over a range of 48-67% SiO<sub>2</sub>. All of the rocks are characterized by high contents of potassium (5-6% K<sub>2</sub>O) and many trace elements, particularly the incompatible elements. Following straight-line correlation trends, Al, Fe, Mg, Ca, Ti, P, Sr and Ba decrease with increasing SiO<sub>2</sub>, whereas Na and Li increase, and K, Rb, Zr, La, Ce, Nb and Y remain virtually constant. The primary mineral assemblage of the inclusions consists of diopsidic pyroxene, forsteritic olivine and mica, and is representative for minettes. Xenocrysts of plagioclase, sanidine, orthopyroxene, clinopyroxene, biotite, ilmenite and olivine occur in increasing amounts in the more siliceous samples. The composition of these xenocrysts is identical to that of the phenocryst assemblage in the rhyodacites. The latitic lavas are rich in xenocrysts and differ from the minettes mainly by the absence of primary mica. The data strongly suggest a magma mixing origin for the minettes, latites and possibly part of the rhyodacites. Injection of mafic magma into a siliceous magma chamber has resulted in the formation of hybrid inclusions and a latitic magma that could only reach the surface after eruption of the voluminous rhyodacitic lavas. The rhyodacites which erupted early and are slightly richer in SiO<sub>2</sub> than most of the other rhyodacites are considered to represent the acid mixing component, whereas the mafic end-member has close affinities to the potassic alkaline lavas of the adjacent Roman Province. The inclusions have the modal composition of a minette and this implies that volatiles were important constituents of the hybrid magmas. This may be attributed to the primary character of the Roman-type end-member involved, or explained by a process of selective enrichment operating

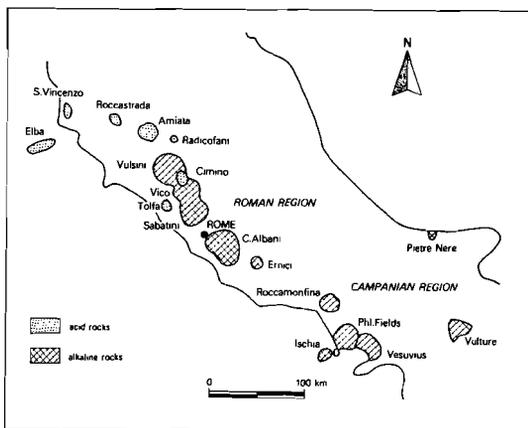
during mixing. Although upper mantle derived Roman magmas have interacted with Tuscan magmas of crustal anatectic origin at Mt. Amiata and probably other volcanic centres in central Italy, the specific chemistry of lavas in both provinces cannot be explained by simple mixing of these magmas in shallow chambers.

## INTRODUCTION

The Pliocene-Quaternary magmatic rocks of Central Italy are classically divided into two provinces. In Tuscany and northern Latium predominantly acid volcanic and intrusive rocks represent the Tuscan Magmatic Province, whereas more extensive potassic alkaline volcanic centres, occurring mainly along the western side of the Apennine fold belt from Latium to the Neapolitan area, form the Roman Magmatic Province (Fig.1). North of Rome several "Tuscan" occurrences are situated in or near the Roman Province indicating a spatial overlap between both provinces.

Since a crustal anatectic origin was proposed for the magmas of the Tuscan Province (e.g. Marinelli, 1967; Barberi et al., 1971), accumulating chemical and isotopic data have led to a general acceptance of this view (e.g. Dupuy and Allègre, 1972; Ferrara et al., 1975, 1976; Taylor and Turi, 1976), which contrasts with the current lively debate concerning the origin of the Roman magmas. In order to explain their high contents of elements like K, Rb, Sr, Ba, REE, Th, as well as their high ratios of  $^{18}\text{O}/^{16}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio several hypotheses have been put forward, which in essence can be reduced to two major groups: one stresses the importance of a chemically and isotopically anomalous upper mantle, the other lays more emphasis on interaction with the crust. A regional N-S variation in isotope compositions (O, Sr, Nd, Pb) exists, which in the area of overlap with the Tuscan Province may reflect either lateral heterogeneity in the upper mantle, or (increasing) assimilation of crustal material (cf. Hurley et al., 1966; Vollmer, 1976, 1977; Cox et al., 1976; Taylor and Turi, 1976; Turi and Taylor, 1976; Hawkesworth and Vollmer, 1979; Vollmer and Hawkesworth, 1980).

Support for contamination in the area north of Rome is largely based on isotope data and relatively few other studies have recently contributed to the argument (e.g. Cundari, 1979; Varekamp, 1979). As a conse-



*Fig. 1. The acid Tuscan Magmatic Province and the alkaline Roman Magmatic Province.*

quence, indications regarding the nature of the possible crustal contaminant are scarce.

In this paper chemical and mineralogical data will be presented on a series of minette inclusions sampled in the rhyodacitic lavas of Mt. Amiata, a Tuscan complex situated about 30 km north of Vulturno, the northernmost Roman centre (Fig.1). Evidence will be provided that the inclusions represent hybrid magmas, and the results will be used to discuss magma mixing as a mode of interaction between Roman and Tuscan type magmas.

#### GEOLOGICAL SETTING

In the Tuscan Magmatic Province, which is represented by a number of scattered plutonic and volcanic centres in Tuscany and northern Latium, acid rock types prevail (Marinelli, 1967; Barberi et al., 1971). Granitic rocks outcrop on the mainland as well as on several islands in the Tyrrhenian Sea, the most important occurrence being the Mt. Capanne granodiorite of Elba. Near San Vincenzo, Roccastrada and Tolfa relatively small volcanic edifices were built by rhyolitic to rhyodacitic lavas, whereas Mt. Amiata and Mt. Cimini are larger and more complex volcanoes. These complexes are mainly composed of rhyodacite lavas and ignimbrites but they also contain smaller volumes of latitic lavas, which together

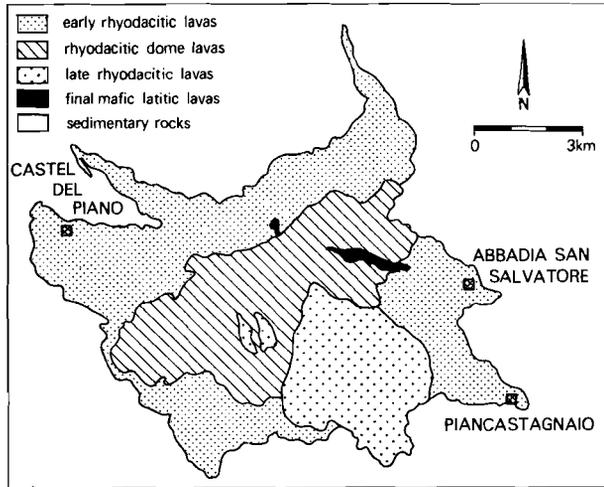


Fig. 2. Geological sketch map of Mt. Amiata volcanic complex (after Mazzuoli and Pratesi, 1963).

with a trachybasaltic volcanic neck near Radicofani and a few dikes and laccoliths are subordinate more mafic rocks in the Tuscan Province.

Magmatism has been active since the Pliocene. K/Ar ages range from 7 m.y. for Mt. Capanne to 0.43 m.y. for Mt. Amiata, and display a decreasing trend from west to east (see review in Barberi et al., 1971). According to recent K/Ar and fission track data (Bigazzi et al., 1981) Mt. Amiata is still younger (0.18 - 0.29 m.y.), and the high geothermal activity in the area demonstrates that magmatic processes have not yet ceased. The southern centres of Mt. Cimino and Tolfa are respectively about 1 and 2.3 m.y. old.

Dating of lavas from Vulsini has yielded ages between 0.04 and 0.88 m.y. (Nicoletti et al., 1979, 1981; Varekamp, 1980), which indicates that Roman and late Tuscan magmatic events are coeval.

In the volcanological evolution of Mt. Amiata (Fig. 2) several stages can be recognized (Mazzuoli and Pratesi, 1963). The earliest rhyodacitic products, now exposed in the peripheral parts, were originally described as rheoignimbrites, but are presently considered as perlitic lavas (Barberi et al., 1971; Marinelli, 1975). Their emplacement was followed by that of more viscous rhyodacitic lavas, giving rise to a number of domes in the central part. They were, in turn, partly covered by some

minor lavas identical to the early rhyodacites, and by two small mafic latitic flows which mark the end of the volcanic activity.

The Mt. Amiata volcanics are characterized by the ubiquitous presence of a variety of rock inclusions, comprising the mafic magmatic inclusions to be described in this paper, as well as polymetamorphic sediments, interpreted as wall rock fragments of the original magmchamber (van Bergen, 1983).

#### PETROGRAPHY AND MINERALOGY

##### Rhyodacitic host lavas

Petrographical data of the host rock rhyodacites have been presented by Rodolico (1935), Mazzuoli and Pratesi (1962, 1963), Dupuy (1970) and Balducci and Leoni (1981). The lavas exhibit little chemical and mineralogical variation, but textures vary according to the volcanological conditions. The dome lavas contain entire phenocrysts and have a usually microcrystalline groundmass, comprising feldspars and clinopyroxene, whereas the other lavas are characterized by intensely fractured and broken phenocrysts set in a mostly perlitic glassy groundmass.

Plagioclase and sanidine are dominant phenocrystal phases, while biotite, two pyroxenes and scarce quartz also occur. Fe-Ti oxide, apatite and zircon are accessory minerals. Sanidine, which in the dome lavas has developed as megacrysts reaching sizes of 3-4 cms, may include the other phenocrysts.

Various combinations of the phenocrystal minerals (except sanidine and quartz) appear in aggregate-like clusters, in some of which we have also observed ilmenite and a fayalitic olivine. Their origin is not clear, but it may be noted that similar assemblages occur in the metasedimentary xenoliths (van Bergen, 1983). Disaggregation and reaction of these xenoliths have indeed resulted in the presence of (clusters of) xenocrysts (e.g. plagioclase containing relicts of green spinel,  $\pm$  opx), but it is as yet uncertain if this mode of origin applies to all of the clusters. Other hypotheses for such aggregates, often found in calc-alkaline rocks, have been discussed by Flood et al. (1977).

## Igneous inclusions

The mafic magmatic inclusions occur in all of the rhyodacitic rocks, but are most numerous in the dome lavas. They have a rounded, subspherical shape and are usually up to a few dm in diameter, although sizes of more than 1 meter have been reported (Barberi and Innocenti, 1967). Contacts with the host rocks are often finely contorted (cf. Fig. 3a). The inclusions are normally porphyric and virtually holocrystalline, and contain globular vesicles. Gradational transitions towards equigranular, more coarse grained types are subordinate. Sometimes small metasedimentary xenoliths, similar to those in the rhyodacites, are present.

Mineralogically the inclusions are dominated by clinopyroxene, ranging in size from large phenocrysts to tiny groundmass crystals. Mica is the second most abundant mafic phase. It varies in grain size and it often has an elongate shape that gives these rocks a distinctive appearance. It crystallized relatively late and its presence is sometimes restricted to the groundmass. Olivine phenocrysts are rare and mainly confined to some of the more mafic samples. One of these samples (MA 26) is exceptional inasmuch as it also contains olivine in the groundmass. Such primary mica is rare.

In addition an assemblage of xenocrystal minerals can be recognized. They occur separately as well as in clusters identical to those in the rhyodacitic host, and their amount increases with increasing  $\text{SiO}_2$ -content of the inclusions. Plagioclase and orthopyroxene are the most frequent, followed by biotite, sanidine and ilmenite. Clinopyroxene and olivine xenocrysts are rare. As will be shown below, all of these minerals are compositionally similar to those in the rhyodacites, and this observation will be used as evidence in support of a magma mixing origin for both the inclusions and the latitic lavas.

Although bimodal mixing may result in an assemblage of xenocrysts supplied by both endmembers, we restrict the term 'xenocryst' to the phases derived from the rhyodacites, because of their more obvious textural and chemical disequilibrium compared with that of the mafic endmember phases (viz. forsteritic olivine and probably part of the diopsidic pyroxene).

Sanidine, clinopyroxene, biotite and sometimes opaques are the groundmass constituents accompanied by plagioclase in the more siliceous inclusions. If a small amount of glass is present, it is preferentially concentrated near vesicles and along rims of sanidine xenocrysts. It also occurs as inclusions in many of the xenocrystal minerals.

In view of the mafic character of the primary phenocrysts, the abundance of biotite, and sanidine as dominating groundmass phase, the inclusions are minettes (Velde, 1971; Wimmenauer, 1973; Rock, 1977). It should, however, be pointed out that, in comparison with other minettes, they are rich in clinopyroxene (cf. Velde, 1971) and have a relatively high content of  $Al_2O_3$  (cf. Métais and Chayes, 1963), see below. In earlier work the Amiata inclusions have sometimes been called 'selagites', because of the textural similarity to the potassic laccolithic bodies in northern Tuscany to which this term has been applied (Washington, 1900). Following Barberi and Innocenti (1967), who already noticed some major chemical differences, we prefer not to use it for the inclusions.

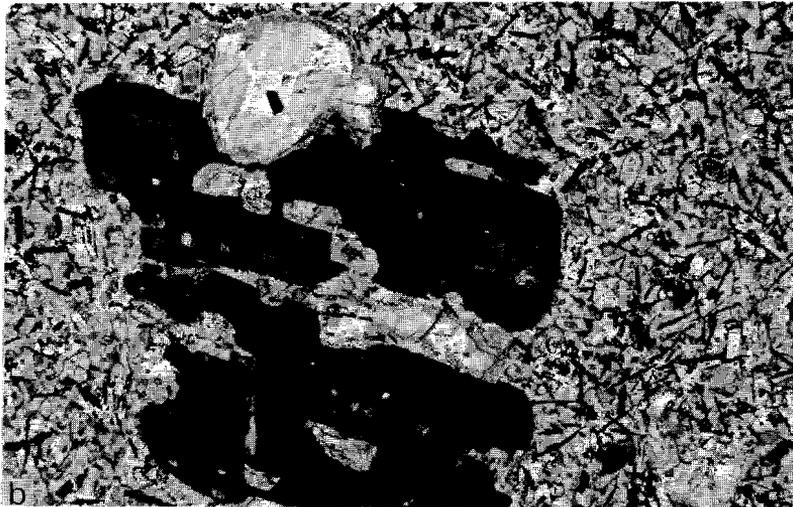
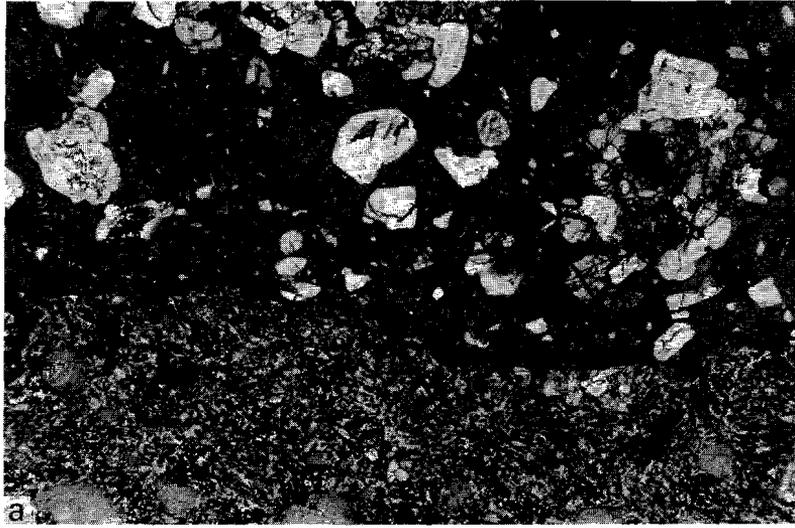
#### Final mafic latitic lavas

The mafic latitic lavas are petrographically comparable to the igneous inclusions. They are porphyric and highly vesicular, and contain abundant clinopyroxene, few large olivines and many xenocrysts. Primary biotite, however, is absent and instead olivine appears in the microcrystalline groundmass in addition to sanidine, plagioclase and clinopyroxene. Plagioclase also occurs as microphenocrysts.

Microprobe analyses were made on six samples of inclusions, two of rhyodacites and one of each latitic lava flow. For comparison the results are plotted in Figs. 4-6, and representative analyses are given in Tables 1-4.

#### Clinopyroxene

In the inclusions clinopyroxenes are euhedral and usually colourless, although greenish rims and groundmass crystals may be observed. Many samples contain skeletal crystals having cores with sanidine and often



*Fig. 3 (a) Irregular contact between minette inclusion (lower part) and perlitic rhyodacitic host lava (upper part). Note globular vesicles (grey) in the inclusion, broken phenocrysts and pyroxene-plagioclase cluster in the lava. Long dimension: 1.15 cm. (b) Heavily corroded biotite xenocryst, associated with plagioclase (note turbid marginal zone) in minette inclu-*



*sion containing clinopyroxene, elongated mica and sanidine. Long dimension: 0.46 cm. (c) Plagioclase xenocryst showing a dark turbid marginal zone and a thin limpid outer rim (crossed polars). Long dimension: 0.46 cm. (d) Rounded sanidine xenocrysts partially enclosing microxenolithic cluster of pyroxene, plagioclase and biotite (lower right). Long dimension: 1.15 cm.*

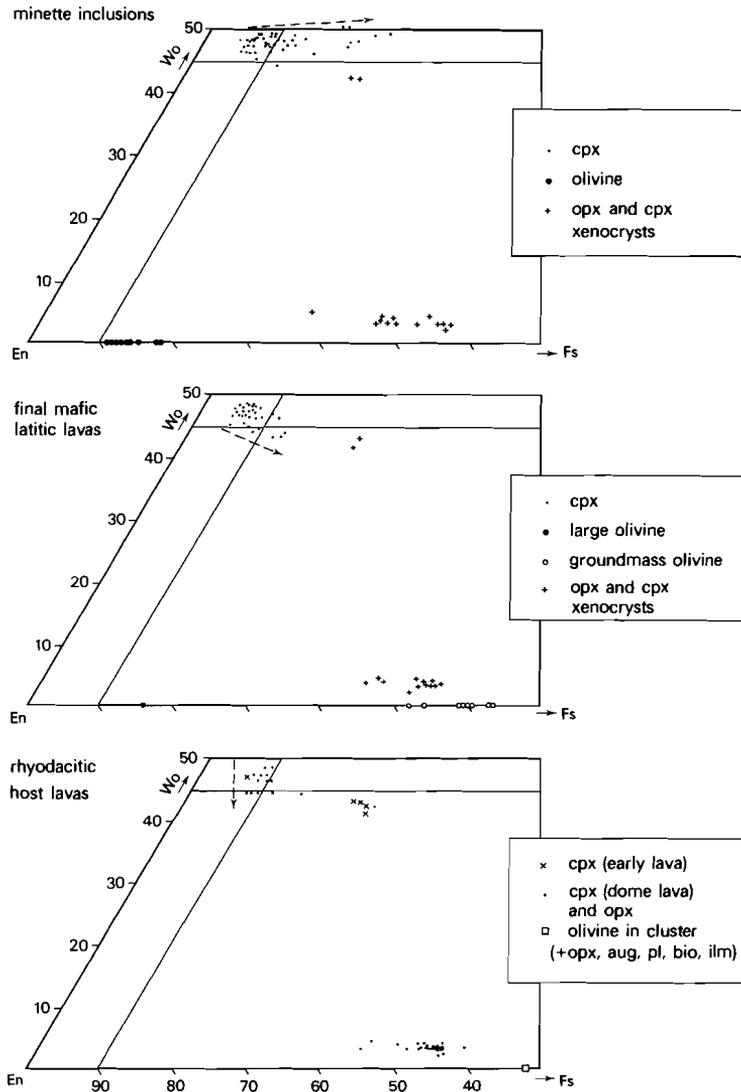


Fig. 4. Ca-Mg-Fe diagrams showing compositions of pyroxenes and olivines in minette inclusions, final mafic latitic lavas and rhyodacitic host lavas. Arrows indicate trends of core-rim and phenocryst-groundmass zoning.

a small biotite, probably crystallized from trapped liquid. The pyroxenes show oscillatory concentric zoning and sometimes sector zoning, and they may be twinned according to (100). Compositions plot in the diopside and salite fields of the conventional Ca-Mg-Fe diagram, and display a general Fe- and Ca-enrichment trend (Fig.4). Diopside (micro-)phenocrysts are ubiquitous and their presence appears to be independent of the Mg/Fe ratio of the rock. Their rims may be salitic and are compositionally similar to the groundmass crystals and the rims jacketing orthopyroxenes. Compared with the cores, rims and groundmass clinopyroxenes are also enriched in Al and Ti.

Al contents are always more than sufficient to fill Si deficiencies in the Z-sites, and in many cases the diopsides have even about enough  $Al^{VI}$  to balance  $Al^{IV}$ . The results suggest that Ca-tschermaks molecule ( $CaAl_2SiO_6$ ) is the main non-quadrilateral component, that is also known to be significant in pyroxenes from lavas of the Roman Province (e.g. Cundari, 1975; Thompson, 1977; Barton et al., 1982). The contents of additional components such as  $CaFe^{3+}AlSiO_6$ ,  $CaTiAl_2O_6$  and  $NaFe^{3+}Si_2O_6$  are relatively low and tend to increase in the salites.

Diopside is also abundant in the mafic latites, whereas it is subordinate in the dome lava rhyodacites and rare in the early rhyodacitic lavas. Compositions of late stage pyroxenes are less different from diopside than in the inclusions. They trend towards the augite field in the latites and more towards endiopside in the rhyodacites. This shift away from the diopside-hedenbergite join coincides with the appearance of an increasing amount of primary plagioclase.

Large crystals of augite have been found in all of the rock types. When occurring in the clusters mentioned above, it is sometimes associated with orthopyroxene. In the inclusions and latites the augites are clearly xenocrysts, whereas with respect to the rhyodacites it can only be stated that their origin must be related to the other cluster-forming minerals.

#### Orthopyroxene

The orthopyroxene has similar characteristics in all of the rock types. It forms large crystals that often contain small euhedral apatites and are sometimes associated with ilmenite. In the inclusions, latites and

	MA 26 core	MA 26 rim	MA 26 grndm	MA 1.15 core	MA 1.15 rim	MA 1.15 rim of opx	MA 1.15 grndm	MA 1.15 xenocr	MA 1.3 core	MA 1.3 rim	MA 1.3 grndm	MA 45 phenocr	MA 45 rim of opx	MA 27 phenocr	MA 27 microph	MA 27 phenocr <sup>2)</sup>
SiO <sub>2</sub>	52.50	50.21	49.64	52.61	51.04	51.10	51.15	51.71	51.56	46.98	50.11	52.37	51.24	49.95	52.91	50.58
Al <sub>2</sub> O <sub>3</sub>	2.56	5.16	5.20	3.70	4.90	4.16	6.31	1.94	4.76	6.29	5.72	3.90	2.91	5.47	1.54	0.67
TiO <sub>2</sub>	0.27	1.23	0.75	0.42	0.71	0.91	0.54	0.43	0.65	0.69	0.83	0.63	0.68	0.55	0.41	0.23
FeO	2.91	5.23	6.58	3.95	5.87	6.78	5.34	13.84	4.38	13.94	5.43	4.02	8.58	5.23	4.86	16.02
MnO	0.05	0.13	0.14	0.11	0.18	0.21	0.10	0.39	0.08	0.36	0.11	0.19	0.35	0.00	0.15	0.35
MgO	16.44	14.24	13.64	16.33	14.50	14.05	14.48	12.07	14.92	8.26	14.71	15.79	15.04	14.99	17.12	10.82
CaO	23.26	22.68	22.09	22.28	22.05	21.56	21.35	19.59	22.78	21.44	22.26	22.90	21.24	22.88	21.68	19.85
Na <sub>2</sub> O	0.15	0.23	0.27	0.26	0.31	0.24	0.25	0.24	0.19	0.28	0.25	0.00	0.32	0.39	0.00	0.39
total	98.14	99.11	98.31	99.66	99.56	99.01	99.52	100.21	99.32	98.24	99.41	100.10 <sup>1)</sup>	100.36	99.46	98.67	98.91
Si	1.944	1.864	1.867	1.921	1.885	1.903	1.876	1.956	1.897	1.834	1.853	1.909	1.902	1.848	1.957	1.968
Al <sup>IV</sup>	0.056	0.136	0.133	0.079	0.115	0.097	0.124	0.044	0.103	0.166	0.147	0.091	0.098	0.152	0.043	0.031
Al <sup>VI</sup>	0.056	0.090	0.098	0.080	0.098	0.086	0.149	0.042	0.103	0.123	0.102	0.077	0.029	0.086	0.024	-
Ti	0.008	0.034	0.021	0.012	0.020	0.025	0.015	0.012	0.018	0.020	0.023	0.017	0.019	0.015	0.011	0.007
Fe	0.090	0.162	0.207	0.121	0.181	0.211	0.164	0.438	0.135	0.455	0.168	0.123	0.266	0.161	0.150	0.519
Mn	0.002	0.004	0.004	0.003	0.006	0.007	0.003	0.012	0.002	0.012	0.003	0.006	0.011	0.000	0.005	0.011
Mg	0.907	0.788	0.765	0.889	0.798	0.780	0.792	0.680	0.818	0.481	0.811	0.858	0.832	0.833	0.950	0.631
Ca	0.923	0.902	0.890	0.872	0.873	0.861	0.839	0.794	0.898	0.897	0.882	0.895	0.845	0.908	0.859	0.827
Na	0.011	0.017	0.020	0.018	0.022	0.017	0.018	0.018	0.014	0.021	0.018	0.000	0.023	0.028	0.000	0.030
Σ	4.00	4.00	4.01	4.00	4.00	3.99	3.98	4.00	3.99	4.01	4.01	3.99 <sup>1)</sup>	4.03	4.03	4.00	4.02
Mg/(Mg+Fe)	0.91	0.83	0.79	0.88	0.82	0.79	0.83	0.61	0.86	0.51	0.83	0.87	0.76	0.84	0.86	0.55

1) contains 0.30% Cr<sub>2</sub>O<sub>3</sub> and 0.009 a.f.u. Cr

2) in cluster with cpx, plag, bio, oliv, ilm

Table 1. Representative analyses of clinopyroxenes. MA 26-MA 1.3: inclusions; MA 45: final lava; MA 27: host lava. All iron taken as Fe<sup>2+</sup>. Numbers of cations based on 6 oxygens. Mineral analyses were carried out with a TPD electron microprobe using wavelength and energy dispersive techniques. Operating conditions were: acceleration potential 15 kV; sample current: 10-25 nA. Corrections for deadtime, background, atomic number, absorption and fluorescence were applied.

some dome lava samples orthopyroxenes are resorbed and overgrown by small rims of clinopyroxene.

The analyses show fairly high Fe contents. Except for one analyzed xenocryst from an inclusion, Mg/(Mg+ΣFe) ratios range between 0.40 and 0.55, while wollastonite contents do not exceed 5% (Fig.4), and Al<sub>2</sub>O<sub>3</sub> is low (between 1 and 2 weight %). Zoning within single crystals is insignificant. Pyroxenes in the clusters could not be clearly distinguished from other by their chemistry.

### Biotite

Two different groups of biotite can be recognized both texturally and chemically. Primary biotites in the inclusions are strongly elongated and xenomorphic, and have variable grainsizes. Mg/(Mg+ΣFe) ratios vary between 0.45 and 0.75 (from which it appears that part of the minette micas are

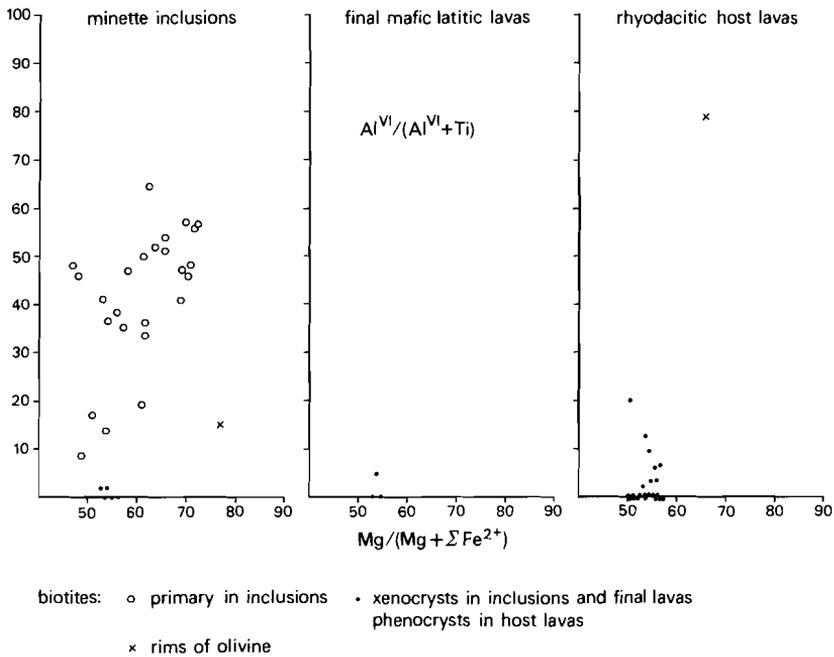


Fig. 5.  $Mg/(Mg+\Sigma Fe^{2+})$  vs.  $Al^{vi}/(Al^{vi}+Ti)$  plots of biotites (phlogopites) from minette inclusions, final mafic latitic lavas and rhyodacitic host lavas.

	MA 26	MA 31	MA 45	MA 45	MA 1
	xenocr	xenocr	xenocr	xenocr	phenocr
SiO <sub>2</sub>	49.57	49.99	50.83	49.95	50.48
Al <sub>2</sub> O <sub>3</sub>	1.61	1.01	1.20	1.30	0.72
TiO <sub>2</sub>	0.19	0.21	0.42	0.43	0.20
FeO	30.39	31.47	27.79	31.44	31.96
MnO	0.19	0.75	1.24	0.87	0.70
MgO	14.72	13.67	16.87	15.10	14.22
CaO	1.26	1.46	1.85	1.33	1.55
Na <sub>2</sub> O	0.10	0.00	0.00	0.00	0.00
total	98.03	98.56	100.20	100.42	99.83
Si	1.966	1.986	1.957	1.948	1.983
Al <sup>IV</sup>	0.034	0.014	0.043	0.052	0.017
Al <sup>VI</sup>	0.041	0.033	0.011	0.008	0.016
Ti	0.006	0.006	0.012	0.013	0.006
Fe	1.008	1.045	0.895	1.025	1.046
Mn	0.006	0.025	0.040	0.029	0.023
Mg	0.870	0.810	0.968	0.878	0.838
Ca	0.054	0.062	0.763	0.056	0.065
Na	0.008	0.000	0.000	0.000	0.000
Σ	3.99	3.98	4.00	4.01	3.99
Mg/(Mg+Fe)	0.46	0.44	0.52	0.46	0.44

Table 2. Representative analyses of orthopyroxenes. MA 26-MA 31: inclusions; MA 45: final lava; MA 1: host lava. All iron taken as Fe<sup>2+</sup>. Numbers of cations based on 6 oxygens.

actually phlogopites), and suggest dependence on the whole rock chemistry. A considerable range of this ratio can be found in a single sample, and large individual crystals may be chemically zoned. Tetrahedral Al varies between 2.34 and 2.73, and octahedral Al between 0.22 and 0.53 a.f.u. (based on 22 oxygens). TiO<sub>2</sub> contents are moderate (2.5 - 5.0 weight %). Crystals enclosed in clinopyroxene fall within a similar range of composition.

Biotites in the rhyodacites are normally large, dark coloured and often deformed. They also occur in the inclusions and latites as heavily resorbed xenocrysts (Fig.3b), and are chemically quite distinct from the first group (Fig.5) inasmuch as they are rich in TiO<sub>2</sub> (5.4 - 8.1 weight %), while Al is often not sufficient to fill Si deficiencies in the tetrahedrons. Mg/(Mg+ΣFe) ratios cover a narrower range: 0.50 - 0.60.

	MA 26 xenocr	MA 2.3 in cpx	MA 2.3	MA 1.15 rim of olivine	MA 1.15 in cpx	MA 1.15	MA 1.15 xenocr core	MA 1.15 xenocr rim	MA 1.3 in cpx	MA 1.3	MA 1 phenocr
SiO <sub>2</sub>	37.03	37.57	36.67	38.29	38.65	37.88	36.51	37.18	37.38	36.75	38.17
Al <sub>2</sub> O <sub>3</sub>	13.20	16.68	16.37	14.96	15.53	16.05	14.19	14.43	17.14	16.38	13.15
TiO <sub>2</sub>	5.88	3.30	2.67	2.52	3.40	4.30	8.05	7.48	2.54	3.61	5.48
FeO	17.36	13.85	10.96	10.69	11.97	15.69	17.09	18.11	14.26	20.09	17.03
MnO	0.06	0.12	0.06	0.13	0.11	0.11	0.11	0.14	0.16	0.15	0.18
MgO	11.54	14.07	16.16	20.29	15.32	11.93	10.66	9.68	13.41	10.24	12.21
CaO	0.14	0.85	0.38	0.39	1.12	0.31	0.43	0.29	0.71	0.17	0.00
Na <sub>2</sub> O	0.51	0.33	0.34	0.32	0.26	0.53	0.52	0.54	0.17	0.37	0.26
K <sub>2</sub> O	9.06	8.86	9.52	9.31	9.55	9.36	9.13	9.04	9.40	9.26	9.32
total	94.78	95.63	94.13	96.80	95.91	96.16	96.69	96.89	95.17	97.02	95.80
Si	5.640	5.543	5.579	5.521	5.656	5.615	5.453	5.549	5.563	5.519	5.727
Al <sup>IV</sup>	2.360	2.457	2.421	2.479	2.344	2.385	2.499	2.451	2.437	2.481	2.273
Al <sup>VI</sup>	0.011	0.443	0.437	0.047	0.334	0.419	-	0.087	0.569	0.418	0.049
Ti	0.674	0.366	0.307	0.273	0.374	0.479	0.905	0.840	0.284	0.408	0.617
Fe	2.211	1.709	1.357	1.289	1.465	1.946	2.135	2.260	1.775	2.523	2.129
Mn	0.008	0.016	0.008	0.015	0.014	0.014	0.014	0.018	0.020	0.020	0.023
Mg	2.621	3.094	3.569	4.361	3.342	2.638	2.374	2.153	2.975	2.291	2.747
Ca	0.023	0.134	0.061	0.060	0.176	0.049	0.069	0.047	0.113	0.027	0.000
Na	0.149	0.095	0.097	0.088	0.074	0.151	0.152	0.158	0.048	0.108	0.077
K	1.761	1.667	1.800	1.713	1.783	1.770	1.740	1.721	1.775	1.773	1.785
Z	8.00	8.00	8.00	8.00	8.00	8.00	7.95	8.00	8.00	8.00	8.00
XY	5.53	5.63	5.68	5.98	5.53	5.50	5.43	5.36	5.62	5.66	5.57
W	1.93	1.90	1.96	1.86	2.03	1.97	1.96	1.93	1.94	1.91	1.86
Mg/(Mg+Fe)	0.54	0.64	0.72	0.77	0.70	0.58	0.53	0.48	0.63	0.46	0.56

Table 3. Representative analyses of biotites/phlogopites. MA 26-MA 1.3: inclusions; MA 1: host lava. All iron taken as Fe<sup>2+</sup>. Numbers of cations based on 22 oxygens.

### Olivine

Forsteritic olivine phenocrysts (Fo<sub>82-90</sub>) are euhedral and only rarely rimmed by a phlogopitic mica. Although they mainly occur in the more mafic inclusions, some have been found in the more siliceous specimen and even in the latites. Groundmass olivines of the latites have compositions between Fo<sub>37</sub> and Fo<sub>48</sub>, while those of sample MA 26 are Fo<sub>82-89</sub>. Analyses of some large greenish olivines in a cluster from a rhyodacite show Fo<sub>32</sub>, which compares well with olivines from the metasedimentary xenoliths (van Bergen, 1983).

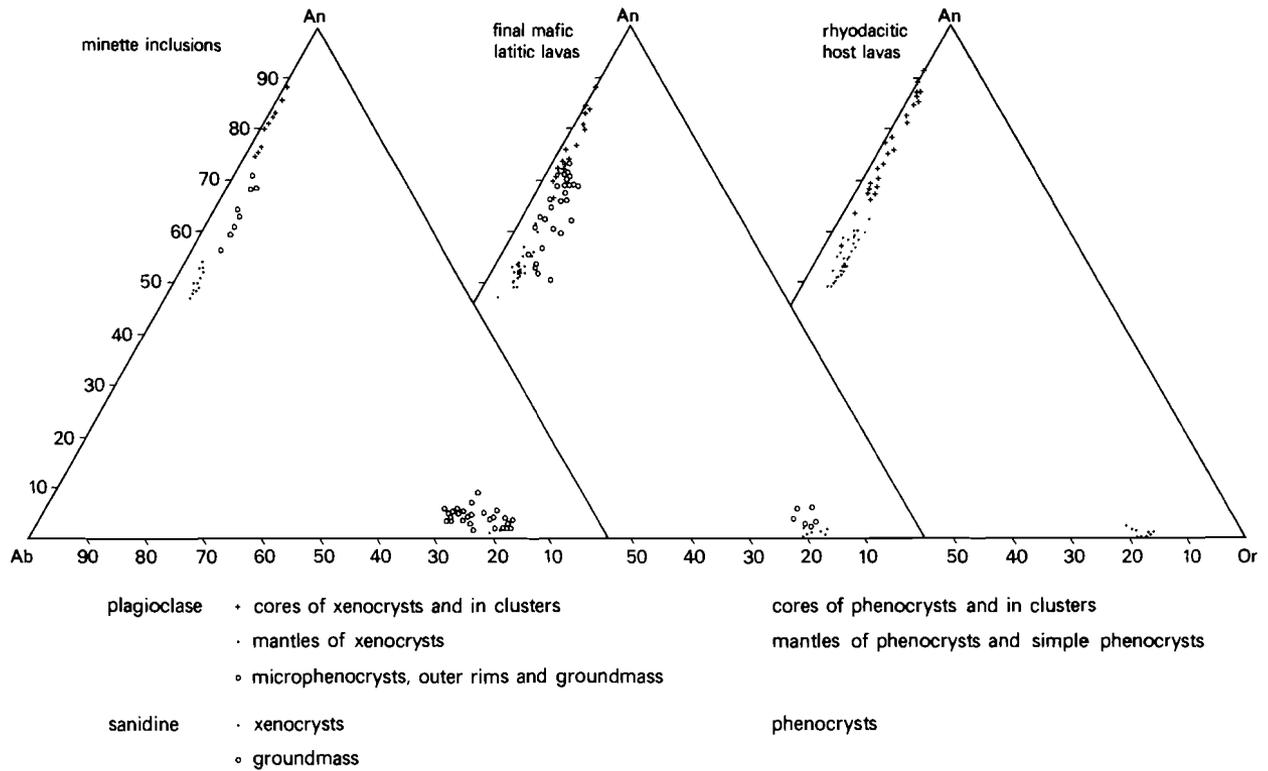


Fig. 6. Ab-An-Or diagrams showing compositions of plagioclase and sanidines. Text on the right applies to the host lavas.

## Feldspars

Compositions of partially analysed feldspars are plotted in Fig.6. Plagioclases appear to be complex. In the inclusions, latites and some dome lava samples they have a turbid resorbed marginal zone which is usually surrounded by a thin outer rim of calcic plagioclase (Fig. 3c) or - in the more mafic inclusions - sanidine. This texture points to a xenocrystal origin, and resembles that described by Eichelberger and Gooley (1977) and Hibbard (1981), and explained in terms of magma mixing.

Except for the resorbed zones and the calcic rims, the plagioclases in these rocks are identical to the common types in the rhyodacites. They are euhedral to subhedral and may be composed of several texturally and chemically different zones (cf. Balducci and Leoni, 1981), which in Fig. 6 are simplified to two major ones, viz. inner cores and 'normal' mantles.

The inner cores are often strongly resorbed, show patchy zoning and sometimes contain inclusions of glass. Similar features are observed in grains associated with orthopyroxene or other cluster minerals. Compositions of cores and grains in the clusters are variable, but generally high An-contents were measured:  $An_{57-92}$ . They are enclosed by mantles similar to the phenocrysts without calcic cores. These simple phenocrysts and the mantle have lower An-contents ( $An_{47-62}$ ) and represent the equilibrium plagioclase crystallized from the liquid.

The outer rims as well as the groundmass crystals in the inclusions and latites are again richer in anorthite ( $An_{57-72}$ ), but also contain slightly more Or-component. Like the microphenocrysts in the latites they are considered to have a post-mixing origin.

Sanidine occurs as euhedral phenocrysts in the rhyodacites, while in the inclusions and latites perfectly rounded outlines (Fig.3d) point to a xenocrystal origin, which is supported by its chemistry. Compositions in all of the rock types show little variation ( $An_{0-2}Ab_{16-21}Or_{79-84}$ ) and zoning in single crystals is negligible. Groundmass sanidines in the hybrid rocks range towards higher Ab-contents and are also richer in An.

	MA 26 phenocr	MA 26 grndm	MA 1.15 phenocr	MA 45 phenocr	MA 45 microph	MA 27
SiO <sub>2</sub>	40.32	39.98	39.79 <sup>1)</sup>	39.74	34.65	32.37
Al <sub>2</sub> O <sub>3</sub>	0.34	1.07	1.06	0.36	0.81	0.00
TiO <sub>2</sub>	0.00	0.06	0.02	0.00	0.24	0.00
FeO	10.50	12.67	14.10	14.68	41.74	53.40
MnO	0.17	0.20	0.22	0.37	0.72	0.87
MgO	46.63	43.80	44.40	44.12	21.66	14.09
CaO	0.48	0.69	0.41	0.59	0.43	0.00
total	98.44	98.47	100.00	99.86	100.25	100.73
Si	1.007	1.008	1.006	0.999	0.995	0.987
Al	0.010	0.032	0.032	0.011	0.027	0.000
Ti	0.000	0.001	0.000	0.000	0.005	0.000
Fe	0.219	0.267	0.298	0.309	1.001	1.358
Mn	0.004	0.004	0.005	0.008	0.018	0.022
Mg	1.735	1.645	1.672	1.653	0.927	0.645
Ca	0.013	0.019	0.011	0.016	0.013	0.000
Σ	2.99	2.98	3.02	3.00	2.99	3.01
Mg/(Mg+Fe)	0.89	0.86	0.85	0.84	0.48	0.32

<sup>1)</sup> by difference

Table 4. Representative analyses of olivines. MA 26-MA 1.15: inclusions; MA 45: final lava; MA 27: host<sub>2</sub>lava (from plag-opx-cpx-bio-ol-ilm cluster). All iron taken as Fe<sup>2+</sup>. Numbers of cations based on 4 oxygens.

#### WHOLE ROCK CHEMISTRY

Major element data representative for 37 analysed inclusions are given in Table 5. Chemical data on the lavas have been reported by Mazzuoli and Pratesi (1963), Dupuy (1970); Dupuy and Allègre (1972) and Bigazzi et al. (1981). Compositional variations are illustrated by means of plots against SiO<sub>2</sub> (Fig.7), which demonstrate the existence of continuous linear trends from the inclusions (48-59 weight % SiO<sub>2</sub>) to the final lavas (56-63 % SiO<sub>2</sub> and the host lavas (62-67 % SiO<sub>2</sub>). The compositional gap between the minette inclusions and the host rock rhyodacites appears thus to be bridged by the final latitic lavas, having overlaps on both sides.

All of the rocks are characterized by high alkali contents ( $\text{Na}_2\text{O} + \text{K}_2\text{O} = 6-9\%$ ) with potassium dominating ( $\text{K}_2\text{O}/\text{Na}_2\text{O} = 2-3$ ). This element displays a particularly striking trend as it remains practically constant (5-6 %  $\text{K}_2\text{O}$ ) over the whole range of  $\text{SiO}_2$ . Consequently, the compositional trends cross-cut dividelines in conventional alkali vs. silica diagrams used to distinguish alkaline from subalkaline volcanic rocks (e.g. Irvine and Baragar, 1971). With increasing  $\text{SiO}_2$  there is a slight increase in  $\text{Na}_2\text{O}$  and a decrease in  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}^{\text{tot}}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{MnO}$  and  $\text{P}_2\text{O}_5$ . Mg-numbers ( $100 \times \text{Mg}/(\text{Mg}+\text{Fe}^{2+})$ ), as calculated using an assumed  $\text{Fe}^{3+}/\text{Fe}^{2+} = 0.15$ , reach values up to 68 in the inclusions, and tend to decrease with increasing  $\text{SiO}_2$ .

The observed chemical variations are further elucidated by CIPW-norm calculations showing the appearance of olivine and minor nepheline in the more mafic inclusions, whereas the other inclusions and the lavas are quartz and hypersthene normative. In addition, the rhyodacites have normative corundum, a common feature in the Tuscan Province (Barberi et al., 1971).

Combination of trace element data of inclusions and lavas also results in straight-line correlations for the whole series (Fig.8). Rb, Zr, La, Ce, Nb and Y, like  $\text{K}_2\text{O}$ , hardly vary with  $\text{SiO}_2$ . On the other hand, with increasing  $\text{SiO}_2$ , Li increases, whereas Sr and Ba decrease and are relatively low in the rhyodacites. The high contents of trace elements, many of which would normally behave as incompatible, is a characteristic of the inclusions that confirms their affinity with (ultra)potassic rocks, including minettes. Inclusion MA 26 is not only the most mafic sample, but is also low in K, Rb and Ba compared with the other inclusions.

## DISCUSSION AND CONCLUSIONS

The present data strongly favour magma mixing as the process which at Mt.Amiata yielded a continuous series inclusions - final lavas - host lavas. The evidence provided by the disequilibrium mineralogy is supported by straight-line correlations in the whole rock chemistry, which cannot be explained by any classic differentiation mechanism. Almost constant

## MINETTE INCLUSIONS

nr.	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sup>+</sup>	H <sub>2</sub> O <sup>-</sup>	tot	Ba	Sr	Rb	Zr	Y	La	Ce	Nb	Li
26	48.00	0.81	17.95	2.79	4.43	0.14	6.84	10.59	1.77	2.64	0.35	2.60	1.09	100.00	775	910	64	197	19.5	74	122	8	n.a.
1.4	48.99	0.73	14.71	5.57	1.69	0.12	7.20	11.06	1.00	4.90	0.39	2.29	0.54	99.19	1100	995	302	245	20	78	139	11	16
2.3	49.49	0.83	16.77	4.74	2.40	0.11	5.54	8.61	1.63	5.70	0.38	2.59	0.61	99.40	1035	730	337	230	25	78	147	15	20
1.19	49.57	0.75	13.97	5.78	1.47	0.12	7.09	10.05	1.17	5.12	0.39	2.46	0.68	98.62	1110	632	313	180	30	81	124	16.5	14
11.1	51.02	0.80	16.40	3.67	2.88	0.12	5.01	9.22	1.84	5.61	0.38	1.83	0.30	99.08	930	760	378	255	17	66	129	14	24
15.21	51.19	0.82	17.29	3.54	3.54	0.12	4.98	8.09	1.77	5.77	0.40	1.62	0.49	99.62	960	750	362	210	17	70	136	13	32
1.18	51.27	0.75	15.69	3.40	3.11	0.12	5.28	8.40	1.42	5.42	0.36	2.29	0.64	99.15	1055	627	297	222	22	71	133	13	40
15.12	51.57	0.79	17.42	4.46	2.18	0.12	4.32	8.59	1.94	5.85	0.40	1.97	0.35	99.96	920	795	373	255	20	70	122	19	34
1.15	52.27	0.78	17.04	3.22	3.18	0.12	4.64	8.06	1.49	5.33	0.39	2.29	0.69	99.50	990	712	283	205	31	75	137	12	26
30	52.45	0.77	17.24	2.82	3.30	0.11	6.14	7.30	2.03	5.38	0.35	1.51	0.60	100.00	940	825	389	242	16	71	129	11	n.a.
12.2	52.72	0.77	17.47	5.14	1.26	0.11	3.74	8.41	1.71	5.65	0.38	2.33	0.60	100.29	855	645	348	225	34	67	129	17.5	90
42	52.82	0.81	16.49	3.03	3.40	0.12	6.04	7.79	1.65	5.28	0.39	1.58	0.60	100.00	960	810	356	180	17	65	130	8.5	n.a.
12.1	52.89	0.78	17.41	3.87	2.52	0.12	3.47	8.39	1.68	5.57	0.34	2.16	0.64	99.84	820	615	353	325	15	65	125	11	14
1.20	53.14	0.79	17.29	3.10	3.46	0.12	4.24	7.50	1.67	5.41	0.35	2.05	0.55	99.67	1005	690	346	220	31	75	129	16	58
1.13	53.29	0.75	17.37	2.74	3.42	0.11	4.29	7.41	1.65	5.33	0.33	2.31	0.69	99.69	945	670	313	230	23	78	144	20	56
40	53.38	0.77	16.76	1.80	4.40	0.12	5.67	7.74	1.67	5.68	0.37	1.32	0.32	100.00	935	712	380	232	15	74	157	7	n.a.
13	53.39	0.80	17.11	2.41	3.90	0.12	4.85	7.56	1.71	5.53	0.36	1.50	0.76	100.00	920	647	304	185	18.5	69	124	14	n.a.
1.3	53.42	0.76	17.25	3.86	2.89	0.12	4.33	8.14	1.66	5.34	0.28	1.63	0.25	100.03	1000	832	340	207	20	71	140	14	34
1.5	53.86	0.69	15.29	4.96	1.29	0.12	5.06	8.05	1.58	5.41	0.36	3.01	0.49	99.17	895	640	335	198	31	71	135	22	76
1.8	54.88	0.70	15.95	5.47	0.79	0.11	4.51	7.86	1.73	5.28	0.34	1.64	0.39	99.65	875	695	348	207	16	66	134	15	76
38	55.54	0.83	16.37	2.34	4.30	0.13	3.38	8.45	1.17	5.80	0.37	1.01	0.31	100.00	935	830	346	232	20	71	128	14	n.a.
11	55.61	0.81	17.70	1.05	4.50	0.11	4.37	5.76	2.09	5.46	0.31	1.65	0.58	100.00	835	770	337	250	20	69	136	13	n.a.
14.1	55.68	0.75	17.07	2.51	3.36	0.11	4.05	6.49	1.96	5.77	0.32	1.89	0.45	100.41	810	600	324	230	14	64	129	14	38
39	55.95	0.82	17.52	2.20	3.02	0.11	4.36	5.67	1.70	5.63	0.34	1.88	0.80	100.00	875	605	324	240	30	72	95	13	n.a.
32	56.26	0.80	16.68	3.80	2.05	0.11	4.13	7.01	1.87	5.65	0.31	0.76	0.57	100.00	780	740	356	220	21	90	136	12	n.a.
43	56.49	0.76	16.85	2.48	2.87	0.10	4.96	5.50	1.96	5.22	0.30	1.80	0.71	100.00	850	610	324	222	21	70	137	12	n.a.
2.1	56.59	0.72	16.65	4.43	1.30	0.11	3.22	5.54	1.72	5.87	0.28	1.71	0.50	98.64	825	580	389	207	27	132	136	15	98
83	57.02	0.79	17.21	1.82	3.75	0.11	3.81	4.97	1.80	5.55	0.29	1.88	1.00	100.00	985	487	318	267	40	78	146	12	n.a.
41	57.20	0.71	17.14	3.20	2.01	0.10	4.20	5.15	1.96	5.51	0.28	1.64	0.90	100.00	870	525	281	230	30	73	140	12.5	n.a.
35	57.63	0.72	16.79	1.36	3.83	0.10	3.95	5.91	2.27	5.62	0.30	0.90	0.62	100.00	835	690	353	240	24	83	134	12.5	n.a.
2.2	57.65	0.69	16.70	2.35	2.87	0.09	2.95	5.49	1.96	5.93	0.27	1.52	0.55	99.02	930	532	351	220	36	119	300	13	58
78	57.80	0.82	17.14	2.39	3.15	0.11	2.77	5.12	2.04	5.51	0.31	1.88	0.96	100.00	825	555	373	217	29	200	165	14	n.a.
77	58.24	0.75	17.63	3.26	2.00	0.10	3.30	5.30	2.18	5.36	0.30	1.17	0.41	100.00	785	560	297	225	19	82	136	11.5	n.a.
74	58.41	0.76	17.47	1.93	3.20	0.10	2.90	4.93	2.18	5.40	0.29	1.75	0.68	100.00	795	585	315	250	25	70	157	17	n.a.
75	58.44	0.78	16.94	3.39	2.16	0.10	3.11	5.91	2.09	5.66	0.30	0.86	0.26	100.00	805	732	418	217	29	102	137	11	n.a.
31	58.72	0.70	16.81	1.74	3.10	0.09	3.30	5.73	2.20	5.68	0.27	1.12	0.54	100.00	785	605	324	250	18	70	127	16.5	n.a.
36	58.82	0.75	16.81	3.75	1.65	0.10	3.44	5.21	2.14	5.71	0.28	0.86	0.48	100.00	820	775	380	205	22	88	128	18.5	n.a.

FINAL LATITIC LAVAS																							
nr.	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> O <sup>+</sup>	H <sub>2</sub> O <sup>-</sup>	Tot	Ba	Sr	Rb	Zr	Y	La	Ce	Nb	Li
14'	59.90	0.70	16.59	0.89	4.03	0.09	3.13	5.39	1.72	5.35	0.24	1.45	0.52	100.00	730	585	362	225	17	67	136	15	n.a.
45'	60.81	0.64	16.08	1.00	3.69	0.09	3.30	5.25	2.01	5.62	0.24	0.96	0.30	100.00	730	725	378	195	15	64	132	15	n.a.
44'	61.64	0.62	16.22	1.17	3.32	0.08	3.35	4.53	1.92	5.66	0.23	0.85	0.40	100.00	705	630	394	230	20	70	139	18	n.a.
RHYODACITIC DOME LAVAS																							
12	64.04	0.63	16.38	0.80	3.18	0.06	1.60	3.59	1.90	5.82	0.23	1.19	0.58	100.00	620	470	421	200	14	66	134	15	n.a.
27'	64.05	0.59	16.76	0.76	3.39	0.08	1.86	3.43	1.99	5.01	0.22	1.31	0.55	100.00	530	360	372	195	19	72	152	21	n.a.
17'	64.84	0.61	16.15	0.82	3.05	0.07	1.70	3.46	2.21	5.14	0.20	1.25	0.60	100.00	460	410	410	200	6	78	145	17	n.a.
LATE RHYODACITIC LAVA																							
24'	65.45	0.56	15.37	0.69	3.45	0.08	1.82	3.50	2.44	4.66	0.10	1.56	0.32	100.00	350	345	356	252	30	82	155	13	n.a.
EARLY RHYODACITIC LAVAS																							
1'	65.37	0.62	15.64	0.76	2.76	0.06	1.66	3.58	2.51	5.25	0.15	1.38	0.26	100.00	430	377	402	220	26	68	133	19	n.a.
19'	65.53	0.60	15.60	0.66	2.77	0.06	1.57	3.40	2.56	5.20	0.14	1.36	0.56	100.00	435	355	394	225	31	68	140	12	n.a.
20'	66.37	0.49	15.57	0.40	2.60	0.06	1.24	2.83	2.49	5.92	0.08	1.38	0.59	100.00	565	390	423	225	27	69	132	16.5	n.a.
89'	66.70	0.48	16.11	1.04	1.85	0.05	1.16	2.47	2.24	5.79	0.20	1.21	0.70	100.00	560	370	367	225	32	70	118	15	n.a.

Table 5. Chemical composition of inclusions and lavas from Mt. Amiata. Analyses were carried out at the Mineralogical and Petrographical Institute, Siena and at the Vening Meinesz Laboratory, Utrecht. Totals of 100.00% generated by correction program used in Siena. All elements (except Na, Mg and Li by AA, and Fe<sup>2+</sup> by titration) analysed by XRF. n.a.: not analysed.  
' major elements from Bigazzi et al. (1981).

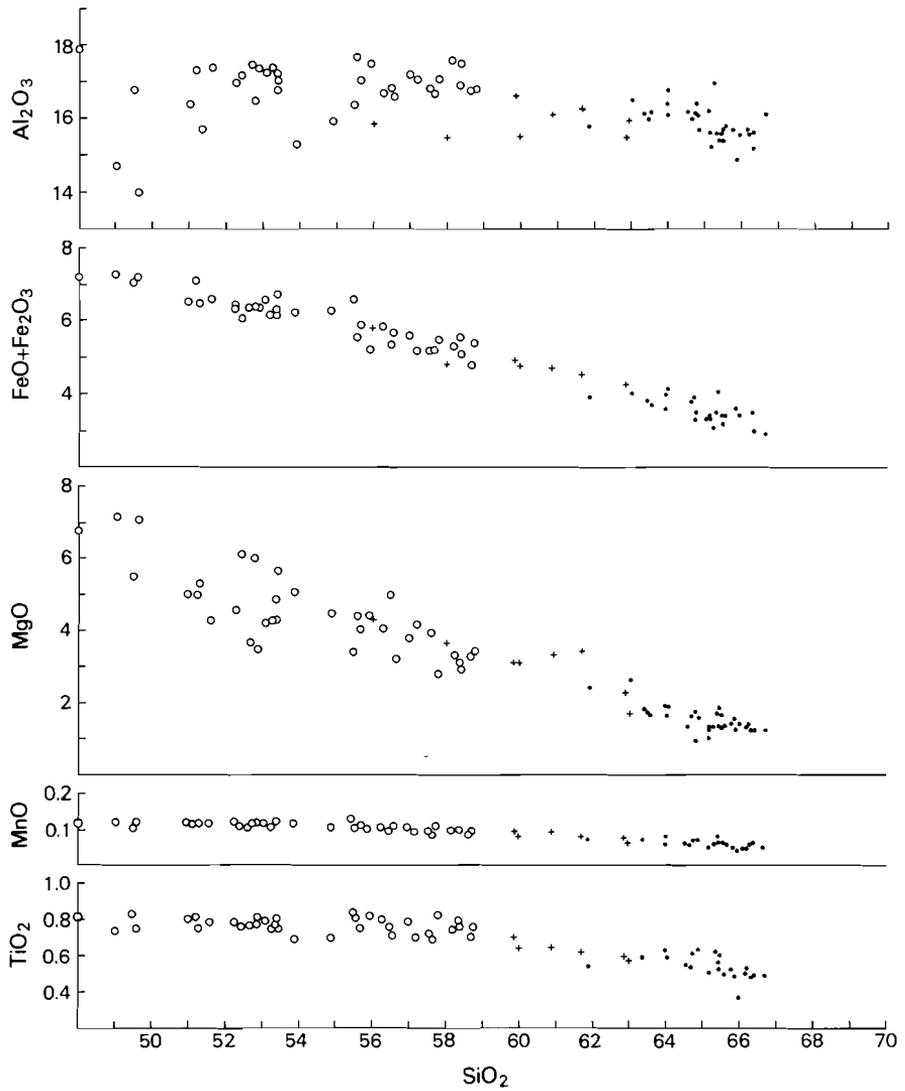
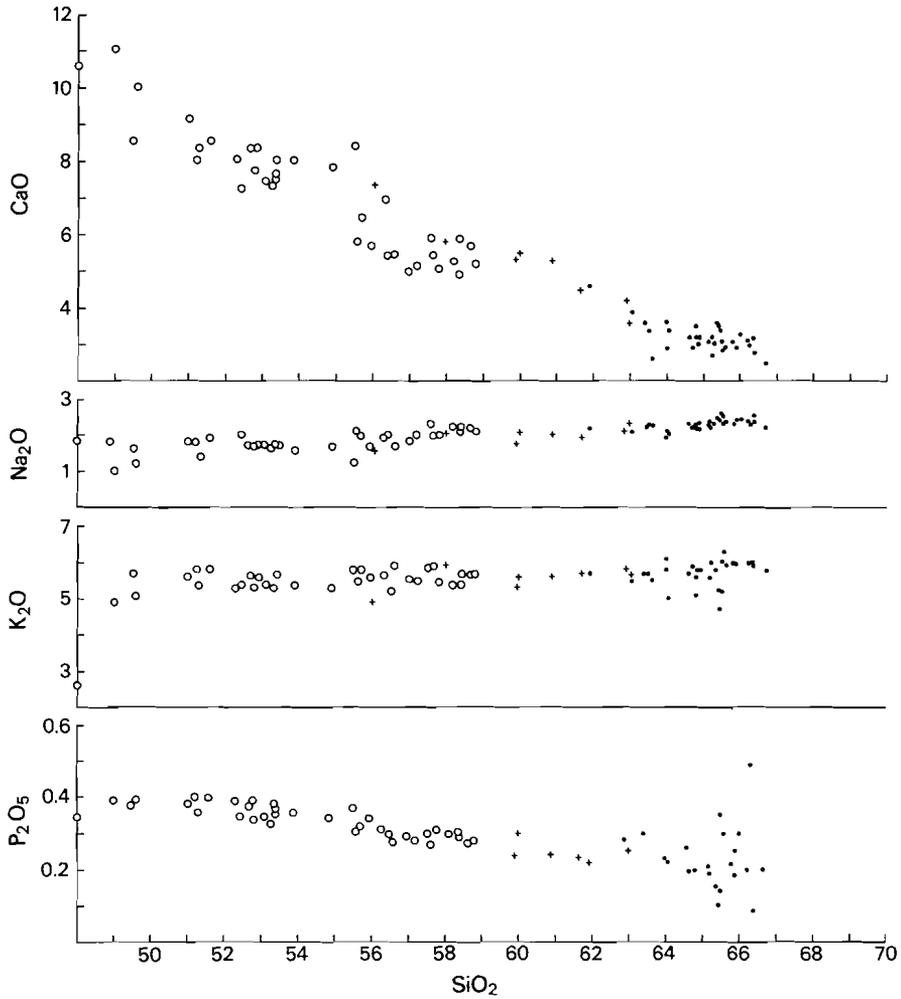
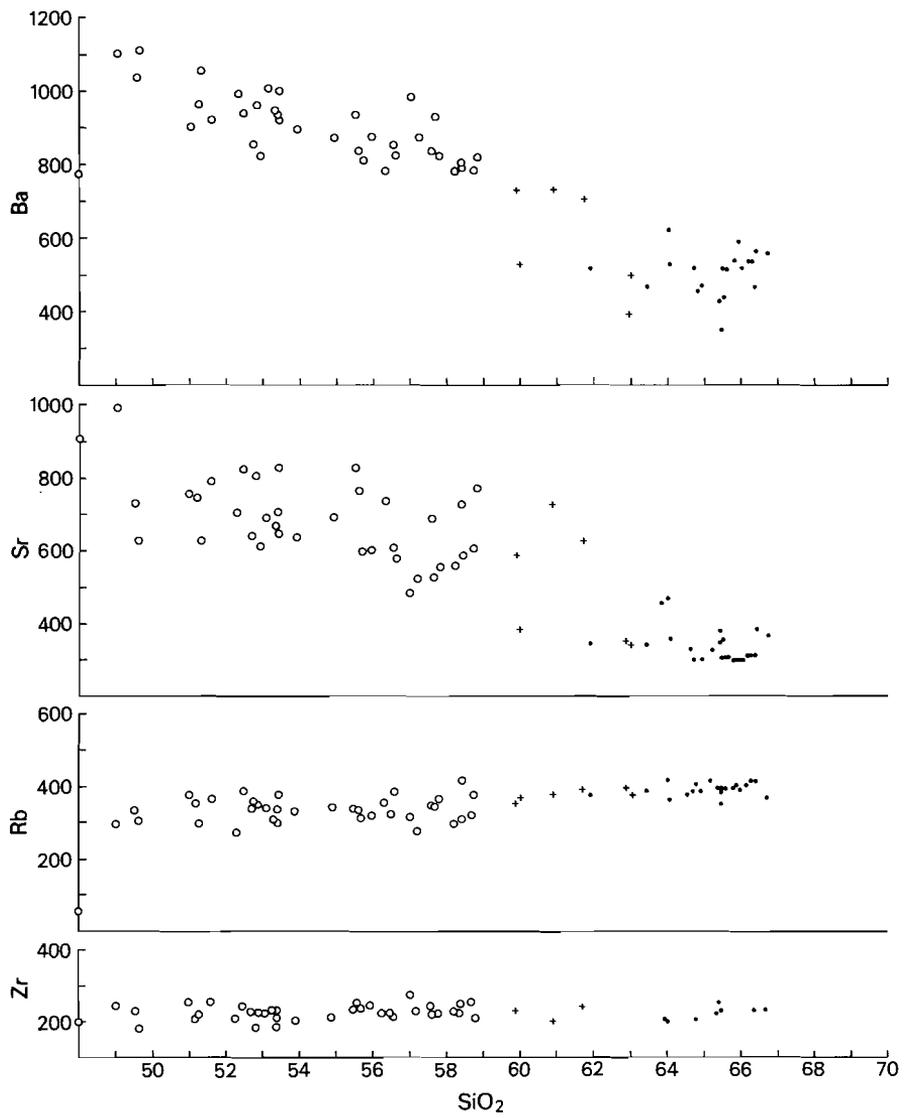


Fig. 7. Variation diagrams of major elements against  $\text{SiO}_2$  for inclusions (open circles), final lavas (plusses), and host lavas (dots) from Mt.



*Amiata. Final lavas and host lavas include data from Mazzuoli and Pratesi (1963), Dupuy (1970) and Bigazzi et al. (1981).*



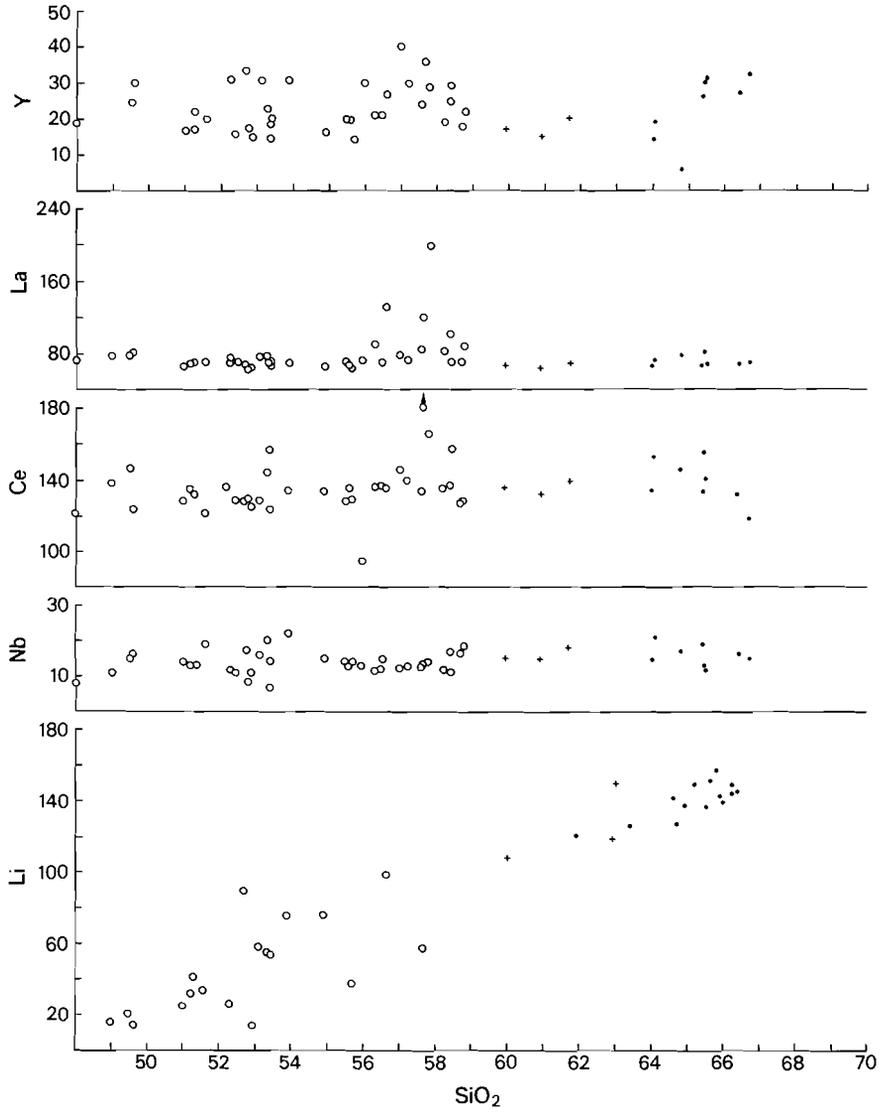


Fig. 8. Variation diagrams of trace elements against SiO<sub>2</sub> for inclusions (open circles), final lavas (plusses) and host lavas (dots) from Mt. Amiata. Final lavas and host lavas include some data from Dupuy (1970).

contents of some elements throughout the whole series could suggest interference with other processes superimposed on mixing, and will be discussed below.

Regarding their porphyric and vesicular texture the Amiata inclusions have been described as fragments of lava, which were incorporated in the rhyodacitic lavas during later eruptions (Mazzuoli and Pratesi, 1963). Several observations are not in accordance with this view:

- (1) the subspherical shape of the inclusions, which is unlike that of accidental xenoliths derived from solid lavas.
- (2) when closely examined, contacts with the host lavas are contorted and not sharp on a microscopic scale, and suggest the former coexistence of two phenocryst-bearing melts.
- (3) the ubiquitous presence of late stage biotite, clearly of igneous origin, and the high degree of crystallinity, suggesting a subvolcanic rather than a volcanic environment.
- (4) concentration of the inclusions in the late stage dome lavas rather than in the early erupted lavas.

Although some of the hybrid magma may have reached the surface to form small lava flows (like the final latitic lavas), or may have crystallized as dikes, the great majority of the inclusions is considered to represent hybrid blobs produced by injection of mafic magma into the acid magma, by which they were later carried upwards.

An origin by magma mixing has been proposed earlier for mafic inclusions in lavas of calcalkaline volcanoes (notably andesites and dacites) and their plutonic equivalents (Walker and Skelhorn, 1966; Eichelberger and Gooley, 1977; Eichelberger, 1978; Heiken and Eichelberger, 1980), and contrasts with an interpretation as cumulates from fractional crystallization (Williams, 1931) or as restites from deep crustal melting (Presnall and Bateman, 1973). Recently Eichelberger (1980) has argued that, when a mafic magma, even with low initial concentrations of water is injected, rapid cooling will result in exsolution of a vapour phase at crustal pressures, and thus cause the formation of vesicles, as observed in inclusions from various calcalkaline volcanoes in the Western United States.

#### Acid end member

The occurrence of rhyolites in Tuscany and Latium would make a magma more acid than the rhyodacites of Mt. Amiata feasible as an end member. However, detailed geochemical studies (Dupuy, 1970; Dupuy and Allègre, 1972) supplemented by isotope evidence (Taylor and Turi, 1976; Hawkesworth and Vollmer, 1979) have shown that the rhyolites of San Vincenzo and Roccastrada form a group clearly distinct from the rhyodacites of Mt. Amiata and Mt. Cimino. These groups cannot be related by any differentiation process, and are considered to reflect differences in crustal source rocks from which they originated by anatexis. Furthermore the rhyolites cannot account for the assemblage of xenocrysts observed in the hybrid rocks as they do not contain pyroxene as a phenocryst and carry, instead, cordierite and fair amounts of quartz (Barberi et al., 1967; Mazzuoli, 1967). Finally, plotting compositions of the rhyolites in diagrams such as Figs. 7 and 8 would result in a kink in the trends of some elements, and is thus inconsistent with a simple two-component mixing model.

Although the Mt. Amiata rhyodacites are quite homogeneous in composition, small differences exist between the two most voluminous lavatypes. The dome lavas are slightly less silicic than the early basal lavas (cf. Table 5, Mazzuoli and Pratesi, 1963; Dupuy, 1970), and, as mentioned earlier, some samples even show compositional overlap with the final hybrid lavas. This implies that (part of) the dome lavas presumably are also the result of mixing. The presence of mantled pyroxenes and feldspars, as well as some resorption of phenocrysts, support this supposition. From these considerations we conclude that the early rhyodacitic lavafloes are the most likely representative of the acid end member magma.

#### Mafic end member

The composition of the mafic end member magma can be estimated by solving best fit correlation lines in the  $\text{SiO}_2$ -oxide/element diagrams of Figs. 7 and 8 at  $\text{SiO}_2 = 48\%$ . The values thus obtained are listed in Table 6, and as a first approximation the end member should have this composition or one at any extrapolated lower level of  $\text{SiO}_2$ .

	Monte Amiata inclusions		LKS				HKS					
	*	MA 26	Ernici		Roccamonfina		Sabatini		Ernici		Roccamonfina	
			mean (n=5)	range	mean (n=6)	range	mean (n=9)	range	mean (n=11)	range	mean (n=17)	range
SiO <sub>2</sub>	48.0	49.84	48.61	47.28-49.65	48.14	47.29-49.21	48.63	47.46-49.74	47.34	46.17-47.83	48.82	46.53-49.99
TiO <sub>2</sub>	0.85	0.84	0.84	0.71- 1.00	1.06	0.86- 1.27	0.84	0.73- 0.91	0.80	0.72- 0.87	0.85	0.76- 1.04
Al <sub>2</sub> O <sub>3</sub>	17.0	18.64	17.52	16.45-18.73	16.17	14.79-17.81	16.11	13.36-18.15	17.81	16.86-18.35	18.12	14.88-20.00
Fe <sub>2</sub> O <sub>3</sub>		2.90	2.27	1.23- 3.30	3.57	2.91- 4.59	4.23	3.25- 6.12	3.59	1.77- 5.94	3.66	1.71- 8.29
FeO	7.5	4.60	5.42	4.57- 7.69	6.03	5.10- 6.58	3.72	1.73- 5.29	3.42	1.80- 4.71	4.65	0.70- 6.12
MnO	0.14	0.15	0.15	0.14- 0.17	0.17	0.16- 0.18	0.15	0.13- 0.18	0.14	0.13- 0.16	0.16	0.13- 0.18
MgO	6.2	7.10	7.79	6.00- 9.09	8.19	6.91- 9.11	5.71	3.50- 7.49	5.80	5.11- 6.40	4.13	2.45- 6.93
CaO	9.8	11.00	11.66	10.39-13.11	13.07	12.54-13.36	11.18	9.78-13.20	10.80	9.96-12.16	9.42	7.40-12.60
Na <sub>2</sub> O	1.4	1.84	2.69	1.65- 3.08	1.90	1.49- 2.30	1.31	0.83- 1.83	2.54	1.99- 2.79	2.18	1.29- 3.04
K <sub>2</sub> O	5.3	2.74	2.77	1.86- 3.38	1.36	1.12- 1.72	7.52	6.52- 8.75	7.31	6.59- 8.15	7.51	5.49- 9.87
P <sub>2</sub> O <sub>5</sub>	0.43	0.36	0.28	0.24- 0.34	0.34	0.28- 0.38	0.61	0.50- 0.67	0.49	0.38- 0.59	0.51	0.40- 0.70
Ba	1093	775	570	500-652	857	640-1130	1564	990-2100	1220	832-1675	1492	1166-1860
Sr	844	910	895	841-981	963	811-1155	1625	1321-2203	1672	1412-1932	1882	1404-2348
Rb	297	64	114	67-148	152	46- 288	458	372- 669	363	335- 421	497	375- 677
Zr	221	197	87	76- 95	95	83- 107	318	266- 430	223	207- 240	260	191- 405
Y	22	19.5		19- 22	30	27- 37	31	28- 35	32	30- 33	51	39- 63
La	76	74	33	29- 40					90	80- 98		
Ce	133	122	72	61- 85	44				188	170- 212		
Nb	13	8	8	6- 9					12	9- 13		

Table 6. Chemical composition of mafic end member in Mt. Amiata mixing event and of inclusion MA 26, compared with least evolved rocks ( $SiO_2 < 50\%$ , contents recalculated to a total of 100%, volatile free) of low-potassic (LKS) and high-potassic series (HKS) from some occurrences in the Roman magmatic province. The mafic end member (indicated by the asterisk) was derived by solving best-fit correlation lines in  $SiO_2$ -variation diagrams (Figs. 7 and 8) at  $SiO_2 = 48\%$ . References: Ernici-Civetta et al. (1981), sample M 1 excluded; Roccamonfina-Appleton (1970, 1972), Ghiara and Lirer (1977); Sabatini-Cundari (1979).

With respect to the rhyodacites the mafic end member is richer in  $Al_2O_3$ ,  $FeO^{tot}$ ,  $MgO$ ,  $CaO$ ,  $MnO$ ,  $TiO_2$ ,  $P_2O_5$ ,  $Sr$ ,  $Ba$ , depleted in  $SiO_2$ ,  $Na_2O$ ,  $Li$ , while they seem to have practically equal high contents of  $K_2O$ ,  $Rb$ ,  $Zr$ ,  $Y$ ,  $Nb$ ,  $LREE$ , assuming that mixing was the only effective process.

The resulting end member has chemical characteristics corresponding to the potassic alkaline Roman Province. In order to illustrate this similarity, chemical data from some of the best documented Roman volcanic centres have been compiled in Table 6. As the end member should have a  $SiO_2$  content about 48% or lower, only the least evolved rocks, i.e. with  $SiO_2$  less than 50%, have been used. Following Appleton (1972) the lavas of the Roman Province are usually divided into two series: a high-potassium series (HKS), which includes the rock types leucite basanite, olivine leucitite, leucitite, tephrite and phonolite, and a low-potassium series (LKS), which includes trachybasalt, latite and trachyte. As can be seen in Table 6 the least evolved lavas of the HKS have a  $K_2O$  content between 5 and 10%, and those of the LKS between 1 and 4%. The contents of other major elements are constant, perhaps with the exception of  $Mg$  which is slightly higher in the LKS. On the contrary, trace elements may show considerable variations in each centre and between different centres, but in general most of the elements listed are higher in the HKS than in the LKS. The available chemical data from other Roman centres, such as Vulcini (being closest to Mt. Amiata) are consistent with these observations (e.g. Varekamp, 1979).

It is difficult to assign the assumed mafic end member to one of both series. Its  $K_2O$  content of 5.3% is slightly low for the HKS, but certainly too high for the LKS. Some trace elements ( $Ba$ ,  $Zr$ ,  $LREE$ ) are also high for the LKS, whereas  $Sr$ , for example, seems to be too low for the HKS. On the other hand 16 partial analyses of HKS lavas from Vesuvius reported by Cortini and Hermes (1981) show an average  $Sr$  content of 976 ppm (range: 773-1117 ppm), similar to usual LKS values, while the contents of  $Rb$  (mean 291, range: 232-340 ppm) are equally low in comparison with other centres. Phenocrysts assemblages of both series also preclude a decisive answer. Porphyritic leucitites and tephrite leucitites (HKS) have a diopsidic clinopyroxene as dominant phenocryst, accompanied with minor forsteritic

olivine (Ernici) or leucite (Sabatini), while leucite-bearing alkali basalts and trachybasalts from Ernici, and olivine-basalt from Roccamonfina (LKS) also carry diopside and subordinate olivine. In these least evolved members plagioclase phenocrysts are usually absent. Consequently the early crystallized mafic phenocrysts in both series are similar to those of the inclusions.

#### Enrichment of volatiles and other incompatible elements

Due to the scarcity or absence of data volatiles have not been included in the discussion so far. Minettes characteristically have a high volatile content, hence they must have been important constituents of the inclusions, especially H<sub>2</sub>O and F which are necessary to stabilize phlogopite/biotite at low pressures. Two explanations for the origin of volatiles can be given: (1) the mafic end member magma was enriched in volatiles prior to mixing with the rhyodacitic magma. If this is true, the Roman magma involved in the mixing process must have been hydrous with a composition similar to that of minette; (2) the enrichment is related to the mixing event.

(1) The compositional relation between many lamprophyres and alkali-basalts has often been noticed in the literature, and specifically the resemblance between minettes and K-rich volcanics has been recognized by several authors (e.g. Velde, 1971; Hyndman, 1972; Wimmenauer, 1973; Rock, 1977; Bachinski and Scott, 1979; Rogers et al., 1982), who observed their common mineralogy, potassic chemistry ( $K_2O > Na_2O$ ), high contents of incompatible trace elements in contrast to low SiO<sub>2</sub> contents, distinctive REE patterns, occurrence in continental environments, association with tensional tectonics, and the occasional association of both rock types (e.g. Navajo Province, USA; Colima, Mexico). The hypothesis that lamprophyres are volatile and alkali enriched alkali-basalts has been frequently advocated (see Hyndman, 1972; Wimmenauer, 1973; Rock, 1977), and is also applied to the potassic varieties. Recently Luhr and Carmichael (1981) noted that, although otherwise similar, the minettes of a basanite-minette suite from Colima (Mexico) are more enriched in incompatible elements (including H<sub>2</sub>O) than the basanites. They attribute this to variations in the relative contributions of incompatible element rich phases during

partial melting of a metasomatically enriched upper mantle. Other recent studies have also stressed that the primary characteristics of minettes are to be related to an origin in the mantle (Kay and Gast, 1973; Beswick, 1976; Ehrenberg, 1977 a, b; Roden, 1977; Bachinski and Scott, 1979; Rogers et al., 1982). Considering that many authors agree on a similar deep source for the potassic lavas of the Roman Province - disregarding the current controversy (see below) - a minette variety of the Roman type magma is clearly a possible mafic end member in the magma mixing model being examined. It is also possible that the mafic end member magma was only apparently enriched in volatiles compared with normal primitive Roman magmas. Under the usual volcanological conditions these magmas may have lost part of their original volatile content during low pressure evolution, or during eruption. In this special case volatile-loss may have been prevented by the enclosing acid magma (cf. Eichelberger, 1980).

(2) An alternative hypothesis is that the Mt. Amiata inclusions obtained their minette character by enrichment of volatiles and possibly other incompatible elements as a result of their mixing origin in an acid magmchamber. In fact, the well known association of minettes and granitic intrusions, and their occurrence in continental environments have often been considered as necessary prerequisites for the origin of the former. Along this line alkali-basaltic magmas are thought to become lamprophyric by enrichment in volatiles during interaction with acid crustal material (see Hyndman, 1972; Wimmenauer, 1973; Rock, 1977). Although the process of volatile transport is difficult to envisage, there are some observations relevant to its possible effectiveness in the evolution of the rocks of Mt. Amiata:

(a) the constant high contents of K, Rb, Zr, Y, Nb, La, Ce throughout the whole series minette inclusions - rhyodacites.

If equal contents of these elements in both end members - implicit in a simple two-component mixing model - cannot be accepted as a coincidence, only a process of selective enrichment could be possible. As such a process must have led to a rapid homogenization of the rhyodacitic and hybrid magmas with respect to (part of) this group of elements, a gas phase transporting volatiles, alkalis and possibly other elements is then likely to have played a role.

(b) the relatively anhydrous character of sample MA 26 and of the final latitic lavas, given the scarcity or absence of mica as a primary phase. The aberrant sample MA 26 is the most mafic inclusion and is remarkably low in K and Rb, which makes it indistinguishable from the Roman LKS (Table 6). Nevertheless it must have undergone a low degree of hybridization as it contains some sanidine xenocrysts. The final lavas are compositionally close to the rhyodacitic end member. Both examples suggest that the enrichment of volatiles and possible associated elements could depend on local factors, connected with the degree of degassing of the rhyodacitic magma.

Due to the lack of experimental data on magmatic processes leading to selective enrichment of this kind we consider any definite conclusion to be premature. It may, however, be noted that from a study of feldspars in the Mt. Amiata rhyodacites Balducci and Leoni (1981) concluded that the sanidine megacrysts crystallized at low  $P_{H_2O}$ , the magma possibly being undersaturated. Transport of  $H_2O$  by an eventually separated gas phase would therefore be questionable

#### Implications for the origin of Roman and Tuscan magmas

Volcanological conditions in Central Italy, such as the presence of shallow magma chambers and repetitive activity of tensional tectonics (Marinelli, 1975; Locardi et al., 1976; Varekamp, 1979, 1980) are highly favourable for magma mixing. The present results indicate that primitive Roman type magmas have coexisted with Tuscan magmas in single volcanic systems where hybrid rocks have been produced by mixing. The evidence for Mt. Amiata is equally applicable to Mt. Cimino, a Tuscan complex situated between the Roman centres of Vulsini and Vico (Fig. 1) and having volcanological and chemical characteristics analogous to Mt. Amiata (Dupuy, 1970; Puxeddu, 1971; Micheluccini et al., 1972), including the occurrence of similar mafic inclusions (Puxeddu, 1971; own observations). In the area of overlap north of Rome, mixing between Roman and Tuscan magmas is also suggested by isotope data (Taylor and Turi, 1976; Taylor et al., 1979; Hawkesworth and Vollmer, 1979) and mixing between different batches of Roman magma by chemical and mineralogical studies (Varekamp, 1979, 1980; Cundari, 1979; Barton et al., 1982).

This close relation and interaction between different types of magma may have important implications for the genesis and evolution of magmas from both provinces. For the Tuscan Province chemical, mineralogical and isotope evidence points to crustal anatexis as the main genetic process. Some of the differences between the distinct magmatic occurrences, with respect to age, geographic situation and chemistry should be reconsidered in the light of possible interaction with Roman material. It should, however, be emphasized that the present data indicate that such a process takes place in a shallow crustal environment, and that they do not support mixing as explanations for some of the major differences (e.g., chemistry and mineralogy of rhyodacites and rhyolites). Nor does it explain why some centres show a potassic tendency. These features are therefore more likely to be attributed to the origin of the magmas at deeper levels.

Among the many theories on the origin of the potassic alkaline suites of the Roman Province (cf. Appleton, 1972; Marinelli, 1975; Civetta et al., 1981) the question of enriched mantle vs. crustal contamination is currently most debated (cf. Hawkesworth and Vollmer, 1979). To account for the fact that even the most primitive volcanic products have high contents of K, Rb, Sr, Ba, LREE and Th, as well as high ratios of  $^{18}\text{O}/^{16}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  and a low ratio of  $^{143}\text{Nd}/^{144}\text{Nd}$ , the hypotheses proposed include a genesis by low degrees of partial melting of a garnet peridotitic mantle previously enriched in LIL elements and appropriate isotope species (Cox et al., 1976; Thompson, 1977; Hawkesworth and Vollmer, 1979; Vollmer and Hawkesworth, 1980; Civetta et al., 1981), or interaction of mantle derived magmas with crustal components (Vollmer, 1976, 1977; Turi and Taylor, 1976; Taylor et al., 1979). In the latter case regional variations in isotope compositions suggest an increasing share of crustal material in the more northern Roman centres, i.e. in the area where Tuscan magmatism is manifest at the surface. Both alternatives basically reflect the enrichment problem outlined above for the mafic inclusions. Nevertheless, evaluation of the mixing trends found (assuming a simple two-component model) precludes magma mixing as an explanation for the general chemical peculiarities of Roman lavas. The Amiata inclusions thus provide the natural evidence for earlier

arguments which pointed to the fact that possible crustal contaminants would have an inadequate chemistry. If any process leading to selective enrichment plays a role between adjacent batches of magma or superimposed on mixing in a crustal environment elements most likely to be involved are K, Rb, Zr, LREE (Nb,Y) - i.e., those showing horizontal linear trends - and not, or substantially less Sr and Ba. The enrichment of (at least) these two latter elements in Roman magmas must therefore be attributed to an anomalous character of the upper mantle.

Because magma mixing, in combination with other processes such as fractional crystallization and assimilation, will have a sensitive influence on trace element contents and isotope ratios (e.g. O'Hara, 1977; De Paolo, 1981), it would be very difficult to determine the nature of the anomalous upper mantle in the area of overlap, and for this purpose more attention has been paid to the southern Roman centres. Indeed, as Tuscan volcanics are absent there, and as the cases of Mt. Amiata and Mt. Cimino suggest that large volumes of uprising mafic magmas are not likely to pass shallow reservoirs of Tuscan melts, this mode of contamination by crystal magmas is improbable. However, evidence for mixing of different batches of Roman magmas has been provided also here (Vollmer et al., 1981; Barton et al., 1982), with the consequence that trace element and isotope data should still be interpreted with care, especially when small variations within one centre or between different centres would seem to reflect heterogeneities of the upper mantle (Vollmer et al., 1981).

Concluding remarks on the evolution of Mt. Amiata

Any model describing the evolution of Mt. Amiata volcanic complex should account for the bimodality of the magmas involved, one rhyodacitic with a crustal origin, the other potassic alkaline basaltic derived from the upper mantle. The arguments suggesting that a silicic magma chamber already existed before the mafic magma invaded shallow crustal levels are:

(1) hybrid products contain all phenocrystal phases from the rhyodacitic end member, indicating that mixing took place at a time when the rhyodacitic magma was at a temperature below its liquidus.

- (2) early unhybridized mafic lavas are absent.
- (3) the polymetamorphic sedimentary inclusions in the rhyodacites represent fragments of a contact aureole (van Bergen, 1983).
- (4) Tuscan magmatism, although partially overlapping in time, generally precedes Roman magmatism.

Several of the features that are characteristic of silicic magma chambers invaded by mafic magmas (cf. Anderson, 1976; Sparks et al., 1977; Eichelberger and Gooley, 1977; Eichelberger, 1980; and related literature) are found in the rocks of Mt. Amiata and the analogous complex of Mt. Cimino. Injection of hot mafic magma, possibly intermittently, has resulted in:

- (a) mixing between both magmas with the formation of a hybrid layer and of hybrid blobs near an unstable interface
- (b) heating of the rhyodacitic magma causing intensified convection and mixing, partial break up of the contact aureole, and assimilation of country rock
- (c) eventual triggering of the rhyodacitic eruptions, which at Mt. Cimino were initially explosive as witnessed by voluminous ignimbrite deposits (cf. Sparks et al., 1977).

From the fact that the volcanic activity ends with the eruption of relatively mafic hybrid lavas, it may be supposed that all rhyodacitic magma originally present has come to the surface. If this is true, then the actual geothermal activity could be due to a cooling batch of Roman magma rather than a Tuscan residue.

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## CHAPTER V

### COMMON TRACE ELEMENT CHARACTERISTICS OF CRUSTAL AND MANTLE DERIVED K-RICH MAGMAS AT MT. AMIATA (CENTRAL ITALY)

Manfred J. van Bergen

*manuscript*

#### ABSTRACT

Rare-earth and other trace element data are reported for K-rich mafic inclusions and siliceous lavas from Mt. Amiata (southern Tuscany, Italy), which form an almost complete mixing series as a result of magmachamber replenishment. Despite a wide range of  $\text{SiO}_2$  contents (48-67 wt.%), most of the rocks are equally enriched in light REE (200-300x) and heavy REE (10-15x) relative to chondritic values, whereas intermediate REE are slightly less abundant in the lavas compared with the inclusions. Eu shows negative anomalies ( $\text{Eu}/\text{Eu}^* = 0.49-0.70$ ) that are most pronounced in the lavas. The compatible elements Cr, V, Sc and Co are found to behave like Sr, Ba and most major elements, as they show a distinct inverse correlation with  $\text{SiO}_2$ , while Cs follows Na and Li, and markedly increases with  $\text{SiO}_2$ . K and a number of other, predominantly incompatible elements, viz Rb, Zr, La, Ce, Yb, Lu, Nb, Y, Hf, Th and U display, however, surprisingly little or no variation, and all of the rocks have unusually high concentrations of many of these elements.

Based on arguments that mixing in the magmachamber was not accompanied by significant selective enrichment of certain elements, these chemical characteristics are attributed to the end-members which can be identified as a silica-saturated Tuscan type magma and a primitive, silica-undersaturated Roman type magma of the high-K series. It is tentatively suggested that the different sources in the lower crust and upper mantle from which the end-member magmas are thought to originate, were metasomatised by the same fluids prior to melting.

#### INTRODUCTION

Despite the commonly accepted origin of the predominantly siliceous magmas in the Plio-Pleistocene Tuscan Magmatic Province (Central Italy) by crustal anatexis and/or large-scale assimilation of sediments, an

increasing number of arguments point to an important role of potassic, silica-undersaturated subcrustal magmas similar to those of the Pleistocene-Recent Roman Magmatic Province, at least in some of the 'Tuscan' occurrences in and near the area where the provinces overlap. Mixing of these distinct types of magma at Mt. Cimino complex, situated between the Roman centres Vulsini and Vico, is suggested by contrasting oxygen isotope ratios of sanidine phenocrysts and host melt (Taylor and Turi, 1976), whereas strong mineralogical and chemical evidence for mixing is displayed by the lavas and a suite of mafic inclusions of Mt. Amiata, a comparable complex in southern Tuscany (Van Bergen et al., 1983). Furthermore, the chemical and strontium isotope characteristics of the effusive rocks from both complexes are consistent with mixing between crustal-derived material and mantle-derived magma, the latter component being similar to lavas of the Roman high-K series (Poli et al., in press).

The high abundances of potassium and related elements that are typical for Roman magmas, as well as their high  $^{18}\text{O}/^{16}\text{O}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $^{143}\text{Nd}/^{144}\text{Nd}$ , are currently explained in terms of metasomatism of the upper mantle source region and interaction with continental crustal material (e.g., Hawkesworth and Vollmer, 1979; Taylor et al., 1979; Civetta et al., 1981; Holm and Munksgaard, 1982). The recognition that these magmas coexisted and mixed with Tuscan magmas in single volcanic systems is thus petrogenetically important, as it indicates one of the possible modes of this interaction.

According to Van Bergen et al. (1983), mixing in both Tuscan complexes occurred by injection of primitive Roman magma into relatively shallow reservoirs of Tuscan magma. The resulting hybrid inclusions and lavas of Mt. Amiata form a complete mixing array from mafic, silica-undersaturated to silica-oversaturated composition over a range of 48-67 wt%  $\text{SiO}_2$ . Nevertheless, the abundances of potassium and a number of related elements (Rb, Zr, La, Ce, Nb, Y) were found to be high and almost constant. If simple two-component mixing is assumed, this implies that the two end-members are nearly equally rich in these elements, and suggests that the crustal and upper mantle derived magmas have certain common chemical characteristics attributable to their sources. Alternatively, the near absence of variation might be the result of some homogenization process

that operated in the magmachamber in addition to mixing.

In order to obtain a more comprehensive insight into the chemistry of both end-members, fourteen selected samples of lavas and inclusions were analysed for a complementary set of trace elements including the rare earth elements. This paper presents and discusses the results in combination with previously published data, and provides arguments in favour of the first-mentioned alternative.

#### GEOLOGICAL AND PETROGRAPHICAL REMARKS

According to recent K-Ar and fission track age-dating (Bigazzi et al., 1981), the volcanic complex of Mt. Amiata is the youngest (0.18-0.29 m.y.) occurrence in the Tuscan Magmatic Province. It is situated on the western upheaval of an approximately NW-SE trending graben structure (Radicofani Graben), that forms part of a regional system of block-faults developed since the end of Miocene times when (still active) tensional tectonics followed the compressive stage of the Apennine orogenesis. The complex is located some 25 km north of Vulturno, the northernmost volcanic area of the Roman Magmatic Province. Following a modified version of Mazzuoli and Pratesi's (1963) subdivision, the complex is composed of four units: early siliceous lavas, siliceous dome lavas, some minor late siliceous lavas and a small volume of final more mafic lavas. The estimated total volume of erupted material amounts to some 25-30 km<sup>3</sup> with the reasonable assumption that pyroclastics were negligible. Abundant metasedimentary xenoliths are associated with the igneous inclusions and represent fragments of a contact-aureole (Van Bergen, 1983). The emplacement of magma in the area was accompanied by Hg-mineralization and gave rise to a present-day geothermal field.

Dominant rocks are K-rich, often corundum-normative lavas (62-67 wt% SiO<sub>2</sub>) which contain plagioclase, sanidine, orthopyroxene, clinopyroxene and biotite as phenocrysts. Because they are difficult to fit into common classification schemes, various rock-names have been used: e.g. quartz-latite, trachyte and rhyodacite. The latter term is adopted here, following Barberi et al. (1971) and others. The final mafic-latitic lavas (56-63 % SiO<sub>2</sub>) and the inclusions (48-59 % SiO<sub>2</sub>) are hybrid products which carry the rhyodacite phenocrysts as xenocrysts, in addition to

	MA 26	MA 1.4	MA 2.3	MA 1.18	MA 40	MA 38	MA 35	MA 78	MA 31	A 33	A 15	A 19	A 3	A 5
La	85	85	88	83	81	92	99	222	81	76	83	77	81	85
Ce	138	151	163	157	154	153	147	188	144	141	137	138	144	147
Sm	14	15	15	14	12.5	14	13	24	12	11	10	10	10	11
Eu	2.9	2.5	2.8	2.6	2.6	2.5	2.3	3.5	2.1	1.7	1.6	1.45	1.6	1.6
Tb	1.4	1.8 <sup>†</sup>	1.5	1.3	1.4	-	1.2	2.4	1.3	0.9	1.0	0.9	1.0	0.9
Yb	2.35	2.2	2.5	2.5	2.7	2.5	2.7	4.9	2.55	2.7	2.2	2.2	2.35	2.95
Lu	0.45	0.32	0.42	0.35	0.42	0.37	0.34	0.81	0.36	0.43	0.45	0.43	0.44	0.47
Sc	32	37	26	27	25	26	18	17	16	16	9	10	9	9
V	229	203	192	157	168	172	113	106	115	87	44	49	48	46
Cr	267	409	130	252	171	142	84	74	78	n.d.	n.d.	n.d.	n.d.	n.d.
Co	36	37	31	29	27	26	18	20	19	16	9	9	9	9
Cs	6	12	19	16	31	25	21	31	36	45	46	22	54	50
Hf	6	6	7	7	7	7	8	8	7	7	7	7	8	8
Th	27	35	32	37	39	35	35	37	37.5	38	39	43	43	45
U	6	8	6	7	8	9	7	11	8	8	8	10	9	10
Eu/Eu <sup>*</sup>	0.70	0.54 <sup>†</sup>	0.61	0.60	0.70	-	0.59	0.49	0.57	0.51	0.55	0.49	0.52	0.51
(Ce/Yb) <sub>Ch</sub>	15.5	18.6	16.7	16.1	14.5	15.7	13.9	10.0	14.8	13.3	16.9	15.5	16.1	12.9
Th/U	4.5	4.4	5.3	5.3	4.9	3.9	5.0	3.4	4.7	4.75	4.9	4.3	4.8	4.5
SiO <sub>2</sub> (%)	48.0	49.0	49.5	51.3	53.4	55.5	57.6	57.8	58.7	60.0	64.6	64.7	65.8	66.2
K <sub>2</sub> O(%)	2.64	4.90	5.70	5.42	5.68	5.80	5.62	5.51	5.68	5.61	5.72	5.87	5.95	6.00

Table 1. Trace-element concentrations (ppm) of inclusions (MA26-MA31), final hybrid lava (A33), late siliceous lava (A15), siliceous dome lava (A19) and early siliceous lavas (A3 and A5). Samples are arranged in order of increasing SiO<sub>2</sub>. Oxides of inclusions are from Van Bergen et al. (1983) and those of the lavas from Dupuy (1970).

<sup>†</sup> note the effect of anomalously high Tb on Eu/Eu<sup>\*</sup> as Eu<sup>\*</sup> is interpolated between Sm and Tb.

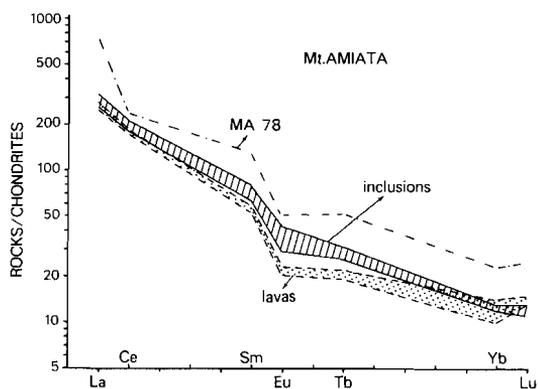
clinopyroxene and minor olivine phenocrysts that may partly originate from the mafic end-member. The inclusions further contain abundant phlogopite/biotite, which gives these rocks the aspect of minettes. More petrographical details are to be found in Van Bergen et al.(1983).

## RESULTS

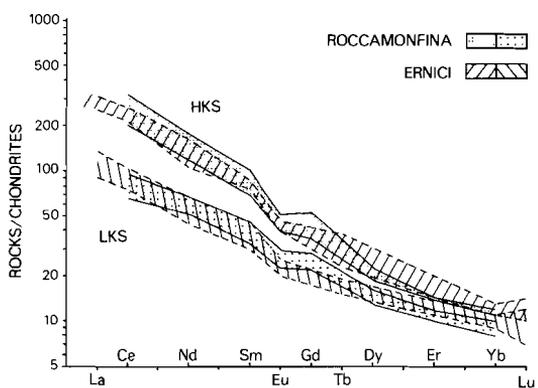
Nine inclusions, one hybrid lava and four host lavas were analysed for 7 REE, Sc,V,Cr,Co,Cs,Hf,Th and U by instrumental neutron activation analysis (INAA) at I.R.I. (Delft). The results are reported in table 1, and fields of chondrite-normalized REE-patterns are given in fig.1a. Average counting uncertainties of one standard deviation are equal to the following percentages of the amounts present: La (1%), Ce (2%), Sm (1%), Eu (3%), Tb (6%), Yb (4%), Lu (6%), Sc (1%), V (4%), Cr (3%), Co (2%), Cs (2%), Hf (2%), Th (2%) and U (5%). One value (Tb in MA38) was rejected because of anomalously poor counting statistics. Some results can be compared with data for the same samples previously obtained by other methods. The contents of La and Ce (by XRF) were on average some 10% lower relative to the present results, which is considered to be within reason. The abundances of Cs in the lavas are some 25% higher than those determined (by flame-spectrophotometry) by Dupuy (1970), which urges some caution in interpreting the absolute values for this element. The determination of Cs in a granite standard (GRAN-1), used by the Geochemical Service Laboratory (Utrecht) was, however, accurate at a level of 4 ppm. Cr was not measured in the lavas, as these samples were contaminated during crushing.

The chondrite-normalized REE-patterns are relatively uniform for both lavas and inclusions (fig.1a) with two exceptions. Inclusion MA78 has REE contents consistently higher than the other samples, which confirms the previous XRF data for La and Ce, and it also shows a somewhat anomalous pattern. Inclusion MA1.4 has anomalously high Tb and is therefore omitted in fig.1a. These deviations are difficult to explain, but could be (partly) due to alteration (cf. Barton et al., 1983).

In general, the Mt.Amiata rocks show a pronounced enrichment in LREE of roughly 200-300 relative to chondritic values and a  $(Ce/Yb)_{ch}$  ratio about 15. Light REE (La,Ce) and heavy REE (Yb,Lu) are virtually constant



a



b

Fig. 1. Chondrite-normalized REE-patterns of (a) Mt. Amiata rocks compared with (b) primitive HKS and LKS lavas from Roccamonfina and Ernici (Hawkesworth and Vollmer, 1979; Civetta et al., 1981). Anomalously high Tb in inclusion MA1.4 omitted.

in all samples, whereas the abundances of intermediate REE (Sm, Eu, Tb) in the inclusions are higher than in the lavas. A significant negative Eu-anomaly is apparent in all analyses ( $Eu/Eu^* = 0.49-0.70$ ) and is most pronounced in the lavas. Sm, Eu, Tb and other trace elements are plotted in fig. 2 as a function of wt. %  $SiO_2$ . It is seen that these REE and the ferromagnesian elements Sc, V, Cr and Co decrease with increasing  $SiO_2$ , and that opposite trends are exhibited by Cs and, to a moderate extent, by the high-valency cations Hf, Th and U. The observed correlations are consistent with the postulated mixing model, perhaps with an exception for Cr, which shows a considerable scatter.

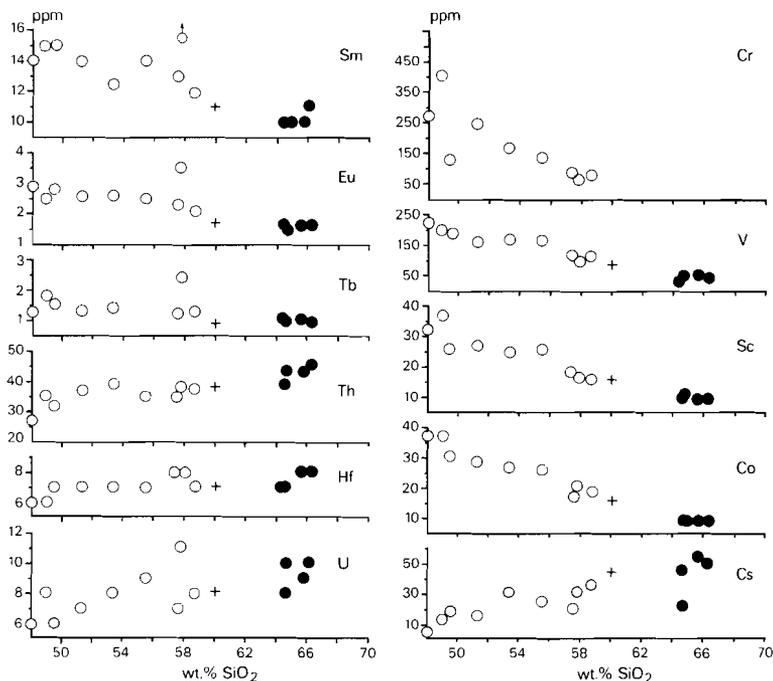


Fig.2. Variation diagrams of trace elements against  $SiO_2$  for inclusions (open circles), final lava (plusses) and host lava (dots) from Mt. Amiata. La, Ce, Yb and Lu are not plotted as these are virtually constant. Lavas were not analysed for Cr.

## DISCUSSION AND CONCLUSIONS

### End-members

If the interaction of magmas in the chamber of Mt. Amiata is assumed to have been a process of simple two-component mixing, then the end-members are approximately represented by those rocks with the highest and lowest contents of  $SiO_2$ . Major and trace element characteristics of the inferred end-members are compiled in table 2. The acid component is best represented by the early rhyodacites which are perlitic lavas with about 66 wt%  $SiO_2$ . In comparison with magmatic rocks with similar  $SiO_2$  contents (cf. Ewart, 1979; Barton et al., 1983; Huijsmans and Barton, in prep.), these lavas are enriched in K, Rb, La, Ce, U and Th, and consequently have high ratios of K/Na, Rb/Sr and LREE/HREE.

Available isotope data for the rhyodacites from Mt. Amiata (Barberi et al., 1971; Taylor and Turi, 1976; Hawkesworth and Vollmer, 1979; Poli et al., in press) indicate high ratios of  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\sim 0.713$ ) and  $^{18}\text{O}/^{16}\text{O}$  ( $\delta \text{O}^{18} = 12.36$ , one determination) and a low ratio of  $^{143}\text{Nd}/^{144}\text{Nd}$  (0.51214, one determination). The acid component has these characteristics grossly in common with the entire Tuscan Magmatic Province, taking into account that minor differences between the distinct occurrences exist.

The approximate composition of the mafic component is established at a level of 48%  $\text{SiO}_2$ , corresponding to the silica-poorest inclusions found. It should, however, be noted that the actual end-member must have been somewhat more mafic, as these inclusions still contain some xenocrysts derived from the rhyodacitic magma, and thus are hybrid products. This K-rich and silica-undersaturated component closely resembles primitive lavas of the potassic alkaline Roman Magmatic Province (see Van Bergen et al., 1983). The present data reinforce this conclusion and, using REE abundances, enable a more precise assessment as to the question whether a member of the high-potassic series (HKS) or low-potassic series (LKS) was involved. Primitive lavas ( $\text{SiO}_2 < 50\%$ ) from both series occur in the southern Roman centres Roccamonfina and Ernici. Apart from their K-contents, the HKS lavas (tephritic leucitites and minor leucitites) are clearly distinguished from the LKS lavas (olivine- or leucite-bearing basalts) by higher contents of LREE (Civetta et al., 1981; Hawkesworth and Vollmer, 1979, as illustrated in fig. 1b). Available data for HKS lavas from other Roman centres yield similar patterns (Sabatini, Alban Hills) but sometimes show depletion (Vesuvius) or some enrichment (Vulsini) of total REE's (Capaldi et al., 1972; Hawkesworth and Vollmer, 1979; Holm et al., 1982). LKS lavas are also found in Vulsini, the centre closest to Mt. Amiata, but unambiguously primitive members seem to be absent despite occasionally low  $\text{SiO}_2$  contents (see Varekamp, 1979; Holm et al., 1982). Comparison of figs. 1a and b strongly suggests that the mafic magma that invaded the magm chamber of Mt. Amiata was a typical primitive HKS magma, such as gave rise to tephritic leucitites in the Roman Province. Although these rocks are in general still somewhat richer in  $\text{K}_2\text{O}$  than the 5-6% inferred for the

	1	2		1	2		1	2
SiO <sub>2</sub>	48.0	66.0	Sc	30	10	Ba	1100	500
TiO <sub>2</sub>	0.85	0.5	V	210	50	La	80	80
Al <sub>2</sub> O <sub>3</sub>	17.0	15.5	Cr	300(?)	-	Ce	145	140
FeO <sub>tot</sub>	7.5	3.5	Co	35	9	Sm	15	10
MnO	0.14	0.06	Sr	850	350	Eu	2.8	1.6
MgO	6.2	1.3	Rb	300	400	Tb	1.6	0.9
CaO	9.8	3.0	Y	22	25	Yb	2.4	2.3
Na <sub>2</sub> O	1.4	2.4	Zr	220	220	Lu	0.4	0.4
K <sub>2</sub> O	5.3	5.9	Cs	12	50	Hf	7	8
P <sub>2</sub> O <sub>5</sub>	0.4	0.2	Li	10	150	Th	35	45
						U	7	10

Table 2. Approximate major-oxide (%) and trace-element (ppm) compositions of mafic (1) and acid (2) mixing end-members at Mt. Amiata. Note that (1) corresponds to the SiO<sub>2</sub>-poorest hybrid inclusions found, but that the actual end-member should have been still more mafic.

mafic end-member, this value is certainly too high for primitive LKS lavas. One inclusion (MA26, which is the most mafic) has an anomalously low K<sub>2</sub>O content (2.74%, see Van Bergen et al., 1983) which could suggest that also LKS magma was involved, but its REE pattern fits well into those of the other inclusions. Considering the hydrous mineralogy of the inclusions, it may further be of interest to note that the REE pattern of the mafic component does not seem to differ much from those of minettes, except that significant negative Eu-anomalies are often absent in these rocks (Jahn et al., 1979; Bachinski and Scott, 1979; Luhr and Carmichael, 1981; Rogers et al., 1982).

#### Selective enrichment

As an alternative for simple two-component mixing, a process leading to selective enrichment simultaneously operating with or closely following mixing may be considered. That such a process could have played a role is suggested by the observation that the abundances of a number of elements show little variation. These elements are K,Rb,Zr,REE (except the intermediate ones), Nb,Y,Hf,Th and U (cf. table 2). Because high contents of most of these elements characterize the Roman Province, this problem also pertains to the question whether mafic magmas could have been selectively enriched by crustal anatectic magmas in a sub-

volcanic environment.

Major chemical modifications of the hybrid inclusions after they formed can be ruled out in view of the high degree of crystallinity and the evidence for rapid crustal growth (see Van Bergen et al., 1983), which is inherent in their origin as hybrid blobs produced by injection of hot mafic magma into a cooler siliceous magma. Any selective exchange with the enclosing rhyodacite should thus have taken place in a very short time. As a second prerequisite, the elements concerned should have been relatively free to move, hence significant proportions should not have been already incorporated into crystalline structures.

Of the processes that are capable to induce selective chemical interaction between coexisting batches of magma, volatile transfer would seem to be a viable mechanism, because indications exist that many of the elements mentioned above can be transported in a volatile phase (Taylor et al., 1981). Diffusion in the liquid state is another potentially effective process, but it can be dismissed because its slowness would render it inadequate under the present circumstances (e.g. Watson, 1982). However, the following points also argue against a substantial enrichment of the hybrid inclusions by means of transport of volatiles derived from the enclosing magma.

1. There is little evidence for the former presence of a volatile phase in the siliceous magma. Vesicles are virtually absent in the rhyodacitic lavas and eruptions were probably non-explosive. Furthermore, the magma was almost certainly undersaturated with  $H_2O$ , at least during its residence in the magmachamber (cf. Balducci and Leoni, 1981). Although all the hybrid rocks are rich in vesicles, this must have resulted from the exsolution of a volatile phase from the mafic component (Eichelberger, 1980), rather than from an influx from outside.

2. Sanidine is a xenocryst in the hybrid inclusions and, according to textural evidence and phase-chemical considerations (Balducci and Leoni, 1981) was the last phenocryst in the crystallization sequence of the rhyodacites. This observation is useful as it implies certain constraints for the proportions of each element that might have contributed to an eventual volatile phase. Significant amounts of K and Rb, for example, must already have been incorporated in sanidine and biotite when mixing

occurred. Also, the role of accessory minerals is of importance, as even trace amounts may concentrate the other elements mentioned (e.g., Gromet and Silver, 1983). The rhyodacites contain ilmenite, apatite, zircon, perrierite and Fe-sulfide, and of these minerals perrierite is of special interest, being a REE-Ti silicate found to contain between 2 and 3 wt% ThO<sub>2</sub> (Van Bergen, 1984). Apatite and zircon also concentrate REE's and, of course, Zr. Textural evidence and low solubilities of apatite and zircon in felsic melts (Watson, 1979; Watson and Capobianco, 1981) suggest that these minerals and perrierite were among the early crystallizing phases or even partially represent unmelted relicts (zircon?).

Element partitioning involving a volatile phase is obviously not known for cases like these, but qualitative indications for the potential mobility of the elements may be obtained from the proportions of each in the glasses. Using available whole-rock analyses (Dupuy, 1970; Ferrara et al., 1975, 1976; Dostal and Capedri, 1975) and an average of 61.4% for the modal amount of glass (Mazzuoli and Pratesi, 1963), the following percentages can be calculated: K- 63%, Rb- 80%, Zr- 41%, La- 61%, Ce- 72%, U- 90%. Considerable but variable proportions of the elements were thus already fixed in crystalline phases and, consequently, it is extremely improbable that the role of a volatile phase would have been such as to lead to significant homogenization of hybrid and host magmas with respect to all of the elements, the more so as this was apparently not the case for the highly mobile elements Li and Cs, of which the glass contains 86 and 96% respectively. Similar lines of reasoning also argue against the opposite case, namely that a K-rich vapour phase separating from the mafic and hybrid magmas due to the pressure drop and rapid cooling (cf. Hernandez, 1982) would have dramatically contaminated the siliceous magma. Although small-scale effects are imaginable, the massif percolation that would be required to induce important chemical modifications in the entire magmachamber seems to be unrealistic.

It is thus concluded that processes of selective enrichment, if operating at all, were ineffective, and that the hybrid products of Mt. Amiata can be regarded as essentially the result of simple two-component mixing.

## Possible petrogenetic implications

There are little or no indications that processes other than simple mixing have substantially contributed to the restricted chemical variation within the siliceous lavas. Low-pressure crystal fractionation was probably insignificant on account of the high viscosity (see also Dupuy, 1970), and the Eu-anomalies may be attributed to the source region of the Tuscan magma or to residual feldspars rather than crystal settling. It should be noted that the lavas contain An-rich plagioclases in apparent disequilibrium with the melt which have an as yet uncertain origin but may well be relicts of melting. The absence of equilibrium plagioclase phenocrysts in the more mafic inclusions (as is consistent with the primary assemblages of primitive Roman HKS lavas) is also of interest in this context. Assimilation of the metasedimentary wall-rock and xenoliths has occurred, but, although its chemical effect is difficult to evaluate, it is believed to be of minor importance (Van Bergen and Barton, 1984).

The recognition that at Mt. Amiata simple mixing was the principle process and that end-members can be identified as Tuscan and primitive Roman HKS magmas, implies that they are essentially unrelated and are derived from different sources. Consequently, the various petrogenetic hypotheses proposed for both provinces are in principle applicable and need not be discussed here at length. However, one particular feature may shed new light on the possible genetic models, namely that magmas commonly considered to have their origin in the crust and upper mantle respectively and occurring in a single volcanic system, are both enriched in the same elements in comparison to 'normal' equivalents from these sources (see also Poli et al., in press). The important corollary that the enrichment in K and related elements could be explained by one process active at the crust-mantle boundary, will be briefly examined, starting from current views on the deep crustal structure and the origin of Roman magmas.

Recent geophysical data from combined seismic refraction and gravimetric studies provide evidence for the presence of two crust-mantle transitions in Tuscany (Morelli et al., 1977), one at a depth of 25-30

km, the other at some 60 km. This configuration could be the result of a low-angle underthrusting of the western margin of the Adriatic microplate by continental crust of the Corsican microplate during compressional stages of the Apennine orogenesis. The magmatic activity in Tuscany and northern Latium is associated with tensional tectonics that followed these stages at the end of Miocene times. It gave rise to a present high heat-flow anomaly in this region, where also anomalous conditions in the mantle-wedge and portions of the overlying lower crust are indicated (see Reutter et al., 1983 and references therein).

A widely accepted genetic hypothesis for the Roman potassic magmas envisages metasomatism of the mantle source with LIL-enriched fluids (Cox et al., 1976; Hawkesworth and Vollmer, 1979; Vollmer and Hawkesworth, 1980) and several authors (Cox et al., 1976; Thompson, 1977; Civetta et al., 1981; Holm et al., 1982) postulated that the ultimate source of the metasomatising fluids is likely to be a subducted slab. In view of the doubling of the crust-mantle boundary in Tuscany, it is believed that this model is not only a viable explanation for the origin of the mafic end-member of Mt. Amiata, but that it can also account for the peculiar chemical characteristics of the siliceous end-member: fluids uprising from the dehydrating deep crustal slab and containing the elements in which both end-members are enriched, may not only have metasomatized the mantle wedge but also areas of the overlying lower crust, a likely source for Tuscan magma.

The possibility that associated magmas are derived from different sources near the crust-mantle boundary that were both invaded by the same fluid prior to partial melting, is envisaged on the basis of isotope systematics also for K-rich volcanics from Virunga, East Africa (Vollmer and Norry, 1983). If, as the evidence suggests, this hypothesis indeed applies to Mt. Amiata (and Mt. Cimino), it is tempting to extrapolate it to other occurrences in the Tuscan Province. It is, however, not intended to set it against other proposed explanations for the geochemical variations in this province (e.g., special conditions and different degrees of partial melting), as they are not necessarily incompatible and as too little is known about the nature of the original source-rocks, but it should be realized that bimodality of the K-rich

magmatism in this region may be more widespread. Relatively mafic rocks and igneous inclusions occur for example near San Vincenzo, and strontium isotopes show a large range in the entire province (Barberi et al., 1971). Furthermore, it may be more than a coincidence that the volcanics of the island Capraia, west of Elba where the crust-mantle boundary is not doubled (Morelli et al., 1977), are geochemically and isotopically very different from those on the Tuscan mainland (Marinelli, 1975). Finally, the recent structural evolution of the Tuscan region is characterized by updoming and distensive tectonics (e.g., Marinelli, 1975), which are thought to be controls for the influx of fluids into source-rocks as precursor of partial melting in continental environments (Lloyd and Bailey, 1975), processes that may explain the anomalous geophysical properties of the mantle-wedge and overlying crust. Assuming that magmas were simultaneously generated in these sources, mixing may have occurred at all levels of the crust. Obviously, further detailed study is required to establish the relationship and interaction of crustal and mantle derived magmas in Tuscany and Latium.

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## APPENDIX A

### GRANDIDIERITE FROM ALUMINOUS METASEDIMENTARY XENOLITHS WITHIN ACID VOLCANICS; A FIRST RECORD IN ITALY

Manfred J. van Bergen

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#### SUMMARY

Grandidierite has been identified in two aluminous metasedimentary xenoliths from quartz-laticitic volcanic rocks from Mt. Amiata and Mt. Cimino, central Italy. Physical and electron microprobe data for the grandidierites and petrological data for the grandidierite-bearing xenoliths are presented. The grandidierites formed by a reaction involving pre-existing aluminium rich minerals, possibly at temperatures of at least 800 °C and at low pressures. The grandidierite from Mt. Amiata replaces sillimanite. Several common characteristics can be demonstrated for magmatic and metamorphic grandidierite-bearing rocks. It is suggested that metamorphic rocks in which grandidierite occurs have often undergone partial melting.

The rare Mg-, Fe-, Al-borosilicate grandidierite has been identified in the course of a detailed study of metasedimentary xenoliths from acid volcanics of southern Tuscany and northern Latium, Italy. The volcanic rocks are part of two Pliocene-Pleistocene volcanic complexes: Mt. Amiata and Mt. Cimino (fig.1). Both belong to the Tuscan-Latian Magmatic Province, which is characterized by extrusive and intrusive acidic rocks of crustal anatectic origin (Marinelli, 1976). The Mt. Cimino complex is surrounded and partly covered by the Quaternary potassic alkaline products of the Roman Magmatic Province. Chemical, petrological, and volcanological data for Mt. Amiata are given by Mazzuoli and Pratesi (1963) and for Mt. Cimino by Puxeddu (1971) and Micheluccini et al. (1972). Most volcanic rocks of the complexes contain abundant, predominantly aluminous, xenoliths of metasedimentary origin.

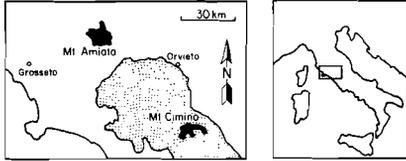


Fig.1. Location of Mt.Amiata and Mt.Cimino. Black areas belong to the Tuscan-Latian Magmatic Province, dotted areas to the Roman Magmatic Province.

Grandidierite was observed in only one xenolith from each complex. Hitherto grandidierite has been described from aplitic and pegmatitic rocks by Lacroix (1922, cited by McKie, 1965) and Zav'yalova et al. (1975), from crystalline rocks associated with charnockites by McKie (1965) and von Knorring et al.(1969), from high-grade regional metamorphic rocks by de Villiers (1940)\*, Krogh (1975), and Vrāna (1979), from rocks in contact aureoles by Black (1970) and Brewer et al.(1979), and from xenoliths in intrusive bodies by de Roever and Kieft (1976) and Semroud et al.(1976). Grandidierite has not been previously described from xenoliths in volcanic rocks, and the samples described in this paper represent the first recorded discovery of grandidierite in Italy.

#### PETROGRAPHY

Mt.Amiata sample.

The hornfels-like xenolith, MA 4.1 (about 15x5 cm), was collected from the Corno di Bellaria flow (Mazzuoli and Pratesi, 1963), which is a quartz-latitude perlitic lava. The xenolith is fine grained and shows a concentric zonation. The central part, in which most of the grandidierite is concentrated, consists mainly of sanidine, green spinel, and biotite, while plagioclase and biotite are the major phases in the ~0.5 cm wide rim. Hypersthene is present in the outer part of this rim. The total amount of grandidierite in the xenoliths is less than 1%.

Accessory minerals are sillimanite, ilmenite, graphite, apatite, and

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\*) de Villiers considered his samples to be of pegmatitic origin. Following Vrāna(1979) it is listed under regional metamorphic rocks, based on the similarities with the occurrence described by this author.

zircon. The spinel occurs both disseminated through the xenolith and in concentrations together with a turbid isotropic mass (presumably altered plagioclase) around grandidierite crystals (fig.2a).

These concentrations have the shape of square prisms, up to 1 cm long, and are believed to be pseudomorphs after andalusite, which is often replaced by sillimanite during high-grade thermometamorphism before complete conversion into the spinel with or without plagioclase has taken place, as observed in other xenoliths (van Bergen, in prep.). Parallel orientated ilmenite grains indicate a weak relict foliation.

Grandidierite occurs almost exclusively within the spinel pseudomorphs. It forms idiomorphic crystals with the shape of slender prisms, up to 1 cm long and less than 1 mm wide. A representative basal section is shown in fig.2b. Locally a poor (100) cleavage is visible. The crystals have irregular cracks, parallel to the basal plane, and they often contain small rounded inclusions (fig.2c). The c-axes of the grandidierites are generally parallel to the long axes of the prism-shaped spinel pseudomorphs. Although closely associated with spinel, grandidierite also shows grain-to-grain contacts with biotite and feldspars. A sillimanite relict, containing several idiomorphic grandidierite crystals was found in the core of one spinel pseudomorph (fig.2d).

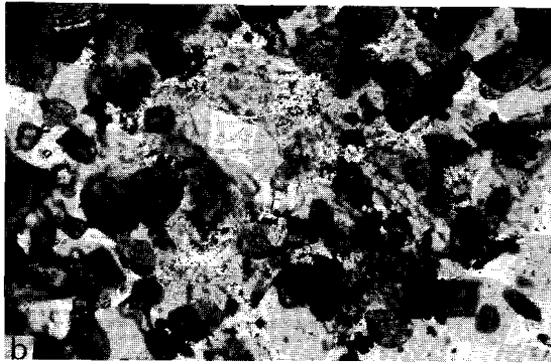
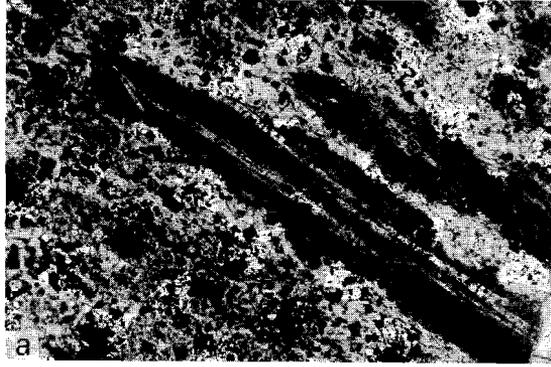
The grandidierite is strongly birefringent and displays a characteristic blue pleochroism. The extinction is straight and the elongation is

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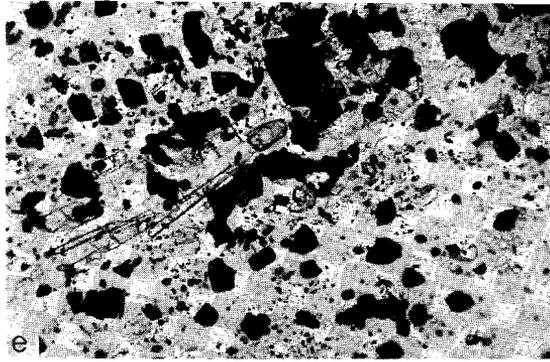
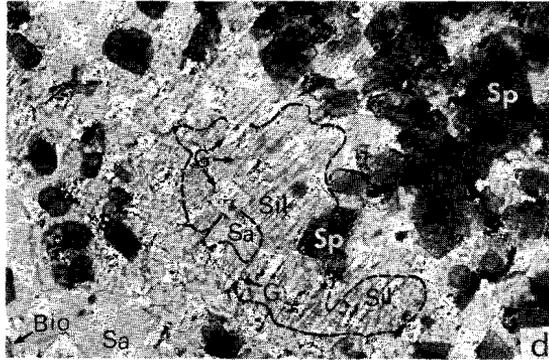
Optical orientation	c $\perp$ optical axial plane
Pleochroism	$\alpha$ = bright blue $\beta$ = colourless $\gamma$ = light greenish blue
Absorption scheme	$\alpha > \gamma > \beta$
Axial angle (U-stage)	$2V_{\alpha} = 32^{\circ} \pm 1^{\circ}$ (MA 4.1) $2V_{\alpha} = 27^{\circ} \pm 1^{\circ}$ (MC 6.9)
Dispersion	r < v clear
Birefringence	$\Delta = 0.0364$
Refractive indices (Na light)	$\alpha' = 1.5982 \pm 0.0002$ $\beta = 1.6290 \pm 0.0002$ $\gamma = 1.6346 \pm 0.0002$ (calculated)

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*Table 1. Optical data of grandidierite from Mt. Amiata and Mt. Cimino. Values for birefringence and refractive indices apply to MA 4.1.  $\alpha$  and  $\beta$  were determined by a double variation method;  $\gamma$  was calculated after determination of the birefringence with an Ehringhaus rotary compensator.*



*Fig.2 (a) MA 4.1. Spinel pseudomorphs after andalusite/sillimanite porphyroblasts, containing slender grandidierite crystals. The matrix consists of sanidine, spinel, and biotite. Nicols parallel. Length of photograph: 5.1 mm. (b) MA 4.1. Eight-sided basal section of grandidierite in an isotropic substance. The long axis of this section is parallel to  $\gamma$ . Nicols parallel. Length of photograph: 0.55 mm.*



(c) MA 4.1. Grandidierite crystal in an aggregate of spinel and an isotropic substance (altered plagioclase?). Note the cracks parallel to the basal plane and the rounded inclusions of green spinel. Nicols parallel. Length of photograph: 1.3 mm. (d) MA 4.1. Small grandidierite crystals in a relict of sillimanite enclosed by plagioclase. Nicols parallel. Length of photograph: 0.55 mm. G=grandidierite, Sil=sillimanite, Sa=sanidine, Sp=spinel, P=plagioclase, Bio=biotite.

(e) MC 6.9. Slender grandidierite crystals in association with two rounded grains of corundum (high relief). Dark grains: green spinel and minor biotite. Light areas: sanidine and corroded plagioclase. Nicols parallel. Length of photograph: 1.3 mm.

variable. The optical axial plane is parallel to (001). Refractive indices and further optical data are given in Table I. The X-ray pattern of a single grain from the Mt. Amiata sample is compared with data from Olesch and Seifert (1976, synthesized Mg end-member grandidierite) and McKie (1965, grandidierite from Sakatelo, Madagascar, with  $Fe/(Fe+Mg) = 0.118$ ) in Table II. This pattern identifies the mineral as grandidierite.

Mt. Cimino (MC 6.9)		Mt. Amiata (MA 4.1)		Sakatelo (McKie, 1965)		Synthetic (Olesch & Seifert, 1976)	
d <sub>obs</sub>	I	d <sub>obs</sub>	I	d <sub>obs</sub>	I	d <sub>obs</sub>	I
5.53	80	5.53	90	5.482	vs	5.451	100
5.17	100	5.21	100	5.17	vvs	5.179	91
		5.05	90	5.04	vvs	5.019	87
4.86	40	4.86	20	4.84	w	4.816	12
				4.59	vw		
		3.97	10	3.97	vw	3.958	12
3.78	70			3.75	vw	3.752	15
		3.71	50	3.708	ms	3.693	55
3.46	50	3.46	20	3.449	w	3.431	18
3.28	10	3.30	10	3.29	vw	3.291	5
3.13	5	3.15	20	3.150	w	3.146	13
				2.99	vw		
2.95	15	2.96	30	2.956	m	2.957	23
2.92	5			2.92	vw		
				2.878	w	2.868	20
2.85	5	2.85	10	2.855	vw		
2.75	85	2.75	80	2.744	vs	2.732	77
		2.66	10	2.66B	vw		
2.60	15	2.60	40	2.602	m		
2.57	20	2.56B	40	2.584	ms	2.595	38
				2.551	mw	2.540	20
		2.51	20	2.515	w	2.512	20
		2.45	10	2.48B	vw	2.468	2
		2.40	5	2.41B	vw		
2.33	5	2.34	10	2.337	vw	2.342	4
		2.29	30	2.287	mw	2.281	21
		2.21	30	2.210	mw	2.202	21
2.15	60	2.16	60	2.166	s	2.165	34
				2.149	m	2.135	20
				2.072	vw		
		2.05	10	2.050	vw		
2.02	20	2.03	20	2.031	mw	2.039	11
		2.01	10	2.012B	vw		
1.948	20	1.949	30	1.946	mw	1.9501	13
numerous weak reflections		numerous weak reflections				numerous weak reflections	

Table 2. X-ray patterns of the grandidierites from Mt. Cimino and Mt. Amiata compared with the grandidierite from Sakatelo ( $Fe/(Fe+Mg)=0.118$ ) and a synthetic Mg end-member grandidierite.

MC 6.9: single crystal in a Debye-Scherrer camera,  $Co-K_{\alpha}$  radiation.

MA 4.1: single crystal in a Gandolfi camera containing a two-axes rotation sample-holder,  $Co-K_{\alpha}$  radiation.

Both determinations were made at the Z.W.O. Laboratory for Isotope Geology, Amsterdam, by R.H. Verschure.

Sanidine is the major phase. It has a variable grain size. The smaller grains tend to form polygonal textures, especially where the sanidine is free of inclusions. Plagioclase grains are irregular in shape and are often separated from each other by a thin glass film. Glass, either alone or around small spinel grains, is also present as inclusions in the plagioclase. Some plagioclase grains show a slight normal zonation. Spinel, abundant and ubiquitous, is dark green and hercynitic. It forms subidiomorphic to idiomorphic crystals. Biotite is

strongly pleochroic:  $\alpha$  yellow and  $\gamma$  dark brown. The randomly orientated crystals often contain ilmenite and spinel inclusions.

Mt. Cimino sample.

The xenolith, MC 6.9 (about 12x6 cm), has roughly the same characteristics as the Mt. Amiata sample. It was found in a quartz-latic ignimbrite near Bagnaia (see map by Micheluccini et al., 1971). The main components are sanidine, green spinel, biotite, and plagioclase. Corundum is present as relatively large anidiomorphic grains, mainly in spinel-rich parts (fig. 2e). The zonation within the xenolith and the accessory mineral content are similar to MA 4.1, except for the absence of sillimanite relicts. The spinel pseudomorphs, which occur in MA 4.1, are also lacking. Grandidierite is disseminated through the rock and is usually accompanied by spinel. It has essentially the same properties as in MA 4.1, but the crystals are considerably smaller and they are corroded along crystal boundaries and cracks. The largest dimensions rarely exceed 100 microns. Several crystals are enclosed in biotite. Apart from contact with biotite there are also grain-to-grain contacts with feldspars and corundum. Optical data are given in Table I and a single-crystal X-ray pattern in Table II. Plagioclase is not limited to a plagioclase-biotite rim. The characteristics of the other main phases do not differ from MA 4.1.

#### MINERAL CHEMISTRY

Electron microprobe analyses of the grandidierites were carried out at two laboratories using different apparatus. The results and mean values are listed in Table III. The boron contents, which are expected to be about 10-12 wt%, could not be determined. The analyses are in good agreement with data in the literature (cf. Semroud et al., 1976, Table I). The Fe/(Fe+Mg) ratios, calculated from the mean values, are relatively high and in fact the MA 4.1 grandidierite is the most Fe-rich natural specimen described to date. The combination of the high Fe/(Fe+Mg) ratio and the high refractive indices (Table I) in this sample is in accordance with the positive linear correlation between the mean refractive indices of grandidierite and its  $X_{Fe}$ , which was demonstrated

	MA 4.1			MC 6.9		
	1	2	mean	3	4	mean
SiO <sub>2</sub>	19.9	19.9	19.9	20.0	19.8	19.9
TiO <sub>2</sub>	n.d.	0.02	0.02	n.d.	0.04	0.04
Al <sub>2</sub> O <sub>3</sub>	50.8	49.9	50.35	50.9	50.3	50.6
FeO	7.8	7.7	7.75	6.6	6.9	6.75
MnO	0.14	0.1	0.12	0.08	0.1	0.09
MgO	9.1	9.3	9.2	9.8	9.7	9.75
CaO	n.d.	0.00	0.00	n.d.	0.01	0.01
Na <sub>2</sub> O	n.d.	0.01	0.01	n.d.	0.00	0.00
K <sub>2</sub> O	n.d.	0.04	0.04	n.d.	0.06	0.06
Total	87.74	86.97	87.39	87.38	86.91	87.20
Numbers of atoms on the basis of fifteen oxygens						
Si	1.99	2.01	2.00	2.00	1.99	2.00
Ti	-	0.00	0.00	-	0.00	0.00
Al	5.99	5.94	5.97	5.99	5.97	5.98
Fe	0.65	0.65	0.65	0.55	0.58	0.57
Mn	0.01	0.01	0.01	0.01	0.01	0.01
Mg	1.36	1.40	1.38	1.46	1.46	1.46
Ca	-	0.00	0.00	-	0.00	0.00
Na	-	0.00	0.00	-	0.00	0.00
K	-	0.00	0.00	-	0.01	0.01
Fe/(Fe+Mg)			0.320			0.281

Table 3. Chemical compositions of the grandidierites from Mt. Amiata (MA 4.1) and Mt. Cimino (MC 6.9).

Electron microprobe analyses on the same polished thin sections were performed both at the electron microprobe laboratory of the Instituut voor Aardwetenschappen, Vrije Universiteit Amsterdam (1 and 3) and at the Vening Meinesz Laboratorium voor Geochemie, Rijks Universiteit Utrecht (2 and 4) by P. Maaskant and the author respectively. 1, 2, 3 and 4: mean values of at least four grains. n.d.: not determined.

by Olesch and Seifert (1976).

Differences in mineral chemistry between the two xenoliths are small. The Mt. Amiata grandidierite has a higher Fe/(Fe+Mg) ratio. The Fe/(Fe+Mg) ratios of seventeen co-existing spinel and biotite grains show varying values. In MA 4.1 the  $X_{Fe}^{spi}$  ranges from 0.75 to 0.79 and the  $X_{Fe}^{bi}$  from 0.44 to 0.53; in MC 6.9 the  $X_{Fe}^{spi}$  ranges from 0.67 to 0.75 and the  $X_{Fe}^{bi}$  from 0.50 to 0.57. The biotites in the plagioclase-biotite rims have the lowest Fe contents. The hypersthene has not been considered because of its isolated position in the outer part of the plagioclase-biotite rims, and because of its probable formation by reaction with the surrounding magma.

As most analyses were carried out on minerals in close proximity to each other, the  $X_{Fe}$  values may be representative of at least local equilibrium, especially regarding the closely associated grandidierite and spinel or part of the spinel. Although total rock equilibrium may not

have been reached, the following general relation holds:

$$X_{\text{Fe}}^{\text{spi}} > X_{\text{Fe}}^{\text{bi}} > X_{\text{Fe}}^{\text{grand}}$$

Microprobe analyses of sanidines yielded  $\text{Ab}_{16}\text{Or}_{83}\text{An}_1$  for MA 4.1 and  $\text{Ab}_{18}\text{Or}_{81}\text{An}_1$  for MC 6.9. An percentages of unzoned plagioclase range from 55 to 58% and from 47 to 73% respectively. An contents increase from the core to the rim of the xenoliths, i.e. towards the volcanic rock.

#### GENESIS OF THE GRANDIDIERITE

The following genetic sequence for the grandidierite-bearing core of sample MA 4.1 is based on textural relations, including those observed in similar xenoliths (van Bergen, in prep.). Sillimanite, which is probably a paramorph after andalusite, is clearly a relict phase. Green spinel partly replaced the sillimanite along crystal boundaries and it formed spinel pseudomorphs. In other xenoliths sillimanite and pre-existing andalusite are often replaced by spinel with or without plagioclase. Subsequently the remaining sillimanite was converted to grandidierite. Some of the spinel was used in this reaction. The often-observed preferential orientation in the pseudomorphs may be the result of some similarity in crystal structure between grandidierite and sillimanite. According to Stephenson and Moore (1968) the structural relationship with andalusite is closer, however. Biotite is generally a late phase, although the presence of an early generation cannot be excluded. Sanidine is clearly the last-formed mineral.

Because in MC 6.9 sillimanite is absent and the grandidierite is more or less randomly distributed, there is no evidence that grandidierite formed by the same mechanism as in MA 4.1. The genetic sequence of spinel, grandidierite, biotite and sanidine is similar. Plagioclase is a late phase but is prior to sanidine. Time relations between corundum and grandidierite and between corundum and spinel are not quite clear. Other xenoliths show corundum to be contemporaneous with or later than spinel. That grandidierite is found in spinel-rich parts of the sample and that it contains small rounded spinel inclusions emphasize a genetic relation with the spinel.

Two stages can be distinguished in the thermometamorphism which in

general affected the Mt. Amiata and Mt. Cimino xenoliths: a contact-metamorphic stage and a subsequent pyrometamorphic stage (Rodolico, 1935). The grandidierite-bearing samples show aspects of both stages. Although a strict separation between these stages is difficult, the generation of grandidierite is most likely to have taken place during the latter.

Crystallization of grandidierite after engulfment of the xenoliths by the magma might point to a metasomatic supply of boron from the magma. However, the scarcity of grandidierite-bearing xenoliths, and the fact that in the same outcrops similar xenoliths do not contain grandidierite (nor tourmaline nor any other boron mineral) make it improbable that the magma was the source of boron. The small amounts of grandidierite may have derived boron from primary tourmaline, either directly by a high-temperature transition of tourmaline into grandidierite (MC 6.9(?)), or after a small-scale redistribution of boron (MA 4.1, MC 6.9(?)) possibly by means of an interstitial melt. Regarding other grandidierite occurrences in metamorphic environments, most authors are also inclined to attribute its presence to a boron enrichment of the original sediments (Krogh, 1975; Semroud et al., 1976; de Roever and Kieft, 1976) although elsewhere boron metasomatism may have taken place (e.g. Black, 1970).

#### COMPARISON WITH OTHER OCCURRENCES

Grandidierite has been described from pegmatitic and aplitic rocks, crystalline rocks associated with charnockites, high-grade regional metamorphic rocks, and thermometamorphic rocks (contact aureoles and xenoliths). Although petrological data on some grandidierite occurrences, especially those in Madagascar, are inadequate, it seems possible to recognize some common characteristics in all of these rocks and to discuss the implications with respect to the formation of grandidierite. All occurrences known to the author are listed in Table IV, together with mineral associations and references. In addition, a recently reported occurrence in the aureole of a hypersthene granodiorite in the Mchinji area, Malawi, may be mentioned (Brewer et al., 1979). Here grandidierite and tourmaline occur sporadically in an originally low-

	quartz	K-feldspar	plagioclase	spinel	corundum	sillimanite	andalusite	cordierite	biotite	garnet	hypersthene	tourmaline	kornerupine
1. Mt. Amiata (Italy)		x	x <sup>1</sup>	x		r			x			x <sup>1</sup>	
2. Mt. Cimino (Italy)		x	x	x	x				x			x <sup>1</sup>	
3. Maratakka (Surinam)		x	x	x	x			x	x				
4. Tizi-Ouchen (Algeria)			x	x	x				x				
5. Blanket Bay (Cuvier Island, New Zealand)											SP	x	s
6. Landing Bay (Cuvier Island, New Zealand)			x					x				x	s
7. Transbaikaliya (USSR)		x	x	x				x	x			x	
(a)	x <sup>2</sup>	x <sup>2</sup>	x										
(b)	x	x	m					x					x
8. Andrahomana (Madagascar)	x	x		x		x	x	x		ALM			
9. Sakatelo (Madagascar)								x					
10. Sahakondro (Madagascar)								PHL					
11. Fort Dauphin area (Madagascar) <sup>3</sup>				x				PHL					
12. Vestpolltind (Norway)	x	x						x	x				
13. Lukusuzi river (Zambia) <sup>4</sup>	x			m	x	x			x			x	x
14. Natal (S. Africa)	x								x	m		x	x

Table 4. Mineral contents of grandidierite-bearing rocks (?a excluded).

1-4: thermometamorphic xenoliths; 5-6: hornfelses from contact aureole; 7: hornfels from contact aureole; without grandidierite (a), containing aplitic and granitic grandidierite-bearing veinlets (b); 8: pegmatitic and aplitic rocks; 9-11: rocks in association with charnockites; 12-14: high-grade regional (poly-) metamorphic rocks.

<sup>1</sup> Present only in outer rims of the xenoliths. <sup>2</sup> Present only in interstitial segregations. <sup>3</sup> With diopside. <sup>4</sup> With dumortierite.

r=relict, m=in minor amounts, s=secondary, SP=spessartine, ALM=almandine, PHL=phlogopite.

References: 1 and 2 - this work; 3 - de Roever & Kieft (1976); 4 - Semroud et al. (1976); 5 and 6 - Black (1970); 7 - Zav'yalova et al. (1975); 8 - Lacroix (1922, cited by McKie, 1965) and Semroud et al. (1976); 9 - McKie (1965); 10 - Christophe-Michel-Lévy et al. (1959) and de la Roche (1963); 11 - von Knorring et al. (1969); 12 - Krogh (1975); 13 - Vrána (1979); 14 - de Villiers (1940).

grade quartz-rich metasedimentary rock, the former only in association with sillimanite that probably originated during the thermometamorphism. The uncertain occurrence recorded by Hlawatsch (1918, cited by McKie, 1965) has not been included.

Apart from the common presence of biotite/phlogopite, the dominant presence of aluminium-rich minerals is striking. The genesis of grandidierite is related to aluminous rocks, which is in accordance with its mineral chemistry (Semroud et al., 1976). These authors pay attention to the fact that in magmatic and metamorphic rocks grandidierite usually crystallizes after the aluminium-rich minerals and before feldspars and quartz (if present). The Mt.Amiata and Mt.Cimino occurrences are good examples of this genetic sequence.

Direct crystallization of grandidierite instead of an  $Al_2SiO_5$  phase in boron-enriched environments is suggested by McKie (1965) for contaminated magmas, and by Krogh (1975) for metamorphic rocks. In experiments Rosenberg and Foit (1975, cited by Olesch and Seifert, 1976) found grandidierite as a high-temperature breakdown product of tourmaline.

For the formation of grandidierite, reaction of aluminium-rich minerals with boron or boron minerals must also be taken into account, especially with regard to the sillimanite-bearing Mt.Amiata rock and the above-mentioned genetic sequence. Evidence for reaction with other boron minerals is scarce. The presence of tourmaline next to grandidierite is reported only from Transbaikaliya (Zav'yalova et al., 1975), while in the New Zealand occurrences tourmaline belongs to a late hydrothermal phase (Black, 1970), and in both the Natal and Lukusuzi River occurrences grandidierite predates kornrupine and tourmaline (de Villiers, 1940; Vrāna, 1979). The reaction with boron must be seriously considered. This element may be derived from a melt phase, the presence of which is obvious for the magmatic occurrences. The former presence of an interstitial melt phase in several other occurrences cannot be excluded. Partial melting could have taken place to a limited extent in the central Italian xenoliths. De Roever and Kieft (1976) suggest partial anatexis for the Maratakka xenoliths and it is interesting to notice the common absence of at least one of the

leucocratic minerals (quartz, plagioclase, K-feldspar) in almost all non-vein rocks (Table IV). In Transbaikaliya grandidierite-bearing aplitic and granitic veinlets cut hornfelses with interstitial segregations of quartz and K-feldspar (Zav'yalova et al., 1975). Partial melting may lead to the aluminous environments favourable for the formation of grandidierite, and the conditions of partial melting are compatible with some independent P-T estimations on the stability of this mineral (see below). Consequently a grandidierite-forming reaction involving aluminium minerals and boron from a melt-phase must be considered for some of the magmatic as well as the metamorphic rock types.

#### STABILITY OF GRANDIDIERITE

The pegmatitic and aplitic occurrences indicate that grandidierite is stable under relatively high-temperature conditions. Estimates of temperatures for the metamorphic occurrences yielded minimum values of 600°C for the Cuvier Island aureole (Black, 1970) and 700°C for the Maratakka xenoliths (de Roever and Kieft, 1976), both based on mineral assemblages. Krogh (1975), using various geothermometers, calculated temperatures of 850-900°C for the Vestpolltind area. Pressure estimates range from less than 300 bars (Cuvier Island) to 10 kb (Vestpolltind). As for the central Italian occurrences Puxeddu (1971) estimated the lower limits of temperature of the Mt.Cimino magma at its origin between 850 and 880°C on chemical grounds, and because of the similarity between the two magmas approximately the same temperatures could apply to the Mt.Amiata magma. The mineral contents of the grandidierite-bearing xenoliths within the volcanic rocks of Mt.Cimino and Mt.Amiata point to temperatures of the sanidinite facies. The occurrence of grandidierite in xenoliths in lavas suggests that at high temperatures this mineral is stable at very low pressures.

In synthetic systems grandidierite was first mentioned by Rosenberg and Foit (op.cit.) as a high-temperature breakdown product of alkali-free tourmalines. Olesch and Seifert (1976) synthesized the Mg end-member at  $P_{\text{H}_2\text{O}} = 1$  kbar and temperatures above 780°C, and a grandidierite with  $X_{\text{Fe}} = 0.1$  at 700°C with QFM buffer. From an experimental study of korner-

upine, Werding and Schreyer (1978) suggested that grandidierite is restricted to environments with relatively high boron/water ratios.

In general grandidierite is a high-temperature mineral, probably stable from very low to high pressures. It is likely to be the natural high-temperature breakdown product of tourmaline and a stable equivalent of this mineral in boron-enriched aluminous rock systems. While tourmaline is a common mineral in contact aureoles around acid intrusives, grandidierite is often associated with thermometamorphic rocks in relation to intrusive bodies which are generally more basic: granodioritic (Tizi-Ouchen, Mchinji area), dioritic (Cuvier Island), essexitic-granodioritic (Transbaikaliya), gabbroic (Maratakka). If the influence of total-rock chemistry (e.g. Na content) can be neglected, this can be explained by temperature differences. The high temperature of more basic intrusions favours the growth of grandidierite rather than tourmaline, provided that enough boron is present in the country rock at the peak of thermometamorphism. If the boron is supplied by the magma during cooling, tourmaline may be expected to be the stable boron mineral also around more basic intrusives.

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## APPENDIX B

### PERRIERITE IN SILICEOUS LAVAS FROM MT. AMIATA (CENTRAL ITALY)

Manfred J. van Bergen

*Mineralogical Magazine, in press*

Perrierite and chevkinite are rare REE-Ti silicates reported from granitic and syenitic pegmatites and igneous rocks, volcanic ash beds, ignimbrites and anorthosite (e.g., Jaffe et al., 1956; Young and Powers, 1960; Mitchell, 1966; Izett and Wilcox, 1968; Raade, 1970; Brooks and Rucklidge, 1976; Segalstad and Larsen, 1978; McDowell, 1979; Harding et al., 1982). The minerals are easily confused because of their close chemical and structural relationships which have been discussed by Bonatti and Gottardi (1954, 1966), Bonatti (1959), Gottardi (1960), Lima de Faria (1962) and Calvo and Faggiani (1974). Experimental studies revealed that perrierite and chevkinite exhibit thermal polymorphism within certain compositional ranges (Ito, 1967; Ito and Arem, 1971). The type-locality of perrierite is Nettuno, Rome (Italy), where Bonatti and Gottardi (1950) found it as a new mineral in shore sands derived from pyroclastics. This communication describes an occurrence in siliceous lavas and, to the best of my knowledge, records the second discovery in Italy.

Routine energy-dispersive microprobe work on the lavas of Mt. Amiata, a Pleistocene volcanic complex in southern Tuscany, which consists of lavas and domes with both calcalkaline and potassic-alkaline affinities, revealed the presence of a REE-Ti silicate with a strong yellowish brown-reddish brown-opaque pleochroism. The mineral was found in studied specimens of the so-called early rhyodacites, which are K-rich lavas containing some 66 wt.% SiO<sub>2</sub>. These mineralogically uniform rocks carry phenocrysts of plagioclase, sanidine, pyroxene (both ortho and clino)

and biotite in addition to about 61 % perlitic glass. Minor and accessory minerals are ilmenite, apatite, zircon, Fe-sulfide and embayed quartz. Chemical and mineralogical details about these volcanics are to be found in Mazzuoli and Pratesi (1963) and Van Bergen et al. (1983). Mazzuoli and Pratesi (1963) reported the ubiquitous presence of very rare crystals of non-metamict allanite with a strong brown-opaque pleochroism. In the thin sections available for microprobe analysis, all grains that conform to this description proved to have the composition of perrierite or chevkinite, whereas allanite was not found. As these minerals are difficult to distinguish optically, this suggests that the REE-Ti silicate is a common accessory phase in all the siliceous lavas of Mt. Amiata. Abundances do not exceed a few tiny grains per thin section, however.

Typical habits are stubby rounded crystals of less than 200  $\mu\text{m}$  which sometimes are included in orthopyroxenes but more often occur along their rims and as discrete grains. Elongate crystals also occur but are extremely rare. Texturally the mineral occupies a position in the crystallization sequence comparable to that of ilmenite, and was probably among the early forming minerals. Young and Powers (1960) reached a similar conclusion for chevkinites in a number of siliceous volcanic ashes from the United States, whereas McDowell (1977) suggested that the chevkinite in the Little Chief Granite, California appeared late in the period of phenocryst crystallization.

Several X-ray diffraction patterns of very small, unheated grains were made in a Gandolfi camera fitted with a two-axes rotating sample-holder. As pointed out by Bonatti and Gottardi (1954), Lima de Faria (1962) and Mitchell (1966), X-ray powder data should be sufficiently diagnostic to distinguish between natural perrierite, chevkinite and allanite. The results correspond well with perrierite, although occasional reflections were found that could also be attributed to chevkinite. The determination as perrierite is based on the consistent presence of two typical strong reflections at d-values between 2.94 and 3.00  $\text{\AA}$ .

Two samples were selected for quantitative analysis. Whole-rock major element compositions and CIPW-norms are given in Table 1.

	1	2		1	2
SiO <sub>2</sub>	65.37	65.53	qz	19.54	19.89
TiO <sub>2</sub>	0.62	0.60	or	31.02	30.73
Al <sub>2</sub> O <sub>3</sub>	15.64	15.60	ab	21.24	21.66
Fe <sub>2</sub> O <sub>3</sub>	0.76	0.66	an	15.90	15.72
FeO	2.76	2.77	di	0.72	0.19
MnO	0.06	0.06	hy	7.31	7.48
MgO	1.66	1.57	mt	1.10	0.96
CaO	3.58	3.40	il	1.18	1.14
Na <sub>2</sub> O	2.51	2.56	ap	0.35	0.33
K <sub>2</sub> O	5.25	5.20			
P <sub>2</sub> O <sub>5</sub>	0.15	0.14			
L.O.I.	1.64	1.92			

Table 1. Analyses and CIPW-norms of perrierite-bearing lavas.

1. Sample MA1
2. Sample MA19

Perrierite analyses were performed with an automated TPD microprobe using wavelength-dispersive techniques and a Tracor-Northern correction program. Operating conditions were 15 kV acceleration voltage, ca. 40 nA sample current and counting times between 20 and 100 seconds. Standards for Y and the rare-earth elements (REE) were the artificial glasses prepared by Drake and Weill (1972) which were moved under the beam during data collection. There are few recent (microprobe) analyses of perrierites and chevkinites (e.g., Brooks and Rucklidge, 1976; Segalstad and Larsen, 1978; McDowell, 1979; Harding et al., 1982). Older (wet chemical) data are summarized in Jaffe et al. (1956) and semiquantitative results for perrierites from occurrences in Virginia are reported in Mitchell (1966). In general, both minerals have variable but fairly similar compositions, except for some Sr, Th or Nb-rich varieties (see Haggerty and Mariano, 1983). However, taking into account that certain 'chevkinites' have been re-identified as perrierites (Bonatti, 1959; Lima de Faria, 1962; Mitchell, 1966) the available analyses suggest that perrierites tend to be slightly poorer in FeO<sup>tot</sup> and richer in Al<sub>2</sub>O<sub>3</sub> and CaO, within limited ranges for other elements. This observation is qualitatively consistent with experimental results which suggest that the transition of chevkinite to perrierite is influenced by the variation in ionic size in the distinct structural sites, and may be accompanied by the coupled substitution of (1) Ce by Ca and of Fe<sup>2+</sup> by Al; (2) Fe<sup>2+</sup> by Al and of Ti<sup>4+</sup> by Al; and (3) Fe<sup>2+</sup> by Al and

	oxides			cations**	
	1	2		1	2
SiO <sub>2</sub>	19.93	19.74	Si	8.045	8.000
TiO <sub>2</sub>	18.89	18.68	Ti	5.737	5.692
Al <sub>2</sub> O <sub>3</sub>	3.36	3.44	Al	1.600	1.647
FeO*	5.42	5.45	Fe	1.832	1.848
MgO	0.66	0.84	Mg	0.399	0.509
CaO	4.71	4.70	Ca	2.038	2.043
La <sub>2</sub> O <sub>3</sub>	9.91	9.28	La	1.477	1.387
Ce <sub>2</sub> O <sub>3</sub>	20.13	20.03	Ce	2.975	2.971
Pr <sub>2</sub> O <sub>3</sub>	2.14	2.18	Pr	0.315	0.323
Nd <sub>2</sub> O <sub>3</sub>	6.74	7.08	Nd	0.972	1.024
Sm <sub>2</sub> O <sub>3</sub>	0.74	0.72	Sm	0.103	0.102
Gd <sub>2</sub> O <sub>3</sub>	0.45	0.44	Gd	0.061	0.060
Y <sub>2</sub> O <sub>3</sub>	0.36	0.39	Y	0.078	0.086
ZrO <sub>2</sub>	0.80	0.71	Zr	0.158	0.141
ThO <sub>2</sub>	2.60	2.90	Th	0.239	0.268
Total	96.84	96.58	Σ	26.029	26.101

Table 2. Electron microprobe analyses of perrierite from Mt. Amiata. \*Total iron listed as FeO. \*\*Cation proportions based on 44 oxygens.

1. Sample MA1 mean of 6 spots in 2 grains

2. Sample MA19 mean of 9 spots in 3 grains

Mn, P and Nb were looked for but not detected. The presence of a few tenths of a percent Sc<sub>2</sub>O<sub>3</sub> was semiquantitatively demonstrated for the perrierite in MA19.

of Si<sup>4+</sup> by Al (Ito, 1967), although it should be noted that the situation in the natural minerals is still a matter of discussion (see Segalstad and Larsen, 1978; McDowell, 1979; Haggerty and Mariano, 1983).

The analysed grains from Mt. Amiata show little variation and agree with this tendency in the chemical characteristics of perrierite, as they are poor in FeO<sup>tot</sup> and fairly rich in Al<sub>2</sub>O<sub>3</sub> and CaO, as well as in ThO<sub>2</sub> (Table 2). Cation proportions are in agreement with the general formula REE<sub>4</sub><sup>3+,2+</sup>(Ti<sup>4+,2+</sup>M<sup>2+</sup>)(TiO<sub>4</sub>)<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub> given by Gottardi (1960). As appears from the partial REE-pattern of chondrite-normalized abundances (Fig.1), the perrierite is extremely enriched in the light REE relative to the heavy REE, with a (Ce/Y)<sub>ch</sub> ratio of 135. This fractionation of the REE compares well with that found in a mineral referred to as REE-rich sphene from the Skye Tertiary granites (Exley, 1980). As tentatively suggested in Harding et al.(1982), this mineral may actually be chevkinite in view of their corresponding compositions. Other analyses of perrierite and chevkinite in the literature also indicate a strong

	Perrierite <sup>1</sup> (%)	Glass <sup>2</sup> (ppm)	Partition coefficient
La	8.18	93	880
Ce	17.13	162	1057
Zr	0.56	149	38

Table 3. Abundances of La, Ce and Zr in perrierite and co-existing glass, and calculated partition coefficients.

1. mean values of MA1 and MA19
2. mean values of four XRF-analyses of glasses separated from samples that were taken from the same lavas as MA1 and MA19 (Ferrara et al., 1976).

preference for the light REE. Possible anomalies of Eu are not apparent because of difficulties in the determination of this element by the methods used.

Several chemical characteristics of the perrierite reflect those of the Mt. Amiata lavas. Whole-rock trace element abundances (e.g. Ferrara et al., 1975 and 1976; Van Bergen et al., 1983; Van Bergen, in prep.) indicate very high contents of Th (37-45 ppm) and strong enrichment in the light REE, although the  $(Ce/Y)_{ch}$  ratio of 12 is considerably lower than that of the perrierite. La, Ce and Zr abundances in the glasses (ca. 73 wt.% SiO<sub>2</sub>) were reported by Ferrara et al. (1976) which allows calculation of perrierite-glass partition coefficients for these elements. Because only averaged compositions obtained from different samples can be used, these coefficients (Table 3) are tentative, but the chemical uniformity of the early rhyodacites should give a good approximation. The expected high coefficients emphasize the importance of perrierite in controlling the distribution of many trace elements in the lavas of Mt. Amiata. This is also illustrated by the large proportions of total whole-rock abundances that the mineral contains, taking an assumed modal amount of only 0.05%: La-49%, Ce-59%, Sm-30%, Th-28%. Nevertheless, the REE-pattern of perrierite is unlike that of the rhyodacite, even disregarding the significant negative Eu-anomaly in the latter (Fig. 1). This implies that other phases substantially contribute to the REE-characteristics of the rock. Apatite and zircon are the most likely candidates in addition to the glass, but due to the relatively low levels of REE in these minerals this could only be qualitatively confirmed in the case

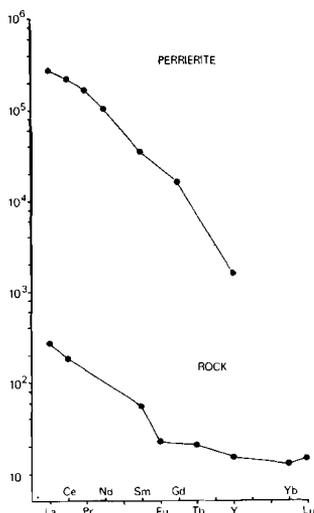


Fig.1. Average chondrite-normalized abundances of REE and Y in the perrierite and in perrierite-bearing lavas (INAA data; van Bergen, in prep.). Note that Y is plotted in the place of Ho, and that the microprobe analyses of the mineral did not include Eu.

of apatite.

Several authors have drawn attention to the role that accessory minerals such as apatite, allanite, zircon, sphene and monazite may play in the evolution of felsic igneous rocks (e.g., Gromet and Silver, 1983), indicating the necessity to include these minerals into petrogenetic models, particularly those involving fractionation of the REE. Because perrierite and chevkinite have been recorded from various types of such rocks and given the fact that trace amounts can be easily overlooked or misidentified, these minerals may be more common and thus petrologically more important than is generally realized. The possible presence of perrierite and/or chevkinite in other occurrences of the Tuscan Magmatic Province should, for example, be taken into consideration.

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*j.b.d.a.v.d.a.*

## CURRICULUM VITAE

(toegevoegd op verzoek van het College van Dekanen van de Rijksuniversiteit te Utrecht)

Manfred J. van Bergen werd op 9 februari 1950 geboren te 's-Gravenhage. Hij doorliep het Openbaar Lyceum 'Schoonoord' te Zeist en behaalde in 1968 het diploma Gymnasium  $\beta$ . In hetzelfde jaar begon hij de studie Geologie aan de Rijksuniversiteit te Utrecht. In mei 1971 werd het kandidaats examen G3 afgelegd en in mei 1977 het doctoraalexamen (cum laude), met hoofdvakken Geochemie en Structurele en Toegepaste Geologie en bijvak Sedimentologie. In de jaren 1971 tot en met 1977 werden assistentschappen vervuld bij het Vening Meinesz Laboratorium (Geochemie) en het Geologisch Instituut (Structurele en Toegepaste Geologie). Van juni 1977 tot september 1980 was hij als wetenschappelijk medewerker verbonden aan de vakgroep Structurele en Toegepaste Geologie. Sindsdien is hij in dienst bij de vakgroep Petrologie, Mineralogie, Kristallografie, Geochemie, Bodemkunde (afdeling Geochemie) van het Instituut voor Aardwetenschappen Utrecht, met als voornaamste taak het werk met de electronen micro-analysator.

author's address:

Vening Meinesz Laboratory  
Dept. of Geochemistry  
Institute of Earth Sciences  
State University of Utrecht  
Budapestlaan 4  
3584 CD Utrecht  
the Netherlands