Stability relations of some titanium-minerals (sphene, perovskite, rutile, anatase)

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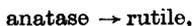Vening Meinesz Laboratory of Geophysics and Geochemistry, Utrecht,
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Abstract—The equilibrium curve for the reaction:

$$\text{calcite} + \text{quartz} + \text{anatase} \leftrightharpoons \text{sphene} + CO_2,$$

has been experimentally determined between 340 and 450°C. Solubility measurements of rutile and anatase at temperatures of 200 and 300°C showed that the free energy of the reaction:

$$\text{anatase} \rightarrow \text{rutile},$$

is of the order of -0.2 to -0.3 kcal, which means that an equilibrium curve for the formation of sphene from calcite, quartz and rutile will be shifted only slightly towards higher temperatures or lower CO_2-pressures relative to the same equilibrium with anatase instead of rutile. Experiments with perovskite and various silicates show that perovskite cannot stably coexist with quartz, enstatite, albite and sanidine, and thus is restricted to very silica-under-saturated rocks (carbonatites, ultramafic rocks and phonolitic extrusives). The value for the free energy of the reaction:

$$\text{perovskite} + \text{quartz} \rightarrow \text{sphene}$$
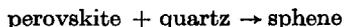
was found to be between -4.75 and -8.6 kcal, which checks well with the calorimetrically determined value for this reaction of -7.05 kcal (TODD and KELLEY, 1956).

As sphene in almost all cases seems to be stable under natural conditions relative to the association rutile + quartz + calcite, this sets rather severe upper limits to the CO_2-pressures which can be reached in nature during epizonal metamorphism.

INTRODUCTION

THE INVESTIGATIONS can be divided into three parts:

1. Experiments.
2. Thermodynamic considerations.
3. Application to natural occurrences.

The experiments were carried out partly at the Dept. of Geology, Princeton University, and partly at the Vening Meinesz Laboratory of Geophysics and Geochemistry of the Utrecht University.

The reaction products were always identified by X-ray diffractometry; the presence of small amounts of calcite was verified under the binocular microscope by the evolution of CO_2 in the powder on addition of a drop dilute HCl. Further details are given below.

EXPERIMENTS

A. *Determination of the sphene equilibrium curve*

The bombs which the Department of Geology, Princeton University, kindly put at the disposal of the senior author, had a limited temperature range. At temperatures higher than

440°C leaks occurred frequently. As it could be expected that reaction rates would be slow for the reaction:

$$CaCO_3 \; + \; SiO_2 \; + \; TiO_2 \; \leftrightharpoons CaTiSiO_5 + CO_2$$
$$\text{(calcite)} \quad \text{(quartz)} \quad \text{(anatase)} \quad \text{(sphene)}$$

at temperatures below 450°C, it was decided from the beginning to use an unconventional technique for the determination of this equilibrium. The 50 ml bombs (Autoclave AG series) were provided with platinum liners; these were loaded completely with a stoichiometric mixture of calcite + quartz + anatase (45 g) to which 10 ml of a 1 N NaCl-solution was added. NaCl-solutions were used instead of distilled water as it was supposed that reaction rates would be enhanced by the addition of NaCl. The bombs were then lowered into pre-heated deep furnaces and brought to the desired temperature. The bombs were continuously connected with Helicoid pressure gauges through a pressure capillary.

By plotting temperature against pressure during the heating period, it was determined that the amount of reaction taking place during the heating period was essentially negligible or only very slight at the higher temperatures. Therefore a "base-pressure" of water vapour pressure only could be established at the start of each run. Thereafter the course of the reaction could be followed by plotting the pressure against time for reaction times varying from 1 day to several months (Fig. 1 and Table 1).
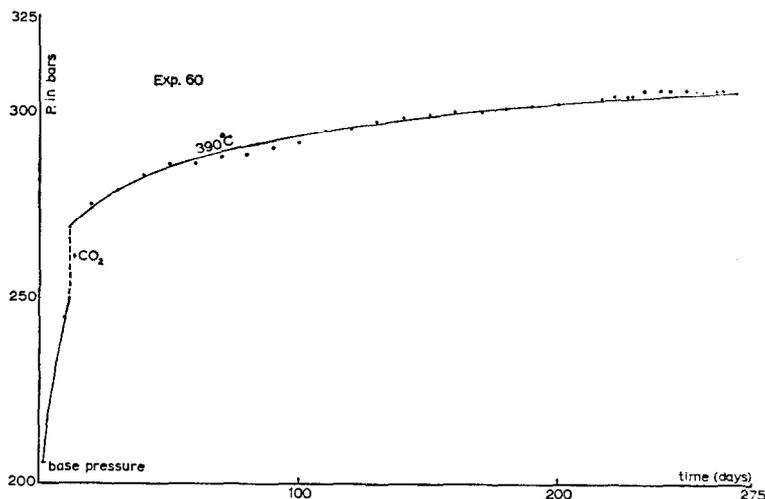

Fig. 1. Example of pressure–time curve for the reaction calcite + quartz + anatase $\leftrightharpoons$ sphene + CO_2.

At higher temperatures after a few hours or days some extra CO_2 was pumped into the pressure vessels (but still well below the expected equilibrium pressure) so that the reaction would not halt because the starting products would be completely consumed. Most runs stopped due to breakdown of the pressure connections or leaks at the copper washer. Equilibrium pressures were deduced by extrapolation of the pressure–time curves to infinite time. This extrapolation was done graphically by considering the maximum and minimum pressures which different smooth concave curves could possibly reach before becoming essentially horizontal. The uncertainty of this extrapolation and the instrumental errors together make up the uncertainty in the determination of the equilibrium fugacities (Fig. 2). That the values thus determined are equilibrium fugacities and not just rate points is further indicated by the fact that the values plot on a straight line on a $\ln f - 1/T$-plot, and that at only slightly higher CO_2-pressures reversals of the reaction have been obtained. Table 1 gives the essential data of the runs by which the equilibrium curve was determined. The temperature was recorded every 2 min by a monitor, and showed generally less than ± 2°C variation. The monitor was not

Table 1. Equilibrium CO_2-pressures and fugacities as deduced from pressure–time experiments, with stoichiometric mixtures of calcite + quartz + anatase, in a 1 mol.NaCl-solution

| Run No.	Temp. (°C)	Time (days)	Extrapolated CO_2-pressures	Equivalent CO_2-fugacities
70	340	124	46·2 ± 9 bars	46·5
57	360	59	67·5 ± 10 bars	69
11	380	15	83 ± 10 bars	85
49	385	8	98 ± 10 bars	102
60	390	261	101 ± 6 bars	104
10	400	16	110 ± 12 bars	113
62	410	25	140 ± 15 bars	145
54	415	6	138 ± 15 bars	143
14	427	15	155 ± 20 bars	162
52	440	4	203 ± 15 bars	210
56	440	4	190 ± 15 bars	197
59	445	7	221 ± 15 bars	250
73	450	1	228 ± 28 bars	260
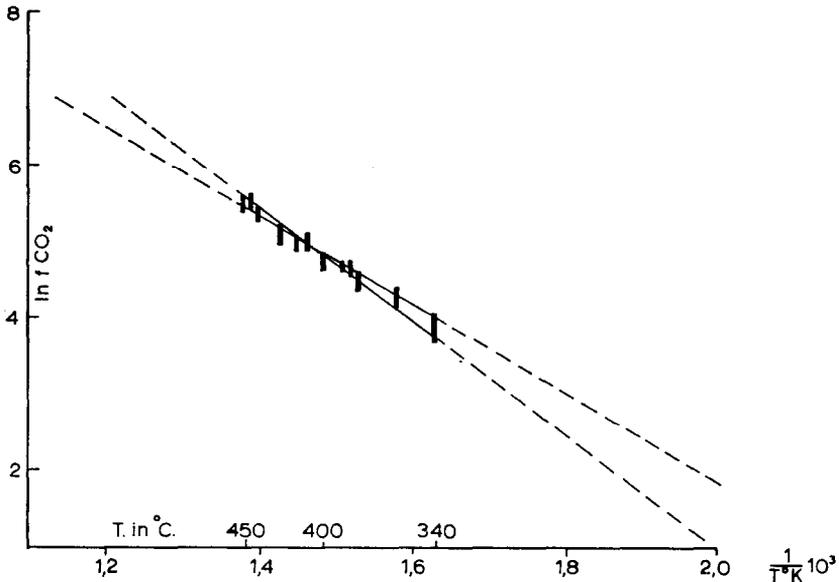
Fig. 2. Results of the experiments on the sphene equilibrium. The size of the rectangles indicates the uncertainty, caused by the extrapolation of the pressure–time curves (Fig. 1), as well as the experimental error.

calibrated for this series of experiments. In all runs it was verified that at the end calcite, quartz, anatase and sphene were all present. In an equilibrium situation the presence of all four solid phases at a fixed temperature would fix the CO_2-fugacity.

Anatase was chosen as a starting product instead of rutile, as this was the form of chemically pure TiO_2 available, and furthermore, it was hoped that the (metastable) anatase would react quicker while at the same time converting into rutile in the hydrothermal runs. This was never the case. Anatase only converted measurably into rutile when rutile was added as seeds. This was not done in the runs which were used for the determination of the equilibrium curve which

therefore applies to the reaction with anatase only. In a few runs the reaction was reversed by putting sphene powder under CO_2-pressures higher than the deduced equilibrium CO_2-pressure for that particular temperature. Although the reversed reaction was slow, and much less than half of the charge had reacted even after some weeks, a reversal could be clearly established (runs 69, 74 in which all three, and runs 19, 47, 75, 40, 43 and 50 in which only two of the three products could be identified—Table 2). Even in these runs it was anatase, and not rutile, that formed from the breakdown of sphene.

Table 2. List of runs in which the sphene equilibrium was reversed or in which reversal was indicated by the presence of 2 out of 3 breakdown phases of sphene (calcite, quartz, anatase) in small amounts in the reaction products.
Identification of phases enclosed in parenthesis is doubtful

Run No.	Temp.	Time (days)	Starting material	CO_2-pressures	Products
19	320	14	Sphene	138 bars	Sphene, calcite, anatase, (quartz), (rutile), (perovskite)
47	360	18	Sphene	124 bars	Anatase, calcite, sphene
69	350	15	Sphene	160 bars	Sphene, quartz, anatase, calcite
74	355	33	Sphene	177 bars	Sphene, quartz, calcite, anatase
75	370		Sphene (on Cu-wire)	197 bars	Sphene, anatase, quartz, (Cu-carbonate)
40	340	16	Sphene	255 bars	Sphene, anatase, calcite
43	355	18	Sphene		Sphene, anatase, calcite
50	380	18	Sphene		Sphene, trace anatase

The difference between the extrapolated pressure which the system would reach at infinite time and the base-pressure is considered to be the equilibrium CO_2-pressure of the reaction at the temperature of the run. From this pressure an equilibrium fugacity can be determined with the aid of conversion tables (MAJUMDAR and ROY, 1956); these calculated fugacities are also given in Table 1.

B. *Solubility measurements of anatase and rutile*

In order to use experimental data on the metastable equilibrium curve involving quartz, calcite and anatase for a calculation of the stable equilibrium curve involving quartz, calcite and rutile, the free energy of the reaction:

$$\text{anatase} \rightarrow \text{rutile}$$
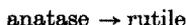
must be known. A value can be found in JANAF's (1960) thermochemical data, to which Dr. R. A. ROBIE kindly drew our attention. This value of the order of -7.4 kcal must clearly be too high by probably an order of magnitude as otherwise one can calculate that rutile + quartz + calcite should be an extremely stable association, reacting to form sphene only at temperatures well above the equilibrium curve of wollastonite.

As it is clear from petrologic experience that sphene forms much earlier in a metamorphic sequence than wollastonite, the existing thermochemical data seem suspect. It was decided therefore to carry out some solubility measurements of the two TiO_2-polymorphs at different temperatures. The bombs were fitted with an extra valve which connected with a silver tube extending down through the solution, and through which samples of solution could be taken at constant temperature and at constant pressure. These solutions were collected through a filter in a pre-weighed amount of dilute HCl to prevent precipitation of TiO_2 during cooling. The solutions were analysed by the Tiron method (SNELL, 1959) in a Beckman colorimeter.

Table 3. Solubility of anatase (run 72) and of rutile (run 77) at temperatures of 200 and 300°C, in a 1 mol.NaCl-solution, under its own vapour pressure

Run No.	Temp (°C)	Time (hr)	Solubility in ppm Ti		
72–1	200	20	1·86	1·68	
72–2	200	115	1·50		anatase
72–3	300	72	2·02	2·07	
72–4	300	315	2·13		
77–1	200	72	1·55	1·33	
77–2	200	115	1·11		rutile
77–3	300	12	1·54		
77–4	300	72	1·78	1·57	
77–5	300	552	1·39		

The analytical data are given in Table 3. Although the amounts of TiO_2 in solution are small, and relative errors therefore large, a systematic but small difference of the solubility of anatase vs. rutile is apparent. As the rutile was prepared from the anatase by prolonged heating above 1000°C, there was no chemical difference between the two modifications.

C. Perovskite–silicate reactions

These experiments were carried out in the Vening Meinesz Laboratory in cold-seal bombs. The reactants, to which 10 mg H_2O was added, were enclosed in welded gold capsules. The reaction products were identified by X-ray powder diagrams, taken with a Nonius camera which permits the simultaneous photography of four samples.

All experiments were carried out under 1000 bars water pressure, in sealed collapsible gold-capsules. Temperatures were between 600 and 800°C (see Table 6) and the duration of the runs was generally three weeks. The principle of the determination of ΔG of the reaction:

$$CaTiO_3 + SiO_2 \rightarrow CaTiSiO_5,$$

was to see from which silica-saturated silicates $CaTiO_3$ is capable of removing SiO_2 to form sphene, and conversely, which undersaturated silicates (or oxides) will react with sphene to form perovskite. Further details are given under the heading "THERMODYNAMICAL CONSIDERATIONS", part C (below).

THERMODYNAMICAL CONSIDERATIONS

A. Calculation of the equilibrium curve for the reaction:

$$CaCO_3 + SiO_2 + TiO_2 \rightleftharpoons CaTiSiO_5 + CO_2$$

The most direct way to calculate the equilibrium curve is by means of the formula:

$$\Delta G_T{}^r = -RT \ln k_T. \tag{1}$$

The equilibrium constant for this reaction being equal to the CO_2-fugacity, the formula is written:

$$\ln f_{CO_2} = \frac{-\Delta G_T{}^r}{RT}, \tag{2}$$

in which:

$$\Delta G_T{}^r = \Delta H_{298}^r + \int_{298}^{T} \Delta c_p \, dT - (298 + \Delta T) \cdot \left(\Delta s_{298} + \int_{298}^{T} \frac{\Delta c_p}{T} \, dT \right). \tag{3}$$

(2) and (3) combined

$$\ln f_{CO_2} = \frac{-\Delta G^r_{298} + \Delta T . \Delta s_{298} - \Delta(H_T - H_{298}) + T . \Delta(s_T - s_{298})}{RT} . \qquad (4)$$

As the standard free energies of formation of sphene and calcite are given (from the oxides), ΔG^r_{298} can be calculated and turns out to be +4560 cal. The influence of the pressure on the solid phases has been neglected in these formulas. As we have restricted our considerations to pressures less than 1000 bars, the error thus introduced is less than 0·5 kcal. $\Delta s_{298} = 37·83$ cal/deg mol (taking rutile as the TiO_2-polymorph). The values of $H_T - H_{298}$ and $s_T - s_{298}$ are tabulated (KELLEY, 1960) for all constituents of the reaction.

As all terms in the right hand side of formula (4) are known, CO_2-fugacities can be calculated for a number of temperatures (Table 4, column E). The calculated reaction between $\ln f_{CO_2}$ and $1/T$ has been plotted in Fig. 3. As the experimental data are not in agreement with the calculated curve, this has been calculated in

Table 4. Equilibrium fugacities at different temperatures for the wollastonite equilibrium curve and the sphene equilibrium curve.
Fugacities are given in bars

Temp (°K)	A $f^a_{CO_2}$ (DAN.)	B $f^a_{CO_2}$ (HARKER)	C $f^c_{CO_2}$ (DAN.)	D $f^c_{CO_2}$ (HARKER)	E $f^c_{CO_2}$ (calc.)	F $f^c_{CO_2}$ (exp.)
298	10^{-7}	10^{-11}	$8·6 . 10^{-4}$	$0·8 . 10^{-6}$	$4·8 . 10^{-4}$	—
400	$10^{-3·1}$	10^{-6}	0·76	$0·8 . 10^{-3}$	0·4	—
500	$10^{-0·8}$	$1·6 . 10^{-3}$	29	0·3	19·1	2·7–6
553	1	$2·5 . 10^{-2}$	103	2·5	80	11·5–20
600	4·4	0·2	295	11	232	30–42·5
633	10	0·6	525	32	435	60–74
700	50	6	1710	190	1290	172–190
738	100	15	2750	430	2200	270–330
800	290	66	5850	1300	4570	494–700
873	810	332	11880	4900	9330	870–1400
933		1090		11750		
973		1940		20150		

Column A. Calculated values for the wollastonite equilibrium curve by DANIELSSON (1950).

Column B. Experimental data from HARKER and TUTTLE (1956); the data, except the last three, are extrapolated from a $\log f_{CO_2} - (1/T) . 10^3$ — diagram.

Column C. Fugacities of the sphene equilibrium curve, calculated with formula (9), using the calculated data of DANIELSSON (1950) of the wollastonite curve.

Column D. Fugacities of the sphene equilibrium curve, calculated with formula (9), using the values from the wollastonite curve, extrapolated from experimental data from HARKER and TUTTLE (1956).

Column E. Fugacities of the sphene equilibrium curve, calculated by means of the formula $\Delta G_T{}^r = -RT \ln k_T$.

Column F. Direct experimental data of the sphene equilibrium curve (this paper), with data extrapolated from a $\ln f_{CO_2} - (1/T) . 10^3$ diagram.

To obtain the calculated fugacities of the columns C, D and E, rutile is used as TiO_2-polymorph. In the experiments (column F) anatase was the TiO_2-modification. (See also part B of THERMODYNAMICAL CONSIDERATIONS, (in text), for the reaction anatase → rutile).

another way, starting from the known equilibrium curve of the reaction:

$$CaCO_3 + SiO_2 \rightleftharpoons CaSiO_3 + CO_2.$$
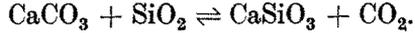
For this curve too, calculation and experiment are not in agreement; the CO_2-fugacities at equilibrium as calculated by DANIELSSON (1950) are much higher than the experimentally determined values of HARKER and TUTTLE (1956). A similar discrepancy is found between the calculated CO_2-fugacities of the sphene equilibrium
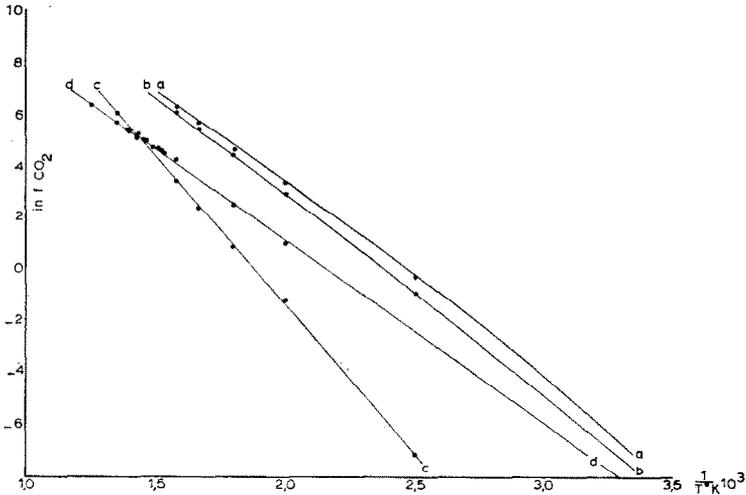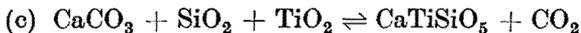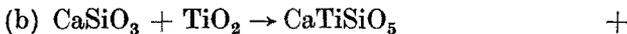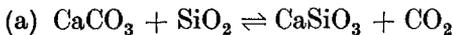

Fig. 3. Equilibrium curves for the sphene equilibrium:
aa. Calculated, using the calculated wollastonite equilibrium data (DANIELSSON, 1950).
bb. Calculated from $\Delta G = -RT \ln k$.
cc. Calculated, using the experimental data on the wollastonite equilibrium (HARKER and TUTTLE, 1956).
dd. Experimental curve, with extrapolated values (this work).

and the experimental values. The calculated fugacities given in Column E of Table 4 are higher by a factor of about three than the values determined experimentally.

It seems likely that these discrepancies are due to inaccuracy of the listed thermodynamical data of the minerals involved.

In order to find another method to calculate the sphene equilibrium curve, we can consider the following reactions:

(a) $CaCO_3 + SiO_2 \rightleftharpoons CaSiO_3 + CO_2$

(b) $CaSiO_3 + TiO_2 \rightarrow CaTiSiO_5$ +

(c) $CaCO_3 + SiO_2 + TiO_2 \rightleftharpoons CaTiSiO_5 + CO_2$

From the reaction (a) is known the $f_{CO_2} - T$ equilibrium curve, as determined experimentally by HARKER and TUTTLE (1956), and as calculated by DANIELSSON (1950). From reaction (b) the heat and free energy of reaction at all temperatures are known (TODD and KELLEY, 1956).

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The following relation holds:

$$\Delta G_T{}^r(c) = \Delta G_T{}^r(a) + \Delta G_T{}^r(b). \tag{5}$$

At temperature T_x and CO_2-pressure P_x, we have at equilibrium:

$$\Delta G_c{}^r(T_x, P_x) = 0. \tag{6}$$

Relation (5) can be applied at all temperatures and pressures:

$$\Delta G_c{}^r(P = 1, T_x) = \Delta G_a{}^r(P = 1, T_x) + \Delta G_b{}^r(P = 1, T_x).$$

If the volume difference between the solid phases $\Delta V_{s,T_x}$ is neglected as it is small as compared to the volume of the CO_2-gas,—in any case at pressures less than 1000 bars—, we can write at equilibrium:

$$\Delta G_c{}^r(T_x, P_x) = \Delta G_a{}^r(P = 1, T_x) + \Delta G_b{}^r(P = 1, T_x) + RT_x \cdot \ln \frac{f_{P_x}{}^c}{f_{P=1}{}^c} = 0. \tag{7}$$

Neglecting the volume change of the solid phases, we can write for reaction (a):

$$\Delta G_a{}^r(P = 1, T_x) = -RT_x \cdot \ln \frac{f_{P_x}{}^a}{f_{P=1}{}^a}. \tag{8}$$

For reaction (b) the heat and free energy of reaction at all temperatures is given (TODD and KELLEY, 1956).

A combination of the formulas (7) and (8) yields:

$$-RT_x \ln \frac{f_{P_x}{}^a}{f_{P=1}{}^a} + \Delta G_b{}^r(P = 1, T_x) + RT_x \ln \frac{f_{P_x}{}^c}{f_{P=1}{}^c} = 0.$$

As at low pressures ($P = 1$) pressure and fugacity are equal for the reactions (a) and (c), the relation $f_{P=1}^a = f_{P=1}^c$ holds, so that the foregoing expression reduces to:

$$\ln \frac{f_{P_x}{}^c}{f_{P_x}{}^a} = \frac{-\Delta G_b{}^r(P = 1, T_x)}{RT_x}. \tag{9}$$

By means of formula (9) the sphene equilibrium curve can be calculated by considering different values for T_x, for which temperature the corresponding $f_{P_x}{}^a$ can be found on the known equilibrium curve of reaction (a). As all data of reaction (b) are given (TODD and KELLEY, 1956), the unknown $f_{P_x}{}^c$ of the sphene equilibrium curve can be found for different values of T_x.

Some CO_2-fugacities at equilibrium at different temperatures for reaction (a) are given in column A of Table 4 (calculated by DANIELSSON, 1950) and in column B of Table 4 (experimental values of HARKER and TUTTLE, 1956). The corresponding CO_2-fugacities of the sphene equilibrium curve are found in columns C and D of Table 4.

Because TODD and KELLEY (1956) use rutile as the TiO_2-modification in their measurements of ΔH and ΔG of the reaction (b), the CO_2-fugacities in columns C and D of Table 4 refer to the sphene equilibrium curve with rutile as the TiO_2 polymorph.

From a consideration of columns C, D, E and F of Table 4 it can be concluded

that a similar discrepancy between calculation and experiment shows up for the sphene equilibrium curve as had been found for the wollastonite equilibrium. Using the tabulated entropies and free energies, the CO_2-fugacities of the sphene equilibrium curve become much higher than the experimentally determined values (Table 4, columns E and F). Using the data from DANIELSSON (1950) for the wollastonite equilibrium curve (thus using indirectly the tabulated standard free energies and entropies), the calculated CO_2-fugacities of the sphene equilibrium curve become also much higher than the values determined experimentally (Table 4, columns C and F). Starting however with the experimental data for the wollastonite curve (HARKER and TUTTLE, 1956) the calculated CO_2-fugacities are in reasonably good agreement with the experiments (Table 4, columns D and F).

B. *Free energy of the reaction; anatase → rutile*

The only data in the literature on the free energy of anatase are found in JANAF's (1960) thermochemical tables. The source of these data is an unpublished ONR-report by ROSSINI *et al.* From these data a free energy of the reaction:
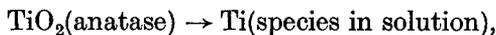
$$\text{anatase} \rightarrow \text{rutile,}$$
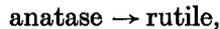
under standard conditions turns out to be $-7\cdot4$ kcal, and as the entropy of reaction is very small, the same free energy of reaction is found at 700°K. These data must be viewed with suspicion; from the fact that sphene has been broken down into calcite, quartz and *anatase* at CO_2-pressures only slightly above the inferred equilibrium CO_2-pressures it is apparent that the equilibrium curve for the reaction:

$$\text{calcite} + \text{quartz} + \text{anatase} \leftrightarrows \text{sphene} + CO_2,$$
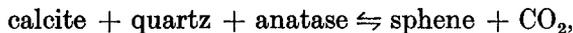
is approximately right. It may not be located lower than the experimentally determined CO_2-pressures which the reactants had built up during reaction. If one would now add a free energy of the reaction anatase → rutile of $-7\cdot4$ kcal, this would make the association quartz + rutile + calcite extremely stable. For a CO_2-pressure of 100 bars the sphene reaction with rutile instead of anatase would be shifted by 200° towards higher temperatures, i.e. well above the equilibrium temperature of wollastonite at the same pressure. In fact sphene would form only at higher temperatures and/or lower CO_2-pressures than does wollastonite from calcite + quartz, which is clearly contradicted by geological evidence. As we are only interested in the free energy difference between anatase and rutile, some solubility measurements of anatase and rutile were carried out. The data are given in Table 3.

Without knowing in what form TiO_2 is present in solution, we can use these data to calculate a free energy of reaction for anatase → rutile.

For the reaction:

$$TiO_2(\text{anatase}) \rightarrow Ti(\text{species in solution}),$$

we can write

$$\Delta G_1 = G_{(\text{Ti-spec. in sol.})} - G_{(\text{an})}. \tag{10}$$

The same can be done for the solution of rutile:

$$\Delta G_2 = G_{(\text{Ti-spec. in sol.})} - G_{(\text{rut})}. \tag{11}$$

Provided that at the same temperature the Ti-species in solution produced by the solution of anatase and of rutile will be the same, it follows that:

$$\Delta G_3 = G_{(\text{rut})} - G_{(\text{an})} = \Delta G_1 - \Delta G_2.$$

As on the other hand:

$$\Delta G_1 = -RT \ln k_1 = -RT \ln (\text{total Ti in sol.})_{\text{an}},$$

and similarly:

$$\Delta G_2 = -RT \ln k_2 = -RT \ln (\text{total Ti in sol.})_{\text{rut}},$$

it follows that:

$$\Delta G_3 = -RT(\ln k_1 - \ln k_2).$$

Using the values of Table 3 we arrive at a free energy of reaction of -221 cal at 200°C and of -316 cal at 300°C. Considering that there is a considerable uncertainty in the determination of the solubilities, we may say that the free energy of the reaction anatase $\rightarrow$ rutile will be -0.25 ± 0.2 kcal, with only a slight variation with temperature. As this value is compatible with geological evidence, the value of -7.4 kcal must be rejected, as being wholly outside the possible range. If the value of -0.25 kcal is accepted, it follows that the stable equilibrium curve for the sphene reaction from calcite + quartz + rutile will shift only to slightly lower CO_2-pressures or slightly higher temperatures relative to the experimentally determined (metastable) equilibrium curve with anatase instead of rutile. This shift amounts to minus 30 bars (from 180 to 150) at a temperature of 700°K.

C. The free energy of the reaction; $CaTiO_3 + SiO_2 \rightarrow CaTiSiO_5$

In Table 5 some reactions between undersaturated silicates or oxides and SiO_2 are listed with their free energy of reaction at 298°K and 973°K. In order to determine the free energy of formation of sphene from perovskite + quartz, mixtures of

Table 5. Free energies of some reactions between undersaturated silicate, or oxide, and quartz, (in kcal), at 298° and 973°K

	$\Delta G^r_{298°K, 1\,bar}$	$\Delta G^r_{973°K, 1\,bar}$
$Mg_2SiO_4 + SiO_2 \rightarrow 2MgSiO_3$	-2.2	-2.1
$\frac{1}{2}NaAlSiO_4 + SiO_2 \rightarrow \frac{1}{2}NaAlSi_3O_8$	-2.6	-2.85
$KAlSi_2O_6 + SiO_2 \rightarrow KAlSi_3O_8$	-4.8	-3.8
$2ZnO + SiO_2 \rightarrow Zn_2SiO_4$	-7.2	-7.6
$2MgO + SiO_2 \rightarrow Mg_2SiO_4$	-15.1	-15.1

perovskite with the saturated silicates at the right hand side of the reactions of Table 5 were treated hydrothermally at temperatures around 700°C. The results of these runs are listed in Table 6. From this table it is apparent that perovskite can react with enstatite, albite and K–feldspar, forming sphene and respectively forsterite, nepheline and leucite. With respect to willemite and forsterite however, perovskite is stable, and sphene reacts with periclase and zincite.

The equation:

$$\Delta G_T{}^r = \Delta H_T{}^r - T \cdot \Delta s_T,$$

Table 6. List of runs of perovskite–silicate reactions

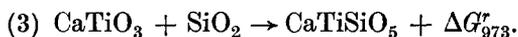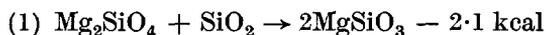| Run No.	Temp.°C	Pressure	Time	Starting material	Products
105 a1	700°	1000 bars	3 weeks	Enstatite + perovskite	Sphene + forsterite
105 a2	700°	1000 bars	3 weeks	Albite + perovskite	Sphene + nepheline
105 a3	700°	1000 bars	3 weeks	K–feldspar + perovskite	Sphene + leucite
105 a5	700°	1000 bars	3 weeks	Forsterite + perovskite	Forsterite + perovskite
170 a1	760°	1000 bars	24 days	Willemite + perovskite	Willemite + perovskite
123 a1	670°	1000 bars	15 days	Sphene + periclase	Forsterite + perovskite
170 a2	760°	1000 bars	24 days	Sphene + zincite	Willemite + perovskite

can be written as:

$$\Delta G_T{}^r = \Delta H_{298}^r + \int_{298}^T \Delta c_p \, dT - (298 + \Delta T) . \left(\Delta s_{298} + \int_{298}^T \frac{\Delta c_p}{T} \, dT \right).$$

Both corrections of ΔH and Δs with Δc_p can be neglected. For reactions between solid phases the role of pressure too can be neglected as the volume changes, and consequently the $P . \Delta v$-terms, are small, at least at the moderate pressures of 1000 bars of the runs described above (100 cal or less). Introducing these simplifications, the above equation becomes:

$$\Delta G_T{}^t = \Delta G_{298}^r - \Delta T . \Delta s_{298}.$$

Consider the following reactions at 973°K:

(1) $Mg_2SiO_4 + SiO_2 \rightarrow 2MgSiO_3 - 2 \cdot 1$ kcal

(2) $\underline{CaTiO_3 + 2MgSiO_3 \rightarrow CaTiSiO_5 + Mg_2SiO_4 - a \text{ kcal}} \quad +$

(3) $CaTiO_3 + SiO_2 \rightarrow CaTiSiO_5 + \Delta G_{973}^r.$

Because reaction (2) proceeds to the right, the free energy of reaction must be negative.

Thus:

$$\Delta G_{973}^r(3) = \Delta G_{298}^r - 675 . \Delta s_{298} < -2 \cdot 1 \text{ kcal}$$

$\Delta s_{298}(3)$ being $-1 \cdot 40$ cal/deg, it follows that $\Delta G_{298}^r(3) < -3 \cdot 0$ kcal. These same calculations can be applied to the perovskite–albite reaction, yields $\Delta G_{298}^r(3) < -3 \cdot 8$ kcal, and for the perovskite–K–feldspar reaction $\Delta G_{298}^r(3) < -4 \cdot 75$ kcal.

For the reactions in which spene reacts to form perovskite, a similar reasoning yields for the zincite–sphene reaction that $\Delta G_{298}^r(3) > -8 \cdot 6$ kcal, and for the periclase–sphene reaction that $\Delta G_{298}^r(3) > -16 \cdot 0$ kcal. So in reality it is the third and the fourth reactions of Table 5 which bracket (by means of runs No. 105 a3, and 170 a2 of Table 6) the free energy of the reaction perovskite + quartz to sphene. This free energy must be between $-4 \cdot 75$ and $-8 \cdot 6$ kcal.; the calorimetrically determined value of $-7 \cdot 05$ kcal, (TODD and KELLEY, 1956) falls within this range.

APPLICATIONS TO NATURAL OCCURRENCES

The main application of the above experimental work on sphene is, in our opinion, the fact that the sphene equilibrium curve allows a delimitation of the maximum

CO_2-pressures that commonly occur in nature, at least for the lower grades of metamorphism (epi- and mesozone). As sphene seems to be nearly always stable and as we have sought in vain for associations of quartz, calcite and rutile/anatase in metamorphic rocks, the conclusion seems warranted that the CO_2-pressures in nature rarely if ever exceed the CO_2-pressures of the sphene equilibrium curve.[*] As on the other hand associations of quartz and calcite are exceedingly common
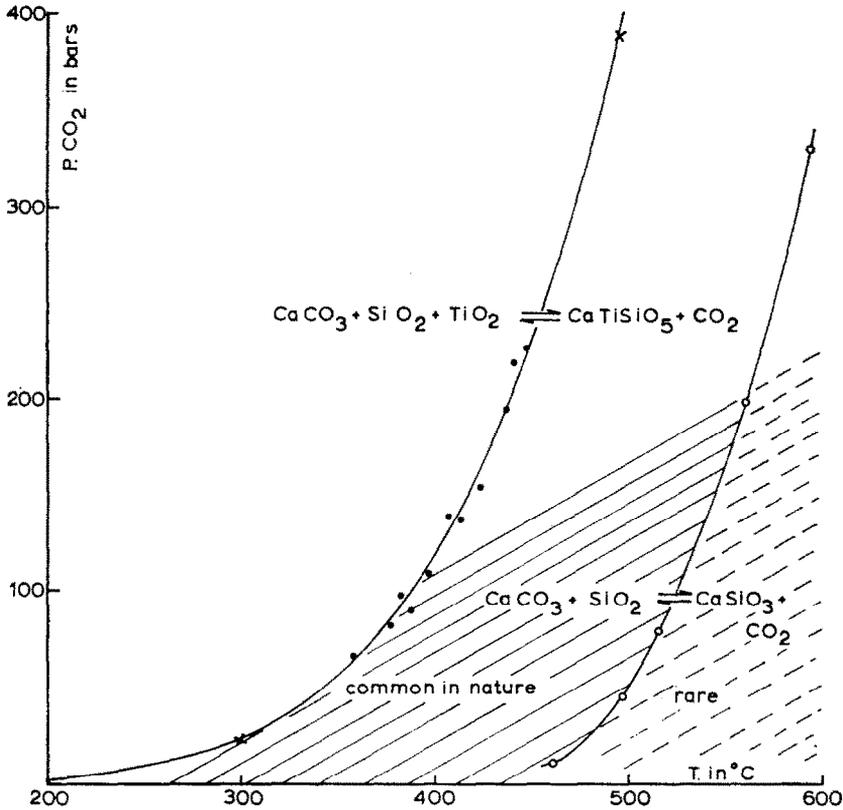

Fig. 4. The experimental sphene equilibrium curve (this paper) and the experimental curve for the wollastonite equilibrium (Harker and Tuttle, 1956), and the range of inferred CO_2-pressures in nature, during epi- and mesozonal metamorphism.

very often in association with sphene, a field of normal CO_2-pressures during metamorphism can be delineated, as has been done in Fig. 4. It seems likely that the CO_2 partial pressures during metamorphism make up only a fraction of the total pressure, at least for the lower grades of metamorphism. ($<500°C$.)

The maximum possible CO_2-pressures for the sphene equilibrium curve at a temperature of 25°C, as extrapolated from the experimental data, fall in the range near 10^{-2} to 10^{-3} atm CO_2-pressure. It follows therefore that authigenic formation

[*] Karpov (1966) observed the reaction calcite + quartz + rutile → sphene + CO_2 in a marble complex of greenschist facies metamorphic grade. His calculated curve for this reaction is close to our calculated curve of Fig. 3, bb.

of sphene in soils and sediments cannot be ruled out as a possibility (MILNER, 1962).

The perovskite cannot crystallize in equilibrium with enstatite, albite or K-feldspar, and its occurrence is therefore restricted to carbonatites, ultrabasic rocks and very undersaturated lavas, in which it occurs commonly (DEER et al., 1965).

The very near equality of the free energies of formation of the TiO_2-polymorphs rutile and anatase, finally, which is indicated by the solubility-experiments, shows why anatase is so commonly formed, especially in low-temperature environments, instead of the stable polymorph rutile. High pressure will strongly favour the formation of rutile; therefore, it can be concluded that anatase has no true stability field.

REFERENCES

DANIELSSON A. (1950) Das Calcit-Wollastonit Gleichgewicht. *Geochim. Cosmochim. Acta* **1**, 50–69.

DEER W. A., HOWIE R. A. and ZUSSMAN J. (1965) *Rockforming Minerals*, Vol IV. London.

HARKER R. I. and TUTTLE O. F. (1956) Experimental data on the P_{CO_2}–T curve for the reaction calcite + quartz ⇌ wollastonite + carbondioxide. *Amer. J. Sci.* **254**, 239–256.

JANAF (1960) *Thermochemical Data*. The Dow Chemical Company, Thermal Laboratory.

KARPOV I. K. (1966) Thermodynamic conditions of rutile and sphene equilibrium in lime–quartz bearing rocks of Mama-beds. *Acad. Sci. U.S.S.R., Siberian Branch Geol. Geoph.* **1**, 125–128.

KELLEY K. K. (1960) Contribution to the data on thermochemical metallurgy. *U.S. Bur. Mines, Bull.* **584**.

MAJUMDAR A. J. and ROY R. (1956) Fugacities and free energies of CO_2 at high temperatures and pressures. *Geochim. Cosmochim. Acta* **10**, 311–315.

MILNER H. B. (1962) *Sedimentary Petrography*, Vol. III: *Principles and Applications*. (4th edition) London, Murby.

ROBIE R. A. (1966) In: Handbook of Physical Constants (editor S. P. Clarke). *Geol. Soc. Am., Mem.* **97**.

SNELL F. D. (1959) *Colorimetric Methods of Analysis*. Van Nostrand.

TODD S. S. and K. K. KELLEY (1956) Heat and free energy data for tricalcium dititanate, sphene, lithium metatitanate and zinc–titanium spinel. *U.S. Bur. of Mines, Rep. Invest.* **5193**, 17 p.