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Reconstruction of Rock Cooling Paths from Kinetic Data on the Fe $^{2+}$-Mg Exchange Reaction in Anthophyllite [and Discussion]

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EXPERIMENTAL PETROLOGY

Reconstruction of rock cooling paths from kinetic data on the Fe^{2+}–Mg exchange reaction in anthophyllite

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The kinetics of the intracrystalline Fe–Mg exchange reaction in anthophyllite can be described by a simple model that permits extrapolation to lower temperatures. Rock cooling rates can be estimated in the vicinity of 300 °C from these data using time–temperature–transformation diagrams. Aluminous orthoamphiboles (gedrites) are expected to yield rock cooling rates at higher temperatures.

Introduction

With the advent of the concept of plate tectonics the dynamics of rock-forming processes have come more and more into focus. Not only maximum pressure–temperature conditions attained by a rock in a metamorphic cycle are of interest but also the pressure–temperature–time history of the entire cycle, i.e. from the deposition of a sediment through the various stages of prograde and retrograde metamorphism to the final cooling and uplifting. Information on the temperature–time or pressure–time gradient derived from rocks could, together with other geological criteria, eventually permit the reconstruction of evolutionary patterns in geosynclines and thus give indirect evidence for processes in the asthenosphere and the lithosphere of the Earth. Because time is one of the critical parameters, kinetic data on reactions in or among minerals of a rock are required to decipher its history.

Most experimental petrologic studies have so far been concerned with equilibrium relationships of heterogeneous reactions. With these data at hand, mineral relics observed in rocks can be used for reconstructing part of the pressure–temperature path followed by a rock (see, for example, Kulke & Schreyer 1973). They do not, however, give any indication of the time elapsed between the different combinations of pressure and temperature corresponding to the relic and the newly formed assemblage, respectively. Kinetic studies on such reactions and their application to natural rocks are greatly hampered by the insufficiently known effects of grain size, catalysis by a gas phase of unknown component activities, shearing stress, etc. On the other hand, homogeneous equilibria in a solid phase (i.e. intracrystalline reactions) are not or only to a minor degree subject to these effects because these reactions proceed within a mineral grain where the basic structure is preserved during cooling.

Such intracrystalline equilibria can occur in all minerals where at least two different ionic species are distributed over at least two structurally distinct sites of slightly different geometry and energetics. Classical examples are the Si–Al exchange in feldspars and the Fe^{2+}–Mg exchange in most ferromagnesian silicates (olivines, pyroxenes and amphiboles).

The theory of intracrystalline exchange reactions has been extensively put forward by, for example, Thompson (1969, 1970) and their kinetics by Mueller (1967, 1969). Searching for suitable substances where the kinetic model proposed by Mueller might be applied it becomes immediately evident that, although intracrystalline equilibria occur in most silicate groups, only a few will be suited for such a study. For ease of evaluation only two cations should be involved in the exchange process, i.e. the phase in question should be a member of a binary solid solution series. Other prerequisites are that no phase transformations occur during cooling and that the energy differences between the sites are large enough to permit a marked temperature dependence of the intracrystalline equilibria. The latter two criteria dismiss the feldspars and olivines, respectively, and from the more common silicate solid solutions only orthopyroxenes, anthophyllites and cummingtonites are left. Kinetic experiments on ordering of Fe and Mg in orthopyroxenes (Virgo & Hafner 1969; Hafner & Virgo 1970) point to rather complicated exchange processes at temperatures around 500 °C and a two-step ordering mechanism has been invoked for these phases by Mueller (1970).

It is the purpose of the present paper to discuss the application of the kinetic model proposed by Mueller (1967, 1969) to the problem outlined above, using data on the kinetics of the intracrystalline Fe–Mg exchange reaction reported by Seifert & Virgo (1974, 1975) for an anthophyllite.

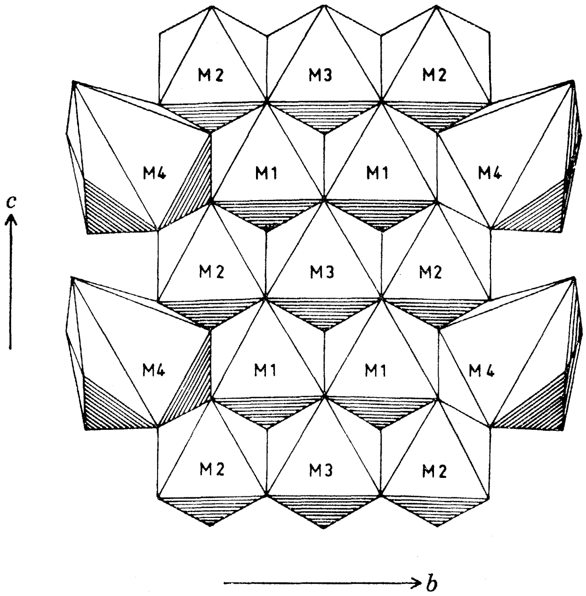

FIGURE 1. Projection of octahedral (M1, M2 and M3) and eightfold coordinated (M4) metal–oxygen polyhedra in anthophyllite on to the *bc* plane. The polyhedra form infinite strips parallel to the *c* axis. Atomic coordinates taken from Finger (1970).

EQUILIBRIUM $\mathrm{Fe^{2+}}$–Mg CATION DISTRIBUTION IN ANTHOPHYLLITE

Anthophyllites can be described by the idealized formula $\mathrm{(Mg, Fe^{2+})_7\,Si_8O_{22}(OH)_2}$. Except for the (soda- and alumina-bearing) gedrites and the (lithium- and alumina-bearing) holmquistite many natural orthoamphiboles closely approach this binary solid solution series, especially those formed by metamorphism of ultrabasic igneous rocks. The anthophyllite crystal structure (Finger 1970) contains a total of seven sites per formula unit occupied by Mg and $\mathrm{Fe^{2+}}$ in eightfold or sixfold coordination, distributed over four structurally distinct equipoints (M1, M2, M3 and M4). These polyhedra form infinite strips in the *c* direction (figure 1). The outer positions M4 are coordinated to 8 oxygens in a very distorted fashion, whereas M1, M2 and M3 are much more regular octahedra of very similar dimensions. The X-ray study of Finger (1970) showed that the distribution of Fe and Mg over these positions is not random, most of the iron being concentrated in M4 and only a small fraction in the M1, M2 and M3 positions. Because no clear-cut fractionation of Fe and Mg exists between the latter positions these will be treated as one position M123 in the following discussion.

It has already been stated by Finger (1970) that the strong site preference of Fe^{2+} for the M4 position indicates a low, but unknown, temperature of equilibration. At higher temperatures the Fe–Mg distribution is expected to become more random through an intracrystalline cation exchange reaction

$$x^{Fe}_{M123} + x^{Mg}_{M4} \rightleftharpoons x^{Fe}_{M4} + x^{Mg}_{M123}. \tag{1}$$

The molecular fractions of Fe^{2+} on the sites M4 and M123, respectively, can be easily determined by Mössbauer spectroscopy and, by difference, also the Mg fractions (Seifert & Virgo 1974). For the anthophyllite specimen studied by Finger (1970) very good agreement between the X-ray method and Mössbauer spectrographic techniques has been found (cf. Table 39 of Seifert & Virgo 1974). Samples heated to elevated temperatures and then quenched showed increased fractions of Fe^{2+} on the M123 position. Reaction (1) thus proceeds to the left with increasing temperature.

The degree of ordering can be described by an ordering parameter p defined as

$$p = \frac{x^{Fe}_{M123}\, x^{Mg}_{M4}}{x^{Fe}_{M4}\, x^{Mg}_{M123}}, \tag{2}$$

that becomes identical to the inverse of the equilibrium constant K of reaction (1) if ideal behaviour of the sites (not necessarily identical to ideality of the solid solution series) is assumed. We can then apply the relations

$$\Delta G = -RT \ln K \tag{3}$$

and

$$\Delta G = \Delta H - T\Delta S, \tag{4}$$

where ΔG, ΔH and ΔS refer to the Gibbs free energy, enthalpy and entropy changes, respectively, of the complete exchange reaction (1), R is the gas constant and T absolute temperature. From (3) ΔG can be calculated and, assuming a temperature-independent ΔH, its temperature dependence can be evaluated with the aid of (4). Heating experiments in the temperature range 550–720 °C (cf. Seifert & Virgo 1974, 1975) indicate that:

(1) Even at the highest temperatures that can be applied without destroying the anthophyllite structure (around 720 °C) Fe^{2+} still shows a marked preference for the M4 position, i.e. the cation distribution is still far from being random.

(2) Equilibrium cation distribution is readily achieved in this temperature range. The same degree of ordering is attained at a given temperature irrespective of the state of the starting material (ordered natural or disordered by preheating at a higher temperature), and this cation distribution is not a function of heating time as soon as the disordered and ordered materials have attained the same cation distribution.

(3) The temperature dependence of the ordering parameter can adequately be described by the simple formulae given above, based on the ideal exchange model. The temperature dependence of ΔG, if any, is only very slight.

(4) The effect of pressure on the equilibrium cation distribution will be negligible for any pressures attained in crustal rocks. Because at constant temperature

$$\mathrm{d}\Delta G/\mathrm{d}P = \Delta V, \tag{5}$$

where ΔV refers to the volume change associated with the exchange reaction (1) the effect of pressure on K can be calculated from

$$\log K_{P2} = \log K_{P1} + \Delta V(P2-P1)/2.303\,RT. \tag{6}$$

The volume of the most ordered (natural) and most disordered material are found to be identical within the limits of error and ΔV certainly does not exceed $10^{-3}\,\mathrm{nm}^3$ (1 Å^3)/mol, corresponding to 0.023 cal (0.1 J)/bar. A ΔP of 5000 bar (500 MPa) would thus change K by less than 0.02 log units at temperatures around 700 °C.

The simple relationships encountered permit the extrapolation of ΔG and thus the equilibrium K towards lower temperatures, where no equilibrium cation distribution can be achieved in experiments of reasonable duration. The highly ordered cation distribution observed in the natural, unheated material indicates an equilibration temperature around 270 °C (cf. Seifert & Virgo 1974, Fig. 129).

KINETICS OF THE EXCHANGE REACTION

The low temperature of equilibration encountered in anthophyllite cannot reflect its crystallization temperature but rather a 'cut off' temperature where the intracrystalline cation exchange was frozen in during cooling of the rock. The conclusion is thus similar to that arrived at by Virgo & Hafner (1969) for orthopyroxenes. Above the cut-off temperature the attainment of intracrystalline equilibrium is assumed to be faster than the rock cooling rate, whereas below the cut-off temperature the cooling rate of the rock exceeds the exchange rate. If the exchange rate at the cut-off temperature were known the cooling rate of the rock at this temperature might theoretically be calculated.

Application of the theory of absolute reaction rates to orthoamphiboles shows that two rate constants are required for description of this second-order competing rate process. Assuming again ideality of mixing the formulation put forward by Mueller (1967, 1969) as applied to the Fe–Mg exchange in orthoamphiboles reduces to

$$-\frac{\mathrm{d}x^{\mathrm{Fe}}_{\mathrm{M4}}}{\mathrm{d}t} = \tfrac{5}{7}k_{4-123}\,x^{\mathrm{Fe}}_{\mathrm{M4}}\,x^{\mathrm{Mg}}_{\mathrm{M123}} - \tfrac{2}{7}k_{123-4}\,x^{\mathrm{Fe}}_{\mathrm{M123}}\,x^{\mathrm{Mg}}_{\mathrm{M4}}, \tag{7}$$

where k_{4-123} and k_{123-4} are the disordering and ordering rate constants, respectively. Introducing the equilibrium constant

$$K = \frac{k_{123-4}}{k_{4-123}}, \tag{8}$$

and the bulk x^{Fe} fraction of the sample

$$x^{\mathrm{Fe}} = \frac{\mathrm{Fe}^{2+}}{\mathrm{Fe}^{2+}+\mathrm{Mg}} = \tfrac{5}{7}x^{\mathrm{Fe}}_{\mathrm{M123}} + \tfrac{2}{7}x^{\mathrm{Fe}}_{\mathrm{M4}} \tag{9}$$

into (7) the change of Fe^{2+} concentration on one position (e.g. M4) with time can be written as

$$-\frac{\mathrm{d}x^{\mathrm{Fe}}_{\mathrm{M4}}}{\mathrm{d}t} = k_{4-123}[c(x^{\mathrm{Fe}}_{\mathrm{M4}})^2 + bx^{\mathrm{Fe}}_{\mathrm{M4}} + a], \tag{10}$$

where

$$a = -Kx^{\mathrm{Fe}},$$

$$b = Kx^{\mathrm{Fe}} - x^{\mathrm{Fe}} + \tfrac{2}{7}K + \tfrac{5}{7},$$

$$c = \tfrac{2}{7}(1-K).$$

The integrated equation takes the form

$$\pm k_{4-123}\,\Delta t = \frac{1}{2(\frac{1}{4}b^2-ca)^{\frac{1}{2}}}\ln\left.\frac{\pm(\frac{1}{4}b^2-ca)^{\frac{1}{2}}+cx^{\mathrm{Fe}}_{\mathrm{M4}}+\frac{1}{2}b}{(\frac{1}{4}b^2-ca)^{\frac{1}{2}}\mp cx^{\mathrm{Fe}}_{\mathrm{M4}}\mp\frac{1}{2}b}\right|^{x^{\mathrm{Fe}}_{\mathrm{M4},\,\Delta t}}_{x^{\mathrm{Fe}}_{\mathrm{M4,\,start}}} \tag{11}$$

(Mueller 1967), where the upper signs refer to ordering, and the lower signs to disordering.

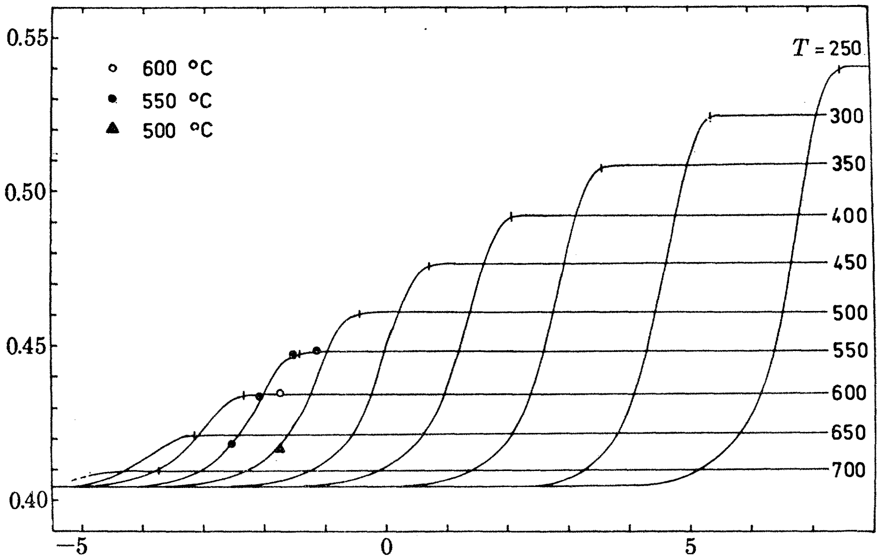

FIGURE 2. Change of $x^{\mathrm{Fe}}_{\mathrm{M4}}$ (ordinate) with time in anthophyllite (abscissa, logarithmic scale) as a function of annealing temperature (in °C). The curves have been calculated from the data points given by Seifert & Virgo (1974, 1975), in part shown as circle, dots and triangle, using the model of Mueller (1967, 1969) as described in the text. As starting material an anthophyllite equilibrated at 720 °C has been assumed. The small vertical bar marks the time required to achieve 99 % of the theoretically possible degree of ordering at the specified temperature.

For an evaluation of rate experiments the following parameters must thus be known either by direct experimental determination or by extrapolation of data obtained at a different temperature: (1) change of Fe concentration with time at a given temperature, (2) equilibrium cation distribution at this temperature, (3) $x^{\mathrm{Fe}}_{\mathrm{M4}}$ value in the starting material, and (4) bulk x^{Fe} value of the sample. The model of Mueller (1967, 1969) has successfully been applied by Seifert & Virgo (1974, 1975) to rate experiments and enabled extraction of the two rate constants at two different temperatures. Combining these, the activation energy of the exchange process, E_{A}, can be calculated using the Arrhenius equation

$$k_{123-4} = C\mathrm{e}^{-E_{\mathrm{A}}/RT}, \tag{12}$$

where C represents a constant (the frequency factor), R the gas constant and T absolute temperature. E_{A} was found to be 62 kcal (251 kJ)/mol for the ordering process. The rate constants can then be calculated at any temperature from

$$\ln\frac{k_{123-4,\,T2}}{k_{123-4,\,T1}} = \frac{E_{\mathrm{A}}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right). \tag{13}$$

Figure 2 shows the expected change of $x^{\mathrm{Fe}}_{\mathrm{M4}}$ with time for a material previously equilibrated at 720°C together with selected values determined experimentally.

It is clear from this figure that the cut-off temperature of a mineral cannot be evaluated from experiments, in which no change of cation distribution is observed. For instance, at 400 °C

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more than a year would be required to change the x^{Fe}_{M4} by a detectable amount. Thus the value of 400–500 °C given by Ghose & Weidner (1972) for the cummingtonite cut off temperature on the basis of 'no reaction' experiments at 398 °C, 672 h, must be considered suspect.

Derivation of cooling rates

The kinetics of the exchange reaction can be conveniently compared to a rock cooling path by means of a time–temperature–transformation diagram (TTT–plot) as in use for the portrayal of time–temperature processes in general (see, for example, Champness & Lorimer 1976) and applied to the kinetics of intracrystalline exchange in anthophyllite by Seifert & Virgo (1975).

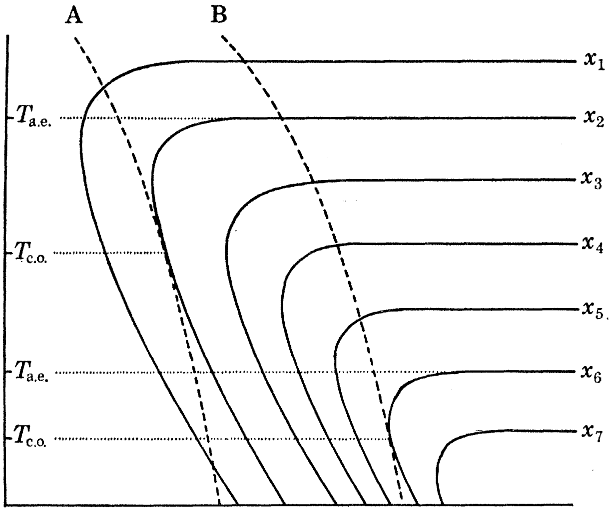

Figure 3. Schematic time (ordinate)–temperature (abscissa, logarithmic scale)–transformation plot for intracrystalline cation distribution. Lines of constant x ($x_1 < x_2 < x_3$, etc.) indicate the x^{Fe}_{M4} that can be achieved at given temperatures and times. Two different rock cooling paths are shown (curves A and B). Where they become tangent to a line of constant x^{Fe}_{M4} ordering stops (true cut-off temperature $T_{c.o.}$) and the degree of order attained at $T_{c.o.}$ indicates an apparent equilibration temperature $T_{a.e.}$. Rapid quenching of a rock (curve A) will result in higher $T_{a.e.}$ and $T_{c.o.}$ values than slow cooling (curve B).

A schematic diagram is given in figure 3. Lines of constant x^{Fe}_{M4} (corresponding to different percentages of transformation from the starting material to the final product) indicate the degree of order that is attained by annealing the starting material for a given time at a given temperature. The time-independent (horizontal) parts of these curves correspond to equilibrium cation distribution. Contrary to the experiments a natural sample will in general not be annealed under a constant temperature and then quenched but rather follow a temperature–time path through the diagram. Two such cooling paths are indicated in figure 3 by dashed lines. Ordering can only occur when the cooling path intersects lines of higher x^{Fe}_{M4} values with decreasing temperature. When the cooling path intersects the equilibrium parts of the constant x^{Fe}_{M4} curves intracrystalline equilibrium will be achieved by the sample at this temperature. In the temperature range where the cooling path intersects the curved parts of the lines and x^{Fe}_{M4} still increases with decreasing temperature along the path ordering is still possible but the equilibrium cation distribution is no longer achieved. The exchange process will eventually stop when the cooling path becomes a tangent to a curve of constant x^{Fe}_{M4}. The end product of this disequilibrium process will be a phase with a cation distribution corresponding to this tangent x_{M4}^{Fe} curve. Because the equilibrium ordering is used for temperature calibration the cation distribution would indicate an 'apparent equilibration temperature' $T_{a.e.}$ that is slightly higher than the true cut-off temperature. Nevertheless there is always a unique correspondence between cooling rate and apparent equilibration temperature.

It is thus possible, at least in principle, to derive the cooling rate of a mineral or its host rock from the intracrystalline cation distribution. So far, the complete determination of all data required has only been made on one anthophyllite specimen (Seifert & Virgo 1974, 1975) but unpublished results indicate that the model forming the basis of the calculations also holds for other anthophyllites of slightly different composition and other provenences (Seifert, in preparation). For the specimen studied by Seifert & Virgo a maximum cooling rate of 1×10^{-4} °C per year is obtained which is geologically reasonable although the inherent errors are hard to estimate at present.

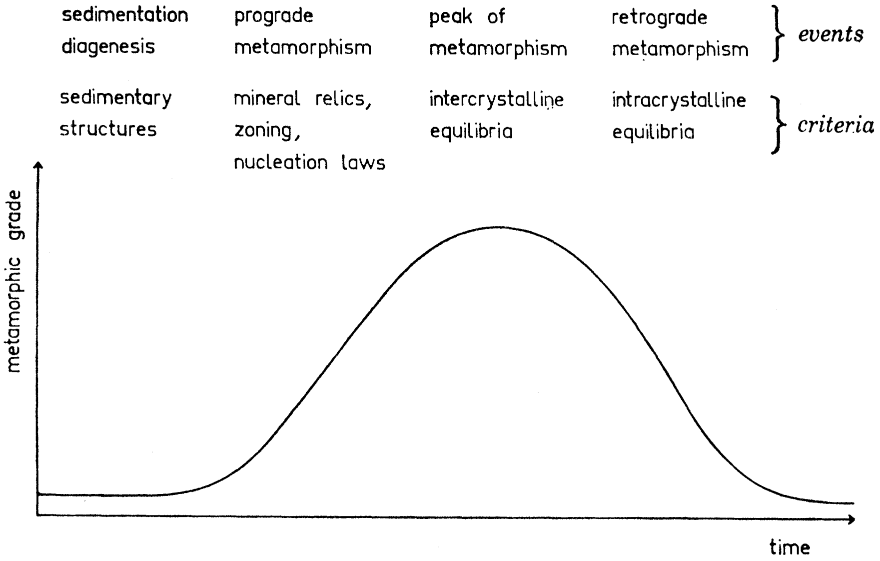

FIGURE 4. Schematic representation of a simple metamorphic cycle, indicating the most important events and the criteria that might be used to estimate the time-dependence of the related processes. For discussion see text.

OUTLOOK

The method presented only gives the cooling rate at one, i.e. the cut-off temperature of the mineral. Any previous event at a higher temperature will not be stored in the intracrystalline cation distribution. The thermal history of a rock during prograde metamorphism and during the peak of metamorphism as well as any polymetamorphism will have to be deduced from other parameters such as zoning and nucleation laws (see, for example, Kretz 1973, 1974) or from the kinetics of heterogeneous reactions. Figure 4 gives a schematic diagram for the processes in a simple metamorphic cycle and the mineralogical methods available to study their time dependence.

A rock cooling path will in general not necessarily be governed by a linear cooling rate but complex temperature–time relations are to be expected. A more complete reconstruction of the rock history might, therefore, be achieved from the order–disorder relation in a variety of minerals belonging to the same rock or rock suite with identical thermal history but different cut-off temperatures. In this context the aluminous varieties of orthoamphiboles, i.e. the gedrites, are most promising. In the few examples studied so far they show higher disorder than anthophyllite (Papike & Ross 1970). Structurally this can be explained by the octahedral Al atoms occupying the M2 position and thus blocking one path of Fe–Mg exchange between the M4 position and the M3 position (cf. figure 1). It is, therefore, suspected that the higher disorder observed in gedrites points to a higher cut-off temperature and that these phases might define thermal histories above the *ca.* 270 °C found for anthophyllite. At even higher temperature, in the vicinity of 500 °C, orthopyroxenes might, after suitable calibration, be used for the same purpose.

In summary, the method proposed represents a promising technique for the determination of rock cooling paths that is independent of other methods known so far. Among these radioactive dating of time intervals between closing temperatures (e.g. Jäger, Niggli & Wenk 1967) and cooling rates from concentration profiles in unmixed nickel-irons (Wood 1964) should be mentioned as the most elaborate methods available at present. It is clear that the complete rock cooling history can only be reconstructed by a combination of all kinetic information stored in the various minerals and by due consideration of all other geological and geophysical criteria (see, for example, Clark & Jäger 1969; Oxburgh & Turcotte 1974).

The basic data for the method proposed were collected during tenure of a fellowship at the Geophysical Laboratory, Washington, in close cooperation with D. Virgo. Additional experimental and theoretical studies at Kiel University have been made possible through a grant by Deutsche Forschungsgemeinschaft. I thank M. Barton for reviewing the manuscript.

References (Seifert)

Champness, P. E. & Lorimer, G. W. 1976 Exsolution in silicates. In *Electron microscopy in mineralogy* (ed. E. Wenk), pp. 174–204. Berlin: Springer-Verlag.

Clark, S. P. & Jäger, E. 1969 Denudation rate in the Alps from geochronologic and heat flow data. *Am. J. Sci.* **267**, 1143–1160.

Finger, L. W. 1970 Refinement of the crystal structure of an anthophyllite. *Carnegie Inst. Wash. Year Book* **68**, 283–288.

Ghose, S. & Weidner, J. R. 1972 Mg^{2+}–Fe^{2+} order–disorder in cummingtonite, $(Mg,Fe)_7Si_8O_{22}(OH)_2$: A new geothermometer. *Earth Planet. Sci. Lett.* **16**, 346–354.

Hafner, S. S. & Virgo, D. 1970 Temperature-dependent cation distributions in lunar and terrestrial pyroxenes. Proc. Apollo 11 Lunar Sci. Conf., *Geochim. cosmochim. Acta Suppl.* 1, **3**, 2183–2198.

Jäger, E., Niggli, E. & Wenk, E. 1967 Rb/Sr Altersbestimmungen an Glimmern der Zentralalpen. *Beitr. Geol. Karte Schweiz N.F.* **134**, 67 pp.

Kretz, R. 1973 Kinetics of the crystallization of garnet at two localities near Yellowknife. *Can. Miner.* **12**, 1–20.

Kretz, R. 1974 Some models for the rate of crystallization of garnet in metamorphic rocks. *Lithos* **7**, 123–131.

Kulke, H. & Schreyer, W. 1973 Kyanite-talc schist from Sar e Sang, Afghanistan. *Earth Planet. Sci. Lett.* **18**, 324–328.

Mueller, R. F. 1967 Model for order–disorder kinetics in certain quasibinary crystals of continuously variable composition. *J. Phys. Chem. Solids* **28**, 2239–2243.

Mueller, R. F. 1969 Kinetics and thermodynamics of intracrystalline distributions. *Miner. Soc. Am. Spec. Pap.* **2**, 83–94.

Mueller, R. F. 1970 Two-step mechanism for order-disorder kinetics in silicates. *Am. Miner.* **55**, 1210–1218.

Oxburgh, E. R. & Turcotte, D. L. 1974 Thermal gradients and regional metamorphism in overthrust terrains with special reference to the Eastern Alps. *Schweiz. Min. Petr. Mitt.* **54**, 641–662.

Papike, J. J. & Ross, M. 1970 Gedrites: crystal structures and intracrystalline cation distributions. *Am. Miner.* **55**, 1945–1972.

Seifert, F. & Virgo, D. 1974 Temperature dependence of intracrystalline Fe^{2+}–Mg distribution in a natural anthophyllite. *Carnegie Inst. Wash. Year Book* **73**, 405–411.

Seifert, F. & Virgo, D. 1975 Kinetics of the Fe^{2+}–Mg, order–disorder reaction in anthophyllites: quantitative cooling rates. *Science, N.Y.* **188**, 1107–1109.

Thompson, J. B. 1969 Chemical reactions in crystals. *Am. Miner.* **54**, 341–375.
Thompson, J. B. 1970 Chemical reactions in crystals: Corrections and clarification. *Am. Miner.* **55**, 528–532.
Virgo, D. & Hafner, S. S. 1969 Fe^{2+}, Mg order–disorder in heated orthopyroxenes. *Miner. Soc. Am. Spec. Pap.* **2**, 67–81.
Wood, J. A. 1964 The cooling rates and parent planets of several iron meteorites. *Icarus* **3**, 429–459.

Discussion

A. D. Law (*Computer Centre, Queen Mary College, University of London*). First may I comment that from my own observations the gedrite spectra are considerably more complex than the spectrum you have shown, and it seems probable that their interpretation is far from straightforward. Secondly, could you say whether the four-peak fit shown is the only one which you attempted – what for example, is the residual for the fit, and is there any evidence that a six-peak fit might be attempted?

J. V. Smith (*Dept. of the Geophysical Sciences, University of Chicago, Chicago, Illinois* 60637 *U.S.A.*).

(*a*) Congratulations on the elegant presentation of the mathematical basis of the relation between cooling and the velocity of the exchange reaction. The cooling rate was assumed to be linear with time. Is such a linear cooling rate to be expected in geological situations, and how would the reaction product vary for non-linear cooling rates?

(*b*) You mentioned that in gedrite, Al in a middle octahedral site might block exchange of Mg and Fe between inner and outer sites. R. C. Clayton's work on oxygen isotopes in minerals from metamorphic rocks indicates mobility of oxygen down to a few hundred degrees Centigrade. Would you comment on the possibility that movement of oxygen might allow the Mg and Fe cations to move without blocking from Al.

In the ensuing discussion, Professor Seifert referred to movement of Mg and Fe in lunar pyroxenes which exist in a dry environment, and he pointed out that the exchange products of his experiments on anthophyllite were the same for wet and dry environments. Dr Smith mentioned the possibility that proton catalysts were involved in migration of oxygen in terrestrial minerals, and pointed out that even in a dry environment anthophyllite contained its own inherent hydroxyl which could yield protons.