

## Hornblende–anthophyllite and hornblende–cummingtonite parageneses

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**SUMMARY.** The associations hornblende and anthophyllite or cummingtonite are dealt with briefly in the light of experimental data and naturally occurring assemblages. On the basis of the distribution of Mg and Fe<sup>2+</sup> in coexisting amphiboles and on the calculated and experimental slopes of a reaction in which the amphiboles hornblende and anthophyllite are formed a tentative *P–T–x* diagram is suggested for these parageneses.

**NATURAL** occurrences of hornblende–anthophyllite and hornblende–cummingtonite have been reported by, among others, Eskola (1914, 1950), Seitsaari (1952), and Tilley (1957). The conditions of formation of hornblende plus anthophyllite have been investigated by Choudhuri and Winkler (1967) in the reaction chlorite + tremolite + quartz → anthophyllite + hornblende + H<sub>2</sub>O, in which natural, analysed minerals were used as starting materials; details of the reaction and experimental runs have already been given. The lower stability of the amphiboles marks the beginning of the hornblende hornfels facies (amphibolite facies at high pressures), and beyond their upper stability the amphiboles break down to clinopyroxene, orthopyroxene, and plagioclase in the K-feldspar–cordierite facies of Winkler (1967). These limits have been used here, together with data on natural and synthetic amphiboles, to put forward a few suggestions for a *P–T–x* diagram for such amphibole pairs.

*Chlorite breakdown and formation of amphiboles.* The course of the experimentally investigated reaction in which chlorite breaks down in stages before it finally disappears leaving only two amphiboles may be given as: chlorite<sub>ss1</sub> + tremolite + quartz → chlorite<sub>ss2</sub> + anthophyllite + hornblende + H<sub>2</sub>O (ss, solid solution). In three runs of the same duration and constant pressure the basal spacing, *d*<sub>001</sub>, of chlorites of run products at successive temperatures was determined with an X-ray diffractometer and compared with the basal spacing of the starting chlorite; quartz present was used as an internal standard. The measurements revealed a noticeable increase in the basal spacings, e.g. from 14·1534 Å for the starting chlorite to 14·1824 Å for the chlorite of the product at 605 °C/2 kb. Since *d*<sub>001</sub> is inversely related to Al<sup>iv</sup> content, the increase in basal spacing suggests a depletion in Al<sup>iv</sup> (to maintain charge balance Al<sup>vi</sup> as well). This would result in a weakening of the layer charge of chlorite, and just as in the case of Greenwood (1963), where talc sheets break down to give the chain

structure of anthophyllite, so also here a similar process may be envisaged for chlorite breakdown. The formation of the amphiboles, however, is much more complex than is implied by these simplified suggestions.

The anthophyllite formed had a very low  $\text{Fe}^{2+}$  and Al content with an  $\text{Mg}/(\text{Mg}+\text{Fe}^{2+})$  ratio of 0.87 to 0.90 as against the gedrite of Akella *et al.* (1966) with  $\text{Mg}/(\text{Mg}+\text{Fe}^{2+}) = 0.65$ . Considering the difficulty involved in synthesizing pure Mg-anthophyllite (Greenwood, 1963), it is significant that an anthophyllite with very low  $\text{Fe}^{2+}$  was readily obtained.

The hornblende was inferred by graphical analysis to be of the type  $\text{Ca}_2(\text{Mg}, \text{Fe})_{6-x}\text{AlSi}_{8-x}\text{Al}_x\text{O}_{22}(\text{OH})_2$  where  $x = 1.1$ . In Mg-Fe amphiboles optical properties

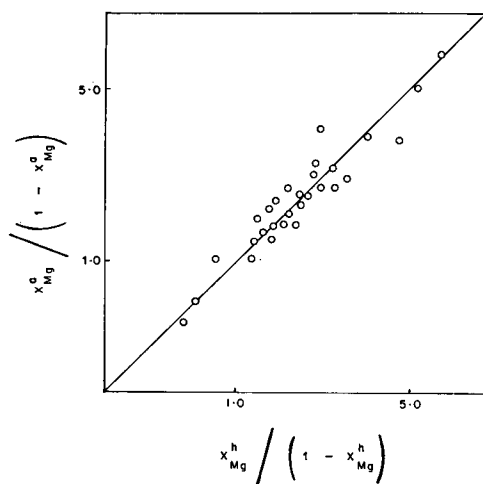


FIG. 1. Distribution of Mg-Fe in coexisting amphibole pairs. Data from Leake (1968), Klein (1968), and Kanisawa (1969).

depend largely on  $\text{Fe}^{2+}$  content, and although Al is a further parameter for orthorhombic amphiboles, the  $\gamma$  refractive index of Al-poor anthophyllites can be related to Mg-Fe content (Deer, Howie, and Zussman, 1965). In common hornblendes, in spite of complexity or composition,  $\gamma$  may also be approximately related to Mg-Fe diadochy, hence the values of  $\gamma$  have been used as an index of Mg-Fe ratio of hornblende and anthophyllite. This is supported by the Mg-Fe distribution in amphibole pairs from natural amphibolites.

*Coexisting amphiboles.* The distribution of Mg-Fe for pairs of coexisting amphiboles, hornblende and anthophyllite or hornblende and cummingtonite, from widely separated regions is found to be very similar. This distribution is shown in fig. 1 in which  $x_{\text{Mg}}^h/(1-x_{\text{Mg}}^h)$  is plotted against  $x_{\text{Mg}}^a/(1-x_{\text{Mg}}^a)$  where  $x_{\text{Mg}}^h$  and  $x_{\text{Mg}}^a$  are mole fractions of Mg in the Y positions in hornblende and in anthophyllite or cummingtonite respectively. The values for the natural pairs have been calculated from various sources (Leake, 1968; Klein, 1968; Kanisawa, 1969); the points representing amphibole pairs scatter close to the line for which the distribution coefficient  $K_{D(\text{Mg})} = 1.0$ , and the value for the experimental pair, estimated from their refractive index, is in fair agreement with the natural pairs (parageneses in which other ferromagnesian minerals are involved have not been considered). There is thus a systematic distribution of Mg-Fe, a phenomenon often observed in coexisting ferromagnesian minerals; in this respect, petrographic evidence also suggests that in most cases such amphibole pairs are in equilibrium. Amphiboles with a particular  $\text{Mg}/(\text{Mg}+\text{Fe})$  ratio have formed in the same physical environment, which leads us to the  $P$ - $T$  conditions of their formation.

Pressure-temperature conditions. Symbols used:

$P_s$ , pressure on the solid phases;

$P_{H_2O}$ , equilibrium pressure of pure  $H_2O$  fluid;

$\Delta G$ , free energy of reaction;

$\Delta S$ , change in entropy;

$\Delta V_s$ , volume change of solid phases;

$V_{H_2O}$ , molar volume of water;

$\Delta H$ , reaction enthalpy;

$f_{H_2O}$ , fugacity of water;

$n_{H_2O}$ , number of moles of water given off in the reaction.

The reaction 7 chlorite+7 tremolite+20 quartz $\rightarrow$ 7 hornblende+6 anthophyllite+22  $H_2O$  may be taken to represent the lower stability of hornblende plus anthophyllite and can be used as a starting point in considering the paragenesis of amphibole pairs. The lower stability of the amphiboles can be shown as a bivariant surface in a  $P$ - $T$ - $x$  diagram, provided  $P_{H_2O} = P_s$ , or by a univariant curve in a  $P$ - $T$  diagram, where  $x$  is the Fe/Fe+Mg ratio. Temperatures for the beginning of the amphibolite facies have been given by Winkler (1967) to be around 540 °C/2 kb, so that the slope of such a reaction at this temperature can be estimated with the help of the relation

$$\left(\frac{\partial P_s}{\partial T}\right)_{G=0} = \Delta S / (\Delta V_s + n_{H_2O} \cdot V_{H_2O})$$

(Thompson, 1955).

In the calculation the change in entropy was obtained from the values for entropy of dehydration given by Fyfe *et al.* (1958); the value of  $V_{H_2O}$  at 540 °C/2 kb was taken from Kennedy (1950). Molar volumes of the minerals at 298.15 °K and 1 bar were taken from Robie (1966), Shirozu (1958), and Greenwood (1963), assuming after Thompson (1955) that the thermal expansion and compressibility of the minerals are not affected by  $P$ - $T$  changes.

The calculated slope is compared with the experimentally determined curve for the reaction in fig. 2 and for the sake of comparison has been drawn through the reaction temperature 560 °C/2 kb. There is no appreciable deviation of the two curves within a reasonable pressure range. It should be pointed out that when  $P_{H_2O} < P_s$  the slope will be steeper;  $P_{H_2O}$  may actually be somewhat less than  $P_s$  under the natural conditions of regional metamorphism. Since the pressure dependence of the curve is small, it gives a fairly narrow range of temperature for the formation of the anthophyllite-hornblende assemblage.

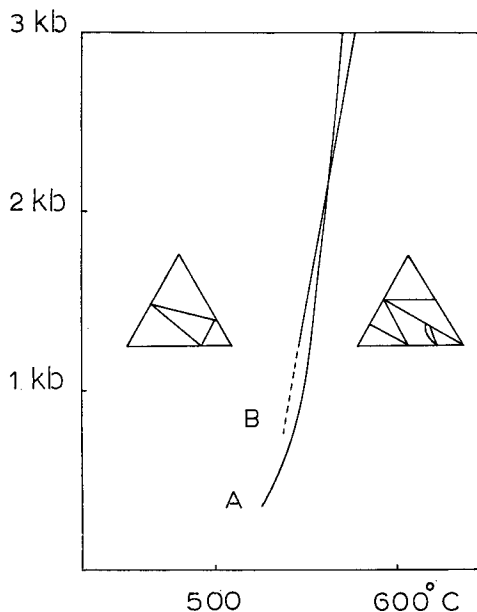


FIG. 2. Calculated slope, B, and determined curve, A, for the reaction chlorite+tremolite+quartz  $\rightarrow$  hornblende+anthophyllite+ $H_2O$ . Triangles represent conventional  $ACF$  diagrams for albite-epidote hornfels facies and hornblende hornfels facies.

In addition the reaction enthalpy for the formation of anthophyllite in the reaction in question and for gedrite (Akella *et al.*, 1966) may be calculated for the sake of comparison with the help of the relation  $d(\log f_{\text{H}_2\text{O}})/d(1/T) = -\Delta H/2.303R$  (Denbigh, 1964).  $f_{\text{H}_2\text{O}}$  was determined from the data of Anderson (1964).  $\Delta H$  is found to be 48 kcal/mole (within the limits of error, i.e.  $\pm 12$  kcal/mole) comparable with 40 kcal/mole for gedrite; this suggests similar conditions of formation (see Fyfe *et al.*, 1958).

The experimental curve or the calculated slope in fig. 2 can thus be used to demarcate the lower stability limit of the amphiboles in a tentative  $P$ - $T$ - $x$  diagram. Inasmuch as amphiboles form more generally from plagioclase and pyroxene of basic rocks in the course of regional metamorphism, their upper stability limit is likely to be the critical boundary under natural conditions. For the representation of this boundary the breakdown curves of the individual minerals (Hinrichsen, 1967; Schürmann, 1967) have been modified based on the breakdown of the hornblende-anthophyllite pair.

Actually hornblende often persists with orthopyroxene in some regional metamorphic terrains (Miyashiro, 1958), but this is disregarded here for the sake of simplicity.

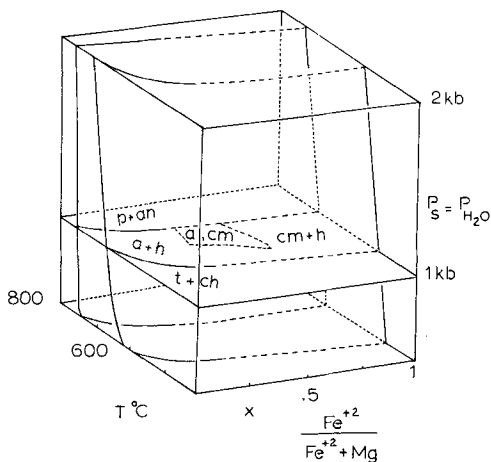


FIG. 3. Tentative  $P$ - $T$ - $x$  diagram for coexisting amphiboles. p, ortho- and clinopyroxenes; a, anthophyllite; cm, cummingtonite; t, tremolite; ch, chlorite; an, plagioclase

$P$ - $T$ - $x$  diagram. Hinrichsen (1967) and Schürmann (1967) have determined stability fields of anthophyllite and cummingtonite in 1 kb isobaric temperature-composition diagrams. In reactions involving other minerals the formation and breakdown temperatures of anthophyllite and gedrite are, however, lower than the temperatures obtained from the  $T$ - $x$  diagrams for orthorhombic amphiboles of corresponding Mg-Fe ratios; similar relations could be expected for cummingtonite, so that the lines bounding

the fields of these amphiboles in a  $T$ - $x$  diagram would shift to lower temperatures.

It was stated earlier that hornblende-anthophyllite and hornblende-cummingtonite pairs must have formed at temperatures appropriate to their Mg-Fe ratios; there are instances in which one of them has formed first, but they would tend to adjust to the given set of conditions as can be seen from the distribution of Mg and Fe between them (fig. 1).

Fig. 3 shows the tentative  $P$ - $T$ - $x$  diagram that has been constructed to serve as a rough model for the coexistence of the amphibole pairs; their field of stability is bounded on the high- and low-temperature sides by bivariate surfaces, which are reduced to lines in isobaric sections. In the 1 kb plane the field of overlap of antho-

phylite and cummingtonite as given by Schürmann (1967) is also shown. (Robinson *et al.*, 1969, have recently reported the equilibrium coexistence of all three amphiboles over a narrow compositional field.) With introduction of  $\text{Fe}^{2+}$  in the system temperatures of formation and breakdown of the amphiboles drop towards the Fe-rich end.

The influence of oxygen partial pressure on the stability of iron-bearing minerals has been considered by Eugster *et al.* (1962), and in dealing with amphiboles  $p_{\text{O}_2}$  will be an additional variable. Under natural metamorphic conditions iron oxides serve as a measure of  $p_{\text{O}_2}$ , and since magnetite is most commonly reported from amphibolites it is possible that  $p_{\text{O}_2}$  lies within the range  $10^{-15}$  to  $10^{-21}$  atm. At higher  $p_{\text{O}_2}$  the field of stability, particularly for iron-rich amphibole pairs, would be expected to shift to lower temperatures (Ernst, 1966).

*Conclusion.* The  $P$ - $T$ - $x$  diagram presented here is a simplified tentative model which indicates the probable field of coexistence of anthophyllite-hornblende and cummingtonite-hornblende pairs, their lower stability limit marking the beginning of the hornblende hornfels facies, or at higher pressures of the amphibolite facies. With increasing pressure the field of the amphiboles broadens, accompanied by a narrowing of the field of their breakdown products, i.e. the field of pyroxenes, so that amphiboles rarely break down completely during regional metamorphism.

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