

The dehydroxylation behaviour of amphiboles

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[Taken as read 9 June 1966]

Summary. The temperature at which dehydroxylation occurs in amphiboles is thought to be largely dependent on the type of cation that occupies the M_3 and M_1 sites. Four amphibole types have been studied in which these sites are occupied, in various proportions, by Mg^{2+} or Fe^{2+} . The temperature of dehydroxylation, in an inert atmosphere, is shown to rise with increasing Mg^{2+} content in these sites.

RECENTLY Hodgson (1965) has discussed the relationship between the chemical composition and the temperature of thermal decomposition of some crocidolites. He concluded from d.t.a. evidence that the position of the high temperature endotherm, that is, the temperature at which structural breakdown of the crocidolite occurs, was dependent on the Fe^{2+}/Mg^{2+} ratio, the temperature of the endotherm rising with rising Mg^{2+} content.

Crocidolite may be unique amongst the amphiboles in that the dehydroxylation process and the structural breakdown process are consecutive rather than concurrent (Freeman, 1962). Thus, in seeking correlations between the composition and thermal behaviour of amphiboles it is important to consider the temperature of dehydroxylation as well as the temperature of final structural breakdown.

In the amphibole structure the hydroxyl group is bonded to the M_3 cation and to the M_1 cations (using Whittaker's (1949) notation). Whittaker (1949) found that in Bolivian crocidolite the M_1 -OH and M_3 -OH bond distances were 2.10 Å. The M_1 -OH bond distance was 2.10 Å and the M_3 -OH distance 2.07 Å in cummingtonite (Ghose and Hellner, 1959). It is to be expected, then, that the strength of the M -OH bond, or the MO -H bond (where M represents the cation on the M_3 or M_1 sites), and consequently the temperature at which bond breakage occurs, will be dependent on the cations which occupy these sites. In order to show the effect of site occupancy on stability the temperature of dehydroxylation of four amphibole types has been determined.

Experimental results. The four amphibole types considered were:

Crocidolite (fibrous riebeckite) from Westerberg, South Africa. This is similar to the specimen described as RS. 7 by Cilliers, Freeman, Hodgson, and Taylor (1961). It has the approximate formula, $\text{Na}_2\text{Fe}_{\frac{3}{4}}^{3+}\text{Fe}_{\frac{3}{4}}^{2+}\text{Mg}_{\frac{3}{4}}\text{Si}_8\text{O}_{22}(\text{OH})_2$. *Amosite* (fibrous grunerite) from Penge, Transvaal. This had the approximate formula, $\text{Fe}_{\frac{2}{4}}^{2+}\text{Mg}_{\frac{1}{4}}\text{Si}_8\text{O}_{22}(\text{OH})_2$. It is similar to the specimen described as PRS.5 by Hodgson, Freeman, and Taylor (1965). *Anthophyllite* from Hillswick, Shetland (Aberdeen University Geology Department Collection, No. G2035). This had the approximate formula, $\text{Fe}^{2+}\text{Mg}_{\frac{5}{4}}\text{Al}_{\frac{1}{4}}\text{Si}_{7\frac{1}{4}}\text{O}_{21}(\text{OH})_3$. It occurred as white, tabular crystals. *Tremolite* from St. Gotthard, Switzerland (Aberdeen University Geology Collection, No. 6988). The composition of this material was very close to $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$. It occurred as white columnar crystals.

The dehydroxylation behaviour was studied, under N_2 atmosphere, in a silica tube furnace. A sample was heated at a series of temperatures between 100° and 1200° C, heating at a particular temperature being continued until the sample had achieved constant weight. In this way curves of weight loss (H_2O loss) versus temperature were obtained. These are shown in fig. 1. The dehydroxylation temperature was taken to be the temperature of maximum rate of weight loss. These temperatures are listed in table I.

Discussion

Occupancy of cation sites. Only a full three-dimensional structure analysis will give, unequivocally, the site occupancy of a particular sample. However, the principles governing the distribution of cations amongst the octahedral sites of the amphibole structure have been discussed by Whittaker (1960) and by Ghose (1965). Using these discussions as a basis it is possible to assign the site occupancy with some assurance.

The principles governing the distribution of cations are based on seven recent structure refinements of which only two, grunerite (Ghose and Hellner, 1959) and cummingtonite (Ghose, 1961), were three dimensional determinations. Ghose (1965) concluded that for anthophyllite, cummingtonite (grunerite), and riebeckite Mg was preferred to Fe^{2+} in the M_1 and M_3 sites; the M_3 site was taken by Mg in anthophyllite and cummingtonite, and by Fe^{2+} in riebeckite; the M_4 site was taken by Fe^{2+} in anthophyllite and cummingtonite, and by Na in riebeckite. Whittaker (1960) pointed out that, in anthophyllite, if M_4 is occupied by Fe^{2+} (radius 0.83 Å) then the cation in M_2 must not be larger than 0.74 Å for orthorhombic symmetry to be retained. If the M_4 site contains Mg (ionic radius 0.78 Å) then there is sufficient room at M_2 for Mg. In the present sample

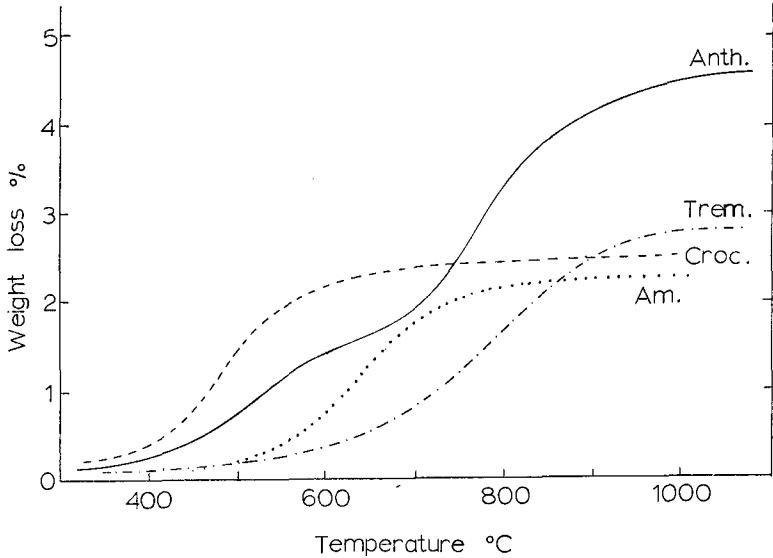


FIG. 1. Dehydration curves for anthophyllite (Anth.), tremolite (Trem.), crocidolite (Croc.), and amosite (Am.)

TABLE I. Site occupancy and dehydroxylation temperature for four amphibole types.

	Crocidolite	Amosite	Tremolite	Anthophyllite
Dehydroxylation temperature:	520° C	610	790	800
M_1 and M_3 {				
Mg	8 %	25 %	100 %	100 %
Fe ²⁺	92	75	—	—
M_2 {				
Mg	12	25	100	63
Fe ²⁺	—	75	—	—
Al	—	—	—	37
M_4 {				
Ca	—	—	100	—
Na	100	—	—	—
Fe ²⁺	—	100	—	50
Mg	—	—	—	50

of anthophyllite this condition can be met by the inclusion of Al³⁺ in M_2 , or by a vacancy at M_2 , since there is a deficiency of metal cations in the structure. The charge balance is maintained by the excess of H⁺ over the required 2(OH) per formula unit. Thus, for the anthophyllite used in this study, it is assumed that all the Fe²⁺ is in the M_4 site, together with Mg²⁺ to complete the balance; the M_2 sites contain all the Al, together with Mg, or may be vacant. The M_1 and M_3 sites contain Mg.

In crocidolite it is assumed that the M_4 sites are filled by Na; the M_2 sites take all $\frac{3}{4}\text{Fe}^{3+}$ ions, the remaining $\frac{1}{4}$ ion is most probably supplied by the Mg ion; the M_1 and M_3 sites are taken by the Fe^{2+} ion and the remaining Mg, which are assumed to be randomly distributed between these sites.

The cation distribution suggested for grunerite (Ghose and Hellner, 1959) may be applied, with little change, to the amosite used in this work. The chemical compositions of these two minerals differ in that the amosite has a slightly higher Fe^{2+}/Mg ratio than the grunerite. With allowance made for this difference the following cation distribution is assumed: The M_4 sites are occupied by Fe^{2+} , and the remaining Mg and Fe^{2+} ions are randomly distributed amongst the M_1 , M_2 , and M_3 sites.

The tremolite used in this work is the almost pure end-member in which Ca takes the M_4 sites and the M_1 , M_2 , and M_3 sites are filled by Mg.

Dehydroxylation behaviour. The dehydroxylation curves for crocidolite, amosite, and tremolite are sigmoid in appearance. The weight losses above 400°C approximate to the values expected for the theoretical $2(\text{OH})$ groups per formula unit.

The curve for anthophyllite differs in two respects; the weight loss is greater than that required for $2(\text{OH})$ per formula unit, and the water is lost in two steps. This two-stage dehydroxylation behaviour has been noted previously by Thilo and Rogge (1939). The first stage may be attributed to loss of hydroxyls bonded to Si and the second stage to hydroxyls bonded to M_1 and M_3 cations.

The temperature of dehydroxylation, as summarized in table I, increases as the proportion of Mg in the M_1 and M_3 sites increases and Fe^{2+} decreases. This behaviour may be compared with the stabilities of the respective hydroxides, since the bonding of the cations at M_1 and M_3 to the OH group is reminiscent of a strip of the brucite structure. In N_2 atmosphere $\text{Fe}(\text{OH})_2$ decomposes below 200° whereas $\text{Mg}(\text{OH})_2$ is stable up to 300°C .

Quite obviously factors other than the type of cation occupancy of the M_1 and M_3 sites play an important part in determining the absolute strength of the $M\text{-OH}$, or $MO\text{-H}$, bond. The present work indicates, however, that the relative strength of the bond, in amphiboles, is dependent on the occupancy of these sites. In four amphiboles studied the M_1 and M_3 site occupancy ranges from 92 % Fe^{2+} in crocidolite to 100 % Mg in anthophyllite and tremolite. The dehydroxylation temperature has a range of about 300°C for these four types.

In this discussion the effects of minor constituents, such as Mn, have been ignored. It is unlikely that small proportions of ions will significantly alter the temperature of maximum rate of water-loss, although they may control the range of temperature over which water is lost. When ions, other than Mg or Fe²⁺, occur in large proportion in the M_1 or M_3 sites, it is to be expected that the dehydroxylation temperature will be similarly related to the decomposition temperature of the respective hydroxide.

Acknowledgements. I wish to record my thanks to Prof. H. F. W. Taylor for stimulating the present work, which was carried out at Aberdeen University. I also wish to thank the Cape Asbestos Company Limited for financial support, and the Geology Department of Aberdeen University for providing specimens.

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[*Manuscript received 4 February 1966.*]
