

Thermal decomposition of amosite, crocidolite, and biotite

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SUMMARY. The oxidation of amosite, crocidolite, and biotite has been determined at temperatures up to nearly 900 °C under both a vacuum (10^{-2} mm Hg) and oxygen (10 and 600 mm Hg). Infrared spectra gave the loss of constitutional hydroxyl under these conditions. The loss of tensile strength of the amphiboles with increasing temperature seems to be due to thermal decomposition. For the three minerals oxidation takes place progressively over a broad temperature range. Under vacuum there is a certain temperature above which the ferric iron previously formed is reduced; this temperature corresponds to the completion of the loss of hydroxyl. The crocidolite anhydride in the literature is most probably an oxycrocidolite formed by dehydrogenation, the truly dehydroxylated zones being amorphous.

WHEN hydrated silicates containing ferrous iron are heated the constitutional hydroxyl decomposes and the iron may also change its valence state. The oxidation may result from either the incorporation of oxygen into the material (oxygenation; Addison and Sharp, 1968) or a dehydrogenation (Brindley and Youell, 1953): $\text{Fe}^{2+} + \text{OH}^- \rightarrow \text{Fe}^{3+} + \text{O}^{--} + \text{H}$. This reaction combines oxidation and dehydroxylation and does not perturb the oxygen packing in the crystals, it involves a migration of protons and electrons (Addison and Sharp, 1962a; Vedder and Wilkins, 1969). At the surface, hydrogen reacts with oxygen to form water or, under inert atmospheres, evolves as H_2 (Hodgson, Freeman, and Taylor, 1965b).

The characteristics of thermal decomposition of crocidolite and amosite may be summarized as follows (Hodgson, Freeman, and Taylor 1965a, b; Patterson and O'Connor, 1966): During a static treatment under non-oxidizing atmosphere (A , N_2 , vacuum), crocidolite dehydroxylates around 500–600 °C. The reaction seems to lead to an anhydrous phase having a structure closely related to the starting material; various new phases appear above 800 °C. Under similar conditions amosite dehydroxylates above 500 °C and produces pyroxene. Upon static heating of crocidolite under oxidizing atmosphere (O_2 or air) a dehydrogenation takes place at 300–450 °C, to form an oxyamphibole. This phase shows structural characteristics very similar to the fresh material; it oxidizes further above 600 °C and decomposes. Under the same conditions amosite oxidizes progressively in the range of 350–800 °C. This oxidation takes place through dehydrogenation, provoking the loss of constitutional hydroxyls, as well as through oxygenation. The formation of an oxyamphibole is also observed; new phases appear at higher temperatures.

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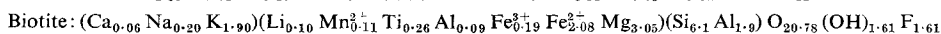
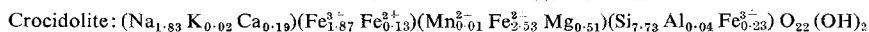
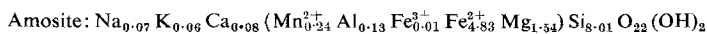
Vedder and Wilkins (1969) have studied the thermal decomposition of biotite by observing the evolution of the OH stretching bands after various pretreatments. The hydroxyls close to an octahedral vacancy, absorbing at low frequency, decompose to form molecular water below 800–900 °C. The other hydroxyls are not decomposed under treatments of macrocrystalline material below 900 °C, but powders are oxidized in air around 500 °C through dehydrogenation.

The purpose of this work was to obtain direct information about the relation between temperature, nature of the atmosphere, oxidation, and hydrogen loss of these minerals. Therefore the quantitative interpretation of the hydroxyl-stretching bands was combined with chemical determination of the iron content.

The *samples* of crocidolite and amosite are due to the courtesy of Dr. A. A. Hodgson, Cape Asbestos Company. They had been defiberized by a hammermill; by sieving under a water current about 95 % of the material passed through the 50 μm sieve.

The biotite studied is from Douglas, Ontario, and was provided by the Geological Survey of Canada. In order to avoid important alteration, grinding was in a Waring Blender containing distilled water to give a particle size of the order of 0.1 to 3 mm.

The following structural formulae were calculated on the basis of analyses performed in this laboratory; for amphiboles an ideal water content was assumed:



Experimental procedure. The three samples, in silica crucibles, were placed in a silica tube connected to a vacuum apparatus. A trap cooled by liquid air or solid CO_2 condensed the water liberated during the heating. The temperature was raised by steps of 50 °C from 250 to 600 °C and by steps of 100 °C above 600 °C, the samples being held for 20 hours at each temperature. After each step a portion of sample was removed for recording infrared spectra and determining the FeO content. Three sequences of experiments were performed under different atmospheres: 600 and 10 mm Hg of oxygen pressure and a vacuum better than 10^{-2} mm Hg. In all cases the sample was put in contact with the appropriate atmosphere before raising the temperature.

The $(\text{Fe}^{2+} + \text{Mn}^{2+})$ content was determined by the method of Ingamells (1960) reported by Schoenfelder (1965). In view of the small amount of Mn present, this content is considered as Fe^{2+} and expressed as FeO (wt. %).

Infrared spectra were recorded in the region of OH stretching bands with a Beckman IR12 spectrograph. The spectra of amphiboles were obtained by the use of KBr pellets. For biotite the flakes were sedimentated on a Büchner funnel from a water suspension and a coherent wafer was obtained after oven drying; the spectra were recorded at various incidence angles, with the light polarized in the plane of incidence.

The characteristics of the OH stretching bands are reported in table I; the cation environment corresponding to each component has been assigned according to Burns *et al.* (1966, 1968) for amphiboles and Vedder (1964) for biotite.

The procedure used for recording the spectra is such that the band area (integrated absorbance) is directly proportional to the integrated parallel absorption

coefficient K (Rouxhet, 1969) and, for a given mineral, to the OH content. The significance of K for micas has been discussed by Rouxhet (1970); the values calculated for Douglas biotite are given in table I. The constancy of K has been checked for the fresh amphiboles over a range of concentrations in the KBr pellets extending

TABLE I. Description, attribution and integrated parallel absorption coefficient K of the stretching OH bands

	Wavenumber	Half band width	Octahedral population	K (wavenumber $\times \frac{\text{cm}^2}{\text{mg}}$)
Amosite	LF 3620	4	3Fe ²⁺	6.0
	MF 3639	4-5	2Fe ²⁺ , 1Mg	6.8
	HF 3656	6	1Fe ²⁺ , 2Mg	2.0
Crocidolite	LF 3621	4	3Fe ²⁺	9.2
	HF 3637	4-5	2Fe ²⁺ , 1Mg	5.5
Biotite single crystals	LF 3545	50-60	1 vacancy, 2 cations	2.1
	HF 3690	35-40	3 cations	12.9

from zero to well above the usual concentrations used; the values reported in table I were estimated by considering the constitutional hydroxyls as randomly oriented in the KBr pellet (Rouxhet, 1969).

Results

Heat treatment of amphiboles. The evolution of the FeO content as a function of the temperature of pretreatment under oxygen atmosphere is illustrated by figs. 1BII and 2BII. For both amphiboles, there is no significant difference between results obtained for the two oxygen pressures (600 and 10 mm Hg). While the FeO content of amosite decreases rather regularly as a function of the pretreatment temperature, crocidolite oxidizes appreciably in a shorter temperature range and the amount of residual Fe²⁺ decreases only slowly as a function of subsequent heat treatments. These static oxidation curves are similar to those obtained by Hodgson *et al.* (1965a); however, here there is no abrupt change in the slope of the curve of crocidolite around 450 °C.

The decrease in intensity of the OH stretching bands under the same conditions is shown in figures 1BI and 2BI. Under these experimental conditions no significant difference was observed either between the evolution of the various bands of a given amphibole or between the results obtained for the two oxygen pressures.

After heat treatments under vacuum (10⁻² mm Hg), a slight oxidation is observed (figs. 1AII and 2AII). However, above some temperature, the value of which depends on the nature of the mineral, the ferric iron formed is reduced. The degree of oxidation is maximum for the temperature where the OH bands have completely disappeared (figs. 1AI and 2AI).

Heat treatment of biotite. The evolution of the FeO content of biotite as a function of temperature is shown in fig. 3II. It is similar to observations by Robert and Pedro (1968) on other biotites. As for amphiboles, no significant difference is observed

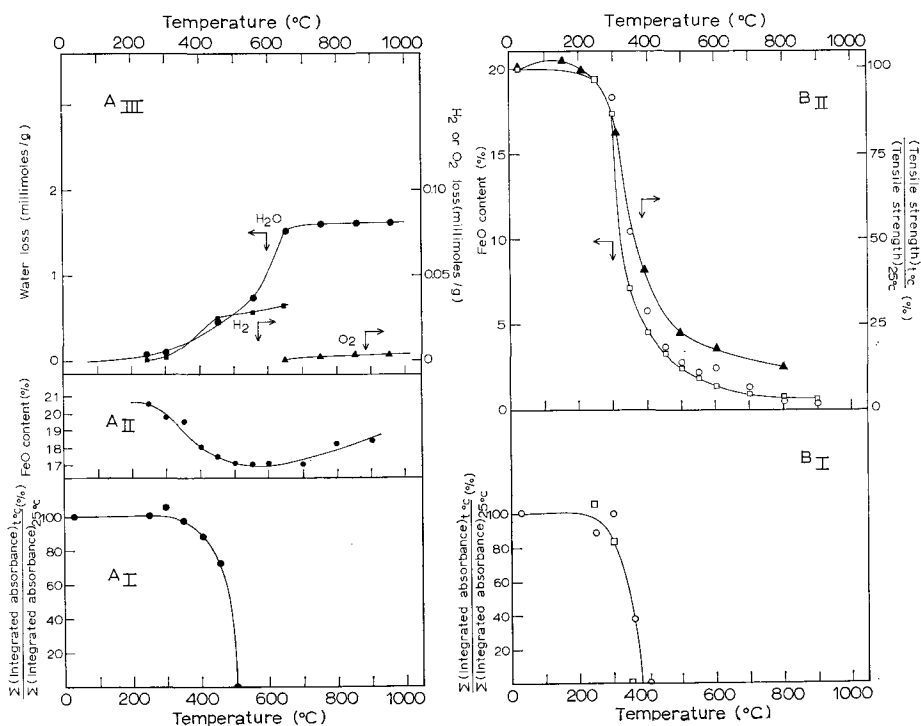


FIG. 1. Variation of *crocidolite* properties as a function of the ultimate pretreatment temperature; the sample was maintained 20 hr at each temperature except when otherwise indicated. A. Treatment under reduced pressure (10⁻² mm Hg). AI. Relative variation (%) of the sum of the integrated absorbances of OH stretching bands, for a fixed amount of material in the infrared beam. AII. Variation of the FeO content (%). AIII. Gas evolved (millimoles/g); treatment of 1 hr at each temperature: ● H₂O; ■ H₂; ▲ O₂. B. Treatment under oxygen pressure: ○ P_{O₂} = 10 mm Hg; □ P_{O₂} = 600 mm Hg. BI. Relative variation (%) of the sum of integrated absorbances of OH stretching bands, for a fixed amount of material in the infrared beam. BII. Left ordinate ○, □: variation of FeO content (%). Right ordinate, ▲: relative variation (%) of the tensile strength; pretreatment in air (Burman, 1967).

between oxidations under 600 and 10 mm Hg oxygen pressures. Oxidation under vacuum takes place in about the same temperature range; heating above a certain temperature reduced the ferric iron formed. Under these conditions the maximum extent of oxidation is higher than for amphiboles.

The intensity of the low-frequency band (fig. 3I) decreases appreciably before oxidation has started; it has vanished after a treatment around 700 °C. The behaviour is the same irrespective of the atmosphere surrounding the samples. This is in agreement with the observations of Vedder and Wilkins (1969), which indicate that hydroxyls

close to an octahedral vacancy, responsible for the low frequency OH band, disappear independently of any oxidation process; they give rise to the formation of molecular water following a classical dehydroxylation process.

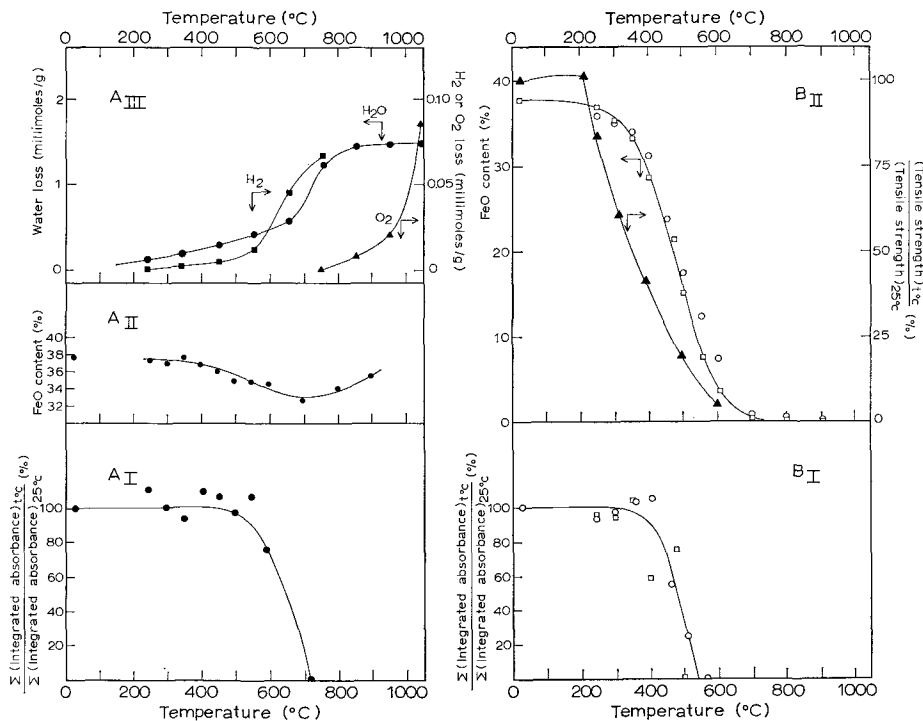


FIG. 2. Variation of *amosite* properties as a function of the ultimate pretreatment temperature; the sample was maintained 20 hours at each temperature except when otherwise indicated. A. Treatment under reduced pressure (10⁻² mm Hg). AI Relative variation (%) of the sum of the integrated absorbances of OH stretching bands, for a fixed amount of material in the infrared beam. AII. Variation of the FeO content (%). AIII. Gas evolved (millimoles/g). Treatment of 1 hour at each temperature: ● H₂O; ■ H₂; ▲ O₂. B. Treatment under oxygen pressure: ○ P_{O₂} = 10 mm Hg; □ P_{O₂} = 600 mm Hg. BI. Relative variation (%) of the sum of integrated absorbances of OH stretching bands, for a fixed amount of material in the infrared beam. BII. Left ordinate ○, □: variation of the FeO content (%). Right ordinate, ▲: relative variation (%) of the tensile strength; pretreatment in air (Burman, 1967).

The intensity of the high-frequency band is not reported on any graph; it does not decrease appreciably below 550–600 °C. However, under the three atmospheres investigated, it becomes very weak after treatment around 700 °C, precisely when oxidation is important.

Gas loss under vacuum. Besides the experiments described above, the amount of gas evolving during heat treatments under vacuum has been measured volumetrically. The temperature was raised by steps, the sample being maintained for one hour at each temperature. The results are shown in figs. 1AIII, 2AIII and 3III. A fraction of

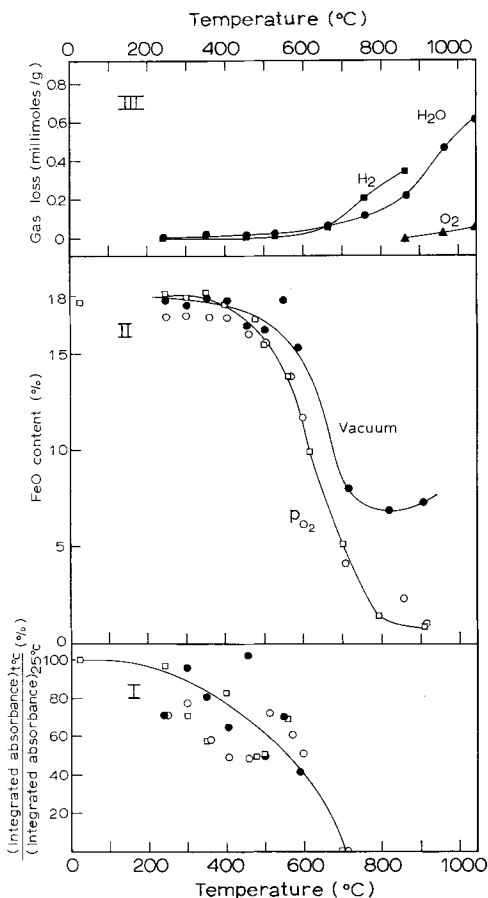


FIG. 3. Variation of the properties of *biotite* flakes as a function of the ultimate pretreatment temperature. The sample was maintained 20 hours at each temperature, except when otherwise indicated. I. Relative variation (%) of the integrated absorbance of the low-frequency OH band, for a fixed amount of material in the infrared beam: ● reduced pressure (10^{-2} mm Hg); ○ $P_{O_2} = 10$ mm Hg; □ $P_{O_2} = 600$ mm Hg. II. Variation of the FeO content (%): ●, ○, □ see I. III. Gas evolved (millimoles/g) under reduced pressure (10^{-2} mm Hg); treatment of 1 hour at each temperature: ● H_2O ; ■ H_2 ; ▲ O_2 .

between amosite and crocidolite. Therefore it seems that the decrease of the tensile strength resulting from a heat treatment is due either to oxidation or to modifications induced by this reaction.

Oxidation under oxygen. Vedder and Wilkins (1969) have studied the oxidation of a biotite (196513) having a chemical composition close to our biotite. The samples

the gas evolved did not condense at liquid air temperature. Mass spectrograph analysis confirms that, for all three minerals, the non-condensable gas liberated below the temperature of maximum oxidation is hydrogen; oxygen evolves at higher temperatures. As gas-loss measurements were performed in separated experiments, no quantitative correlation can be made between these data and the oxidation curves.

The results for amphiboles indicate an anomalously high water content. Hodgson *et al.* (1965a) attribute this excess to water molecules tightly held between the fibres.

Discussion

Tensile strength of the amphiboles. Burman (1967) has measured the tensile strength of an amosite and a crocidolite after pretreatment in air at various temperatures. These minerals, the amosite from Penge and the crocidolite from Pomfret, have chemical compositions very close to those of samples studied in our work; the fibres used for the determination had an equivalent diameter of the order of $10\text{--}20\ \mu\text{m}$. The relative decrease of the tensile strength observed by Burman as a function of the pretreatment temperature is shown in figs. 1BII and 2BII. For both amphiboles the resulting curve has a shape similar to the variation of the FeO content, whilst the two types of curves differ appreciably

studied here had a particle size intermediate between sheets and powder used by them. The temperature (600–700 °C) at which oxidation occurs and the high-frequency band disappears is also intermediate between those observed for sheets (above 900°C) and powder (500 °C). Such an important variation of reaction temperature as a function of the particle size excludes the possibility of studying the oxidation kinetics by experiments performed on powders, unless the distribution of particle sizes is extremely narrow.

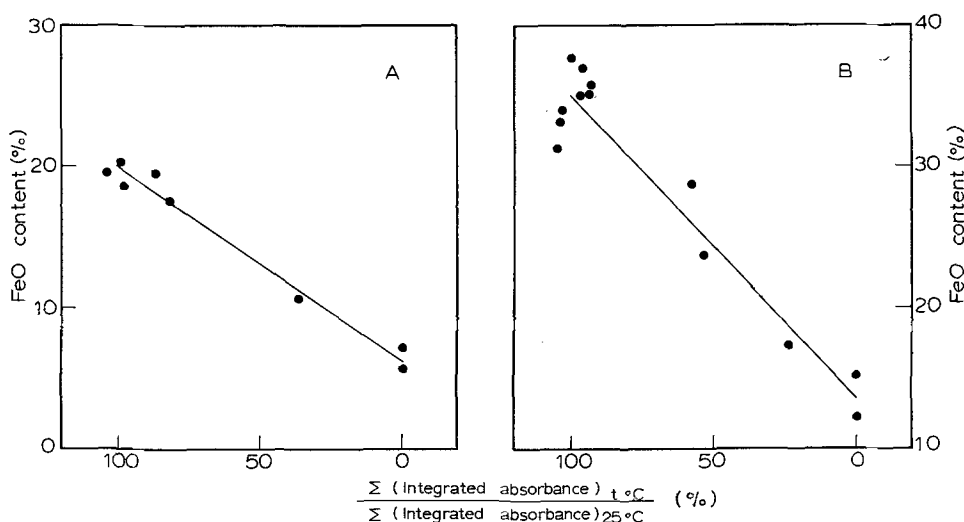


FIG. 4. Relationship between the decrease of the FeO content (weight percent) and the relative diminution (%) of the sum of the integrated absorbances of OH stretching bands; data obtained after pretreatment at various temperatures under P_{O_2} of 600 or 10 mm Hg. A. Crocidolite. B. Amosite.

Fig. 4 shows for both amphiboles a plot of the FeO content as a function of the sum of the integrated absorbances of OH bands, related to its value for the fresh material. The slope of the straight lines drawn allows an estimation of the atomic ratio H-liberated/ Fe^{2+} -oxidized. On the basis of an original constitutional water content of 1.9 %, this ratio is found to be of the order of 1 for crocidolite and 2/3 for amosite, from the beginning of oxidation to the disappearance of constitutional hydroxyls. This confirms observations that as long as hydroxyls are present the oxidation of crocidolite is essentially a dehydrogenation, while for amosite dehydrogenation and oxygenation occur together (Addison, Addison, Neal, and Sharp, 1962; Addison and Sharp, 1968; Addison and White, 1968; Hodgson, Freeman, and Taylor, 1965; Ernst and Wai, 1970).

Once all hydroxyls have been lost, amosite still contains about 13 % and crocidolite 6 % FeO. For both amphiboles, as well as for biotite, the completion of oxidation must therefore proceed through oxygenation.

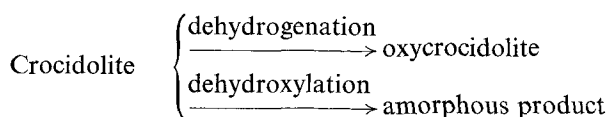
Addison *et al.* (1962) and Addison and White (1968) have observed that the oxidation of crocidolite around 450 °C stops at some degree. They attribute that behaviour to Mg ions blocking some diffusion processes involved in the progress of the reaction. The same effect of Mg ions would limit the extent of dehydrogenation of amosite (Addison and Sharp, 1968). Figs. 1BII and 2BII show that even with a particle size smaller than the one used in those works a limitation of the reaction extent is in fact observed in a very wide temperature range; therefore reaction stopping at some point does not seem to be significant by itself. Amosite does not even show any sharp decomposition step at any temperature.

The apparent extension of reactions over a broad temperature range may as well be due to a trivial kinetic effect resulting from a slow diffusion process. Moreover it should be kept in mind that thermodynamic reasons may condition the stability of compounds having intermediate oxidation degrees. It has been shown that the thermal stability of hydroxyls depends very strongly on their close environment (Wilkins and Vedder, 1969); the same might be true for the oxidation conditions of Fe²⁺. In this respect, not only the chemical composition but also cation ordering (Ernst and Wai, 1970) may be important factors. As far as the effect of magnesium is concerned, a general observation is that the temperature of decomposition increases when the Mg content rises (Freeman, 1966), but this must be related to the thermodynamics of the minerals.

Heat treatment under vacuum. The oxidation taking place under vacuum rules out the possibility of determining the water content of these silicates by weighing the samples after pretreatment below 1000 °C under vacuum; this can be done by measuring volumetrically the amount of gas evolved. However, the reduction observed above a certain temperature indicates that a treatment at sufficiently high temperatures does possibly not change the valence state of iron.

Wilkins and Vedder (1969) have pointed out the problem raised by the apparent existence of a crystalline crocidolite anhydride resulting from a heat treatment of crocidolite under vacuum, whilst there is no vacancy in the octahedral layer. As such a treatment provokes a partial dehydrogenation it is most probable that the X-ray pattern attributed to crocidolite anhydride (Hodgson *et al.*, 1965*a*) is due in fact to oxycrocidolite, which must represent up to 10 % of the material under the conditions used here. The zones that have lost hydroxyls through condensation into water molecules, i.e. the truly dehydroxylated zones, would be amorphous. This point is supported by the observation (Addison and Sharp, 1962*b*) that a crocidolite heated at 615 °C under a reducing atmosphere is amorphous.

Therefore the evolution of crocidolite under vacuum is considered not to be the same through the whole sample; the two possible reactions may be schematized as:



In the case of amosite the formation of oxyamphibole under vacuum was not observed by X-ray, possibly because of the nature of the dehydrogenated and dehydroxylated zones distribution or because of an immediate crystallization into pyroxene.

Conclusion

The present work suggests that the loss of tensile strength of preheated amphiboles is associated with the thermal decomposition of the minerals.

Correlations between the FeO and OH contents confirm that, as long as hydroxyls are present, the oxidation of crocidolite takes place essentially through dehydrogenation, while for amosite dehydrogenation and oxygenation take place together. For both amphiboles, as well as for biotite, the completion of oxidation proceeds through oxygenation.

It is thought that reaction stopping apparently at some degree at any temperature has not much significance by itself. The shape of the oxidation curves as a function of temperature might have some meaning in a comparison of minerals together; however, it is not practically possible to decide whether the extension of reactions over a broad temperature range is due to kinetics or stability effects.

Biotite and amphiboles have fairly similar behaviours. When heated under vacuum (10^{-2} mm Hg) they oxidize progressively; however, above a certain temperature at which there is no hydroxyl left in the lattice the ferric iron formed is reduced.

The crocidolite anhydride mentioned in the literature is most probably an oxy-crocidolite formed by dehydrogenation, the truly dehydroxylated zones being amorphous.

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