THE STRUCTURAL DISINTEGRATION OF SOME AMPHIBOLES*

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ABSTRACT

The structural disintegration characteristics of some selected species of amphiboles were investigated by thermal, *x*-ray, optical, and chemical methods. Except for some limited cases of fusion all of the reactions involving structural collapse occur in the solid state and are heat absorbing (endothermic). In the temperature range 900°–1125° C most species have heats of reaction of the order of 5 calories per gram.

Monoclinic amphiboles yield the following substances among the products of structural disintegration: monoclinic pyroxenes, cristobalite, hematite, magnetite, olivine, plagioclase feldspar, water, and glass. The magnetite and olivine minerals occur as disintegration products of hastingsite at 1145° C. Orthorhombic amphiboles collapse above 900° C. to form orthopyroxenes, cristobalite, water, and glass.

The amphiboles containing Al that proxies for Si in the double-chains have higher disintegration temperatures than the non-aluminous types. The heats of reaction at these higher temperatures are lower, however, than those for the pure silicon types.

The amphiboles that contain large amounts of Na and F undergo extensive fusion near the breakdown temperatures. Fluorine remains in the glass product of disintegration and is not driven off at temperatures up to 1125° C. due to its high electronegativity.

The oxidation of ferrous iron at temperatures bordering near structural collapse make calorimetric measurements of the disintegration process less accurate in those specimens bearing ferrous iron.

INTRODUCTION

Thermal studies of the amphiboles were initiated more than fifty years ago by Doelter and Hussak[1] when they determined that green hornblende broke down into magnetite plus augite, or olivine, at a high temperature. These observations were made without the benefit of a precise knowledge of the structure and composition[2,3] of the amphiboles which remained undetermined for many years. The dehydration experiments with tremolite[4] and magnesian anthophyllite[5] confirmed the previously established presence of 2 (OH,F) ions per mole formula. In these same experiments it was shown that the removal of hydroxyl groups

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[1] Doelter, C., and Hussak, E., Ueber die Einwirkung geschmolzener Magmen auf verschiedene Mineralien: *Neues Jahr. für Min., Geol.*, und *Pal.*, Band **1**, 18–44 (1884).

[2] Warren, B. E., The crystal structure and chemical composition of the monoclinic amphiboles: *Zeit. für Krist.*, **72**, 493–517 (1930).

[3] Warren, B. E., and Modell, D. I., The structure of anthophyllite, $H_2Mg_7(SiO_3)_8$: *Zeit. für. Krist.*, **75**, 161–178 (1930).

[4] Posnjak, E., and Bowen, N. L., The role of water in tremolite: *Am. Jour. Sci.*, **22**, 203–214 (1931).

[5] Thilo, E., and Rogge, G., Chemische Untersuchungen von Silikaten, mitteil VIII: *Ber. der Deut. Chem. Gesell.*, **72**, 341 (1939).

in the form of water was closely associated with the disintegration of the crystal structure.

The investigation described here is a re-examination of some of the previous experiments by a quantitative method[6] of differential thermal analysis that permitted the heats of reaction for the structural disintegrations to be measured. In addition, *x*-ray, optical, and spectrochemical methods of analysis were employed as supplementary tools in the investigation.

The chemical analyses for the eight specimens tested are shown below. Several differential thermal analyses of diverse members of the amphibole group indicated that the range of stability of these minerals lies between 600° and 1125° C., a region of high efficiency for the thermal equipment used in this investigation. No changes were observed below 600° C. and so only the thermographic records above that temperature are exhibited. A heating rate of 30° C. per minute with a furnace evacuated to a pressure of 1 mm. Hg was used to obtain the thermographic curves.

The structural disintegration of all the specimens analyzed occurred in the temperature range 925°–1125° C., and this reaction is designated by the peaks (y) in Figs. 1 and 2. Only the thermographic peaks so designated are concerned in this investigation. In all cases the transformation is a solid state reaction requiring heat absorption (endothermic). Other reactions, such as inversions[7] in the magnesian varieties, and oxidation of Fe^{++} in the ferrous varieties, are thermographically recorded at temperatures below the disintegration level.

TREMOLITE

Posnjak and Bowen[8] demonstrated the role of water in tremolite by static weight-loss experiments. At 900° C. the theoretical water content (2.22%) is driven off, and the following reaction takes place in the solid state:

$$\underset{\text{tremolite}}{Ca_2Mg_5Si_8O_{22}(OH)_2} + \Delta H = \underset{\text{diops.-clinoenst.}}{2CaSiO_3 \cdot 5MgSiO_3} + \underset{\substack{\text{cristo-}\\\text{balite}}}{SiO_2} + H_2O$$

A thermographic record of the removal of hydroxyl groups from tremolite (Fig. 1) gives a graphical representation of this dissociation reaction. The specimen from which the analysis was obtained was a portion of the

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[6] Wittels, M., Some aspects of mineral calorimetry: *Am. Mineral.*, **36**, 760–767 (1951).

[7] Wittels, M., Structural transformations in amphiboles at elevated temperatures: *Am. Mineral.*, **36**, 851–858 (1951).

[8] Posnjak, E., and Bowen, N. L., *op. cit.*

Specimen	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	FeO	MnO	Na_2O	CaO	K_2O	H_2O	F	Total
Tremolite[1]	58.59	0.10			24.78			0.12	13.95	0.10	2.31	—	99.75
Richterite[2]	57.74	0.37	tr	0.29	23.67	tr	2.40	3.14	9.01	0.64	2.39	0.37	99.86
Soda-Trem.[3] Glaucophane (A)	54.30	2.02	0.04	7.37	17.71	2.96	0.52	7.80	3.30	2.10	0.61	2.14	100.87
Soda-Trem.[3] Glaucophane (B)	52.28	4.34	0.57	4.32	18.14	5.30	0.26	5.56	6.74	2.18	0.15	n.d.	99.86
Anthophyllite[4] (A)	57.02	1.40	—	—	28.81	8.71	0.09	0.66	1.48	—	1.59	—	99.76
Anthophyllite[4] (B)	48.49	13.26	0.41	1.28	20.56	14.60	—	0.11	0.04	—	1.48	—	100.23
Hastingsite	43.60	11.33	2.09	4.02	12.41	9.88	0.19	1.38	12.03	1.34	1.63	—	99.95
Pargasite[3]	40.18	14.26	1.79	4.73	14.87	5.76	0.22	2.22	12.88	1.86	0.60	0.79	100.19

Note: Glaucophane (A), glaucophane (B), and pargasite are designated IH39, U-184e, and U-1993, respectively, in the paper by Larsen. Anthophyllite (A) and anthophyllite (B) are designated CC 200A and CC 121, respectively, in the paper by Rabbitt.

[1] Posnjak, E., and Bowen, N. L., *op. cit.*

[2] Sundius, N., The position of richterite in the amphibole group: *Geol. Förh.*, Band **67,** 266–270 (1945).

[3] Larsen, E. S., Alkalic rocks of Iron Hill, Gunnison County, Colorado: *U.S.G.S.P.P.* **197A** (1942).

[4] Rabbitt, J. C., A new study of the anthophyllite series: *Am. Mineral.*, **33,** 263–298 (1948).

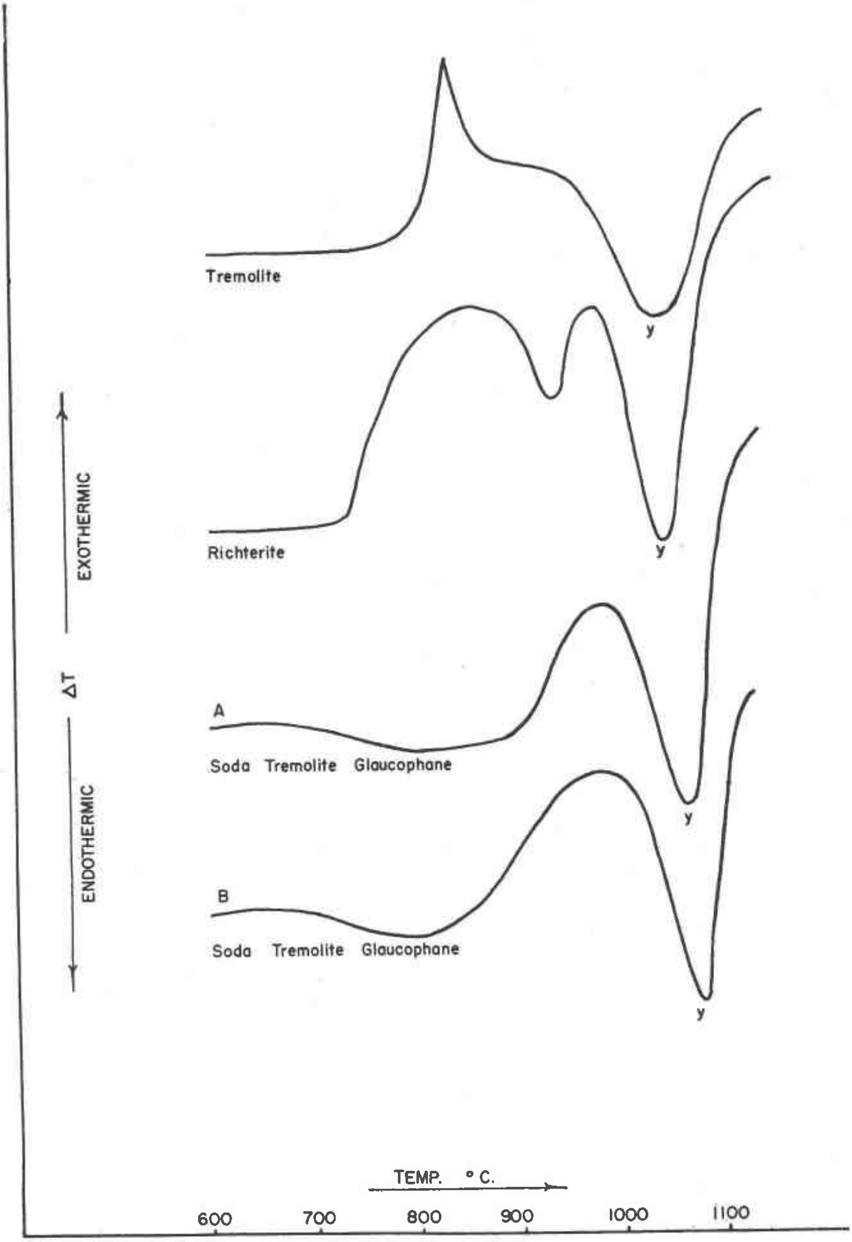

FIG. 1. Thermographic curves of amphiboles.

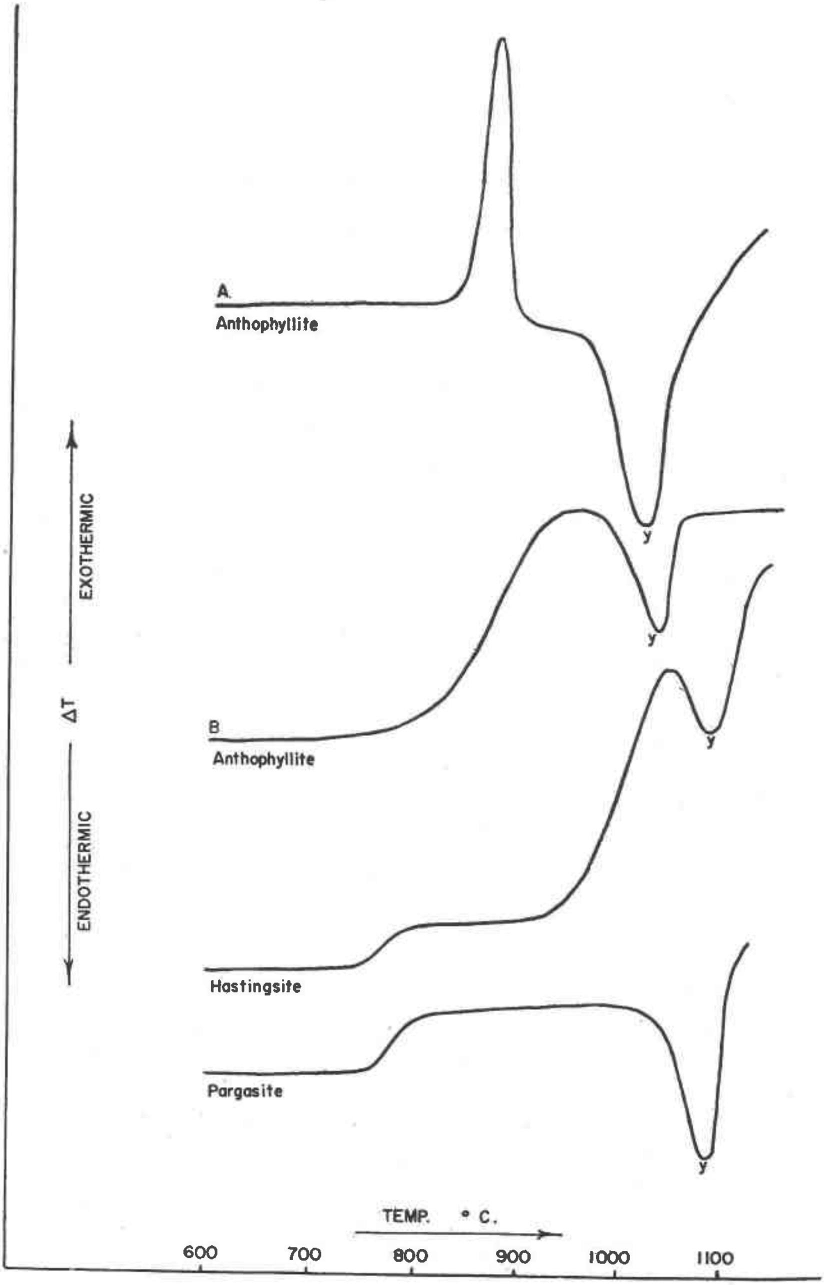

FIG. 2. Thermographic curves of amphiboles.

very pure material investigated by Posnjak and Bowen. The results are in complete accord with those described in the earlier investigation, where the reaction went only to partial completion after 24 hours at 900° C.

Specimens heated to 960° C. and immediately cooled showed no structural changes upon *x*-ray examination. This observation was a reflection of the dynamic nature of differential thermal analysis in that there is a noticeable reaction-temperature lag which static tests do not give. Where the reaction is not instantaneous and when high heating rates (30° C. per minute) are employed, this relation is all the more evident.

At 1125° C. the disintegration reaction is completed. It was noted that an original 200 mesh amphibole powder transformed into reaction products which were still part of the original powder. This material did not melt, fuse, or cohere. Each grain became a pseudomorph of pyroxene plus cristobalite after amphibole in a simple reaction of solid state disintegration. The close relation of the amphibole and pyroxene structures reveals a mechanism of structural collapse whereby the double-chain units split into single-chain units plus a residue which are stable at these elevated temperatures. The heat absorbed (ΔH) in the reaction was 6.40 calories per gram, and the accuracy of the determination is estimated at $\pm 15\%$.

RICHTERITE

The disintegration reaction for this specimen was similar to that for tremolite, except that a more complex pyroxene formed due to the presence of Mn, plus a glassy residue from the Na and F constituents. A hypothetical reaction for the thermal collapse of the mineral is

$$\underset{\text{richterite}}{2\mathrm{NaCa_{1.5}Mg_{4.5}Mn_{0.5}Si_{8}O_{22}(F)(OH)}} + \Delta H = \underset{\text{pyroxene}}{\left|\begin{array}{l}3\mathrm{CaSiO_3}\\ 9\mathrm{MgSiO_3}\\ 1\mathrm{MnSiO_3}\end{array}\right|} + \underset{\text{glass}}{2\mathrm{NaF\cdot 3SiO_2}} + \mathrm{H_2O}$$

The reaction products included a complex pyroxene with a composition in the diopside-clinoenstatite-johannsenite series, water, and an alkali fluor-silicate glass. A heat of reaction of 6.85 calories per gram was determined and the accuracy of the measurement was somewhat lower (approximately $\pm 20\%$) as a result of the errors imposed by the slight sintering action.

SODA-TREMOLITE-GLAUCOPHANE

The structural disintegration of amphiboles whose composition includes portions of tremolite and glaucophane end-members was parallel to the rupture of tremolite and richterite samples. The breakdown products included a pyroxene of the acmite-augite series, hematite, cristobalite, and water. A hypothetical reaction for this process is

$$\underset{\text{soda-trem.-glaucophane}}{Na_2Mg_2Fe^{2+}Fe_2^{3+}Si_8O_{22}(OH)_2} + \tfrac{1}{4}O_2 + \Delta H = \underset{\text{polyaugite}}{\left|\begin{array}{l} 2NaFe^{3+}Si_2O_6 \\ 2MgSiO_3 \\ \tfrac{1}{6}Fe_2O_3 \end{array}\right|} + \underset{\text{hematite}}{\tfrac{1}{3}Fe_2O_3} + \underset{\text{cristobalite}}{2SiO_2} + H_2O$$

This reaction will vary in amphiboles of this variety depending upon the chemical composition of each specimen. Small amounts of Ca and Al alter the reaction only slightly since both are acceptable constituents of the augite reaction product. Indeed, the ability of the augite structure to accept small amounts of Al^{+++}, Fe^{+++}, and Ti^{++++}, in addition to regular amounts of Ca^{++}, Mg^{++}, Fe^{++}, and Mn^{++}, makes it almost impossible for any precise reaction to be written. Slight differences in the amounts of the isomorphous constituents of the amphibole minerals definitely alter the proportional amounts of the reaction products. The presence of fluorine causes, at the distintegration temperature, the formation of a glass, and may eliminate the cristobalite component. In a limiting case hematite may not form if the iron content of the amphibole is so low that all of the iron goes into the formation of pyroxene. In any case, the bulk of the disintegration products always consists of a complex pyroxene of the acmite-augite-clinoenstatite series while the remaining substances described above form in minor amounts or are absent.

Both specimens fused into glassy masses at 1100° C., and as a result, the accuracy of the calorimetric measurement was reduced to about ±25%. The peculiar heat effects accompanying glass formation is detrimental to the type of heat analysis employed in this investigation where the test specimen must maintain its physical characteristics if accurate measurements are to be made. The high alkali and fluorine contents of both samples was largely responsible for this glass formation. Spectrochemical analyses of the disintegration products revealed no loss of fluorine in samples heated to 1125° C. This might be expected in view of the very high electronegativity of fluorine. The heat absorbed by specimens A and B in the disintegration reaction was 4.68 and 5.24 calories per gram, values of the same order as those determined for tremolite and richterite.

PARGASITE-HASTINGSITE

These amphiboles are members of the lime-alkali varieties of hornblendes that are high in calcium as well as aluminum. At 1100° C. the disintegration products included some plagioclase feldspar flakes in addition to polyaugite, hematite, and water. The complex composition of both the amphibole and its reaction products prohibits the writing of an exact expression for the reaction but a possible reaction may be expressed as follows:

$$\underset{\text{hornblende}}{\mathrm{2NaCa_2MgFe_3^{2+}Fe_{1.5}^{3+}Al_{1.5}Si_6O_{22}(OH)_2}} + \tfrac{3}{2}\mathrm{O_2} + \Delta \mathrm{H}$$

$$= \left|\begin{array}{l} \mathrm{NaFeSi_2O_6} \\ \mathrm{2MgSiO_3} \\ \mathrm{3CaSiO_3} \\ \text{polyaugite} \end{array}\right| + \left|\begin{array}{l} \mathrm{CaAl_2Si_2O_8} \\ \mathrm{NaAlSi_3O_8} \\ \text{plagioclase} \end{array}\right| \begin{array}{l} \mathrm{Fe_2O_3 + 2H_2O.} \\ \text{hema-} \\ \text{tite} \end{array}$$

The hastingsite specimen heated to 1145° C. reacted to form all the products above plus some olivine and magnetite. Evidently temperatures greater than 1100° C. are necessary for the formation of these reaction products.

The differential thermal curve for hastingsite (Fig. 2) reveals a disintegration peak temperature of about 1090° C., approximately 40° C. higher than the peak temperature for tremolite. Buerger[9] stated that the presence of aluminim proxying for silicon in a silicate increases the disintegration temperature for that silicate. Comparing the disintegration temperatures of tremolite and the aluminous hastingsite we see that this relation holds true in this instance.

The heats of reaction for the pargasite and hastingsite specimens are 2.83 and 0.83 calories per gram, respectively. These heats are noticeably lower than those determined for the other monoclinic amphiboles and should be interpreted with care. Since the disintegration temperatures for aluminous species are considerably higher than for non-aluminous types direct comparison of the reaction heats at different temperatures are not justifiable. In addition, the oxidation of ferrous iron at temperatures closely bordering on the disintegration temperatures is an exothermic reaction that interferes with the heat determination of disintegration. The accuracy of these determinations is probably no better than ±50%.

The thermographic curves of pargasite and hastingsite show that some transformation is occurring in the 750°–800° C. range. It is possible that this is supporting evidence for the inversion reported by Kozu, *et al.*[10]

MAGNESIAN ANTHOPHYLLITE

The disintegration of magnesian anthophyllite closely parallels the collapse of tremolite, its monoclinic counterpart. The products of structural disintegration are orthopyroxene, cristobalite, and water.

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[9] Buerger, M. J., The role of temperature in mineralogy: *Am. Mineral.*, **33**, 101–121 (1948).

[10] Kozu, S., Yoshiki, B., and Kani, K., Note on the transformation of common hornblende into basaltic hornblende at 750° C.; *Sci. Rept. Tohoku Imp. Univ.*, Ser. 3, No. **2**, 143 (1927).

The reaction[11]

$$\underset{\text{anthophyllite}}{Mg_7Si_8O_{22}(OH)_2} + \Delta H = 7\underset{\text{enstatite}}{MgSiO_3} + \underset{\text{cristobalite}}{SiO_2} + H_2O$$

has a peak temperature of about 1020° C., and absorbs 4.50 calories per gram. The estimated accuracy of the heat measurement is the same as that for tremolite (±15%). Rabbitt's[12] thermographic curve for anthophyllite (A) was described as "a vague continuing loss . . . of H_2O at 1050° C." From the present investigation it is seen that his interpretation overlooked the fact that the more extensive reaction, shown above, was taking place.

FERROUS ANTHOPHYLITE

Specimen (B), Fig. 2, gave orthopyroxene, cristobalite, and water as disintegration products according to the reaction

$$\underset{\text{anthophyllite}}{\left|\begin{matrix}Mg\\Fe^{++}\\Al^{+++}\end{matrix}\right|_7 \left|\begin{matrix}Si\\Al\end{matrix}\right|_8 O_{22}(OH)_2} + \Delta H = 7\underset{\text{hypersthene}}{\left|\begin{matrix}Mg\\Fe^{+++}\\Al^{+++}\end{matrix}\right|} \left|\begin{matrix}Si\\Al\end{matrix}\right| O_3 + \underset{\text{cristobalite}}{SiO_2} + H_2O$$

where the pyroxene is hypersthene, the variety that accommodates Fe and Al in its structure. Once again ferrous iron oxidation interferes with the calorimetric measurement of the disintegration reaction, and makes the heat determination of 2.00 calories per gram accurate to about ±30%. It may be expected that alkali fluoriferous specimens would yield a glass among the disintegration products.

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[11] Thilo, E., and Rogge, G., *op. cit.*

[12] Rabbitt, J. C., *op. cit.*

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