STRUCTURAL TRANSFORMATIONS IN AMPHIBOLES AT ELEVATED TEMPERATURES*

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ABSTRACT

A thermal investigation of the amphiboles revealed some structural transformations occurring in three magnesian varieties at about 830° C. *X*-ray and optical methods of analysis were employed in the study of these transitions, in addition to a differential thermal technique that was used for calorimetric determinations.

Magnesian anthophyllite undergoes a reversible crystallographic contraction of about 0.45% in the *c*-axis direction at 830° C. The heat evolved by the transformation is of the order of 3 calories per gram.

At 825° C. tremolite contracts in the *c*-axis direction. The transformation is irreversible and evolves 2.76 calories per gram.

By an *x*-ray method of analysis the approximate axial contractions of richterite near 825° C. were determined. The calculated contractions are $a_0=0.33\%$, $b_0=0.44\%$, and $c_0=0.55\%$. The transformation is not reversible and evolves an undetermined amount of heat. Between the temperatures of 700° C. and 825° C. the average coefficient of linear thermal contraction is 2.8×10^{-5} per deg. C. This coefficient is of the same order of magnitude as the linear coefficients of expansion for many metals.

Further investigation by high temperature *x*-ray, optical, and dilatometric methods are necessary to define the transformations more precisely.

INTRODUCTION

At temperatures below those required for structural disintegration certain species of amphiboles undergo characteristic transformations. Magnesian anthophyllite, tremolite, and richterite are three varieties which exhibit these properties. The chemical analyses of five specimens studied are shown below.

Spec.	Reference	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	FeO	MnO	Na_2O	CaO	K_2O	H_2O	F	Total
A	CC200A[1]	57.02	1.40	—	—	28.81	8.71	0.09	0.66	1.48	—	1.59	—	99.76
B	U. S. Nat. Mus. No. 13895	n.d.	0.28	n.d.	n.d.	n.d.	3.35	n.d.	n.d.	0.36	n.d.	n.d.	n.d.	—
C	Harvard No. 97956	n.d.	0.13	0.08	n.d.	24.8	n.d.	0.26	—	13.7	n.d.	n.d.	0.27	—
D	Posnjak and Bowen[2]	58.59	0.10	—	—	24.78	—	—	0.12	13.95	0.10	2.31	—	99.95
E	Sundius[3]	57.74	0.37	tr	0.29	23.67	tr	2.40	3.14	9.01	0.64	2.39	0.37	99.86

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

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

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

The evidence for describing these transformations was collected by these methods: (1) differential thermal analysis, (2) *x*-ray powder diffrac-

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* An investigation as part of a Ph.D. thesis by the author.

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tion, and (3) optical studies. This paper is a presentation of the initial investigation of these phenomena.

MAGNESIAN ANTHOPHYLLITE

The differential thermal analyses in this investigation were made at a heating rate of 30° C. per minute in a furnace evacuated to 1 mm. Hg pressure. Thermal analyses under these conditions revealed a transformation occurring in magnesian anthophyllite at about 830° C. Thermographic curves *A* and *B* in Fig. 1† show a major exothermic reaction at this temperature. The general nature of the reaction peak has the earmarks of a displacive[1] transformation except for the fact that heat is evolved with rise in temperature.

The reaction was not reversed thermographically (by cooling), but this may be due to its proximity to the reaction temperature for structural disintegration. Initial rupturing of a few bonds at temperatures slightly above 850° C. may prevent the thermographic reversal of this transformation.

Quenching experiments failed to indicate that any high form exists above 830° C. and this added to the difficulty in determining the nature of the transformation. The evolution of heat attending the rise in temperature from 800° C. to 850° C. can be explained if the mineral is in a high form at 20° C., but the stability of a high form at this low temperature is very difficult to explain on thermodynamic grounds.

Additional evidence for a structural change at 830° C. was obtained by a high temperature optical examination in the nature of a dilatometric test. A contraction in the direction of the *c*-axis was recorded at 830° C. and was found reversible when the temperature 830° C. was not exceeded. This observation correlates well with the thermographic nonreversibility at slightly higher temperatures. The optical analysis was simple. A single needle of anthophyllite was heated on a platinum resistor and was observed through a microscope as the temperature rose. An eyepiece equipped with a scale enabled the observer to record linear changes. A shrinkage of 0.45% in the *c*-axis direction was recorded at 830° C. The data shown below is in proper sequence reading downward and indicates the reversibility of the transformation when 830° C. is not exceeded.

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† The endothermic reactions occurring above 1000° C. are the thermographic records of the structural disintegration of the amphiboles. These will be discussed in a later paper which will include a study of some ferrous amphiboles.

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

Specimen	*Temp.* °C. (±10°)	*Length* (*c*)
B	100	100.00
	300	100.00
	500	100.00
	800	100.00
	830	99.55
	775	100.00
	830	99.55
	930	99.55
	1050	99.55

Estimated accuracy ±15%

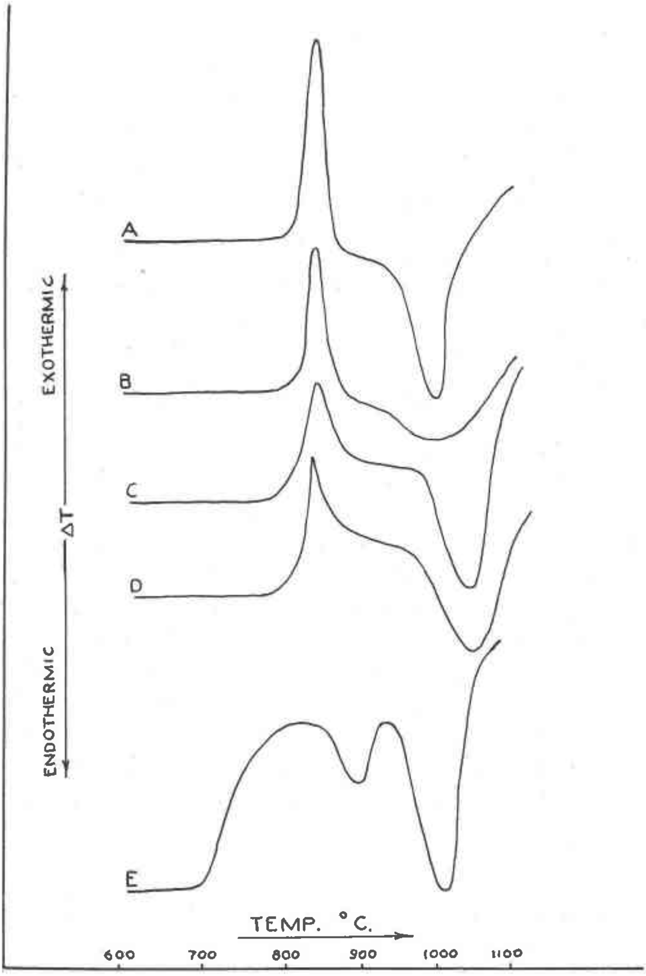

Fig. 1. Thermographic curves of amphiboles.

The thermographic investigation also included the determination of the heat evolved by the transformation. The accuracy of these determinations are high as a direct result of the negligible baseline deviation[2] in the thermographic curves.

Specimen	*Heat Evolved Cal. per gram* (±10%)
A	3.50
B	2.84

The difference in the heat determinations for the two specimens is probably due to slight variations in the chemical compositions.

TREMOLITE

The thermographic curves for tremolite (C and D) reveal a sharp exothermic reaction taking place about 825° C., with a base-line shift at the completion of the reaction. The general configuration of the reaction peaks are similar to the thermal curves showing the alpha→beta quartz inversion; both occur over a narrow range of temperature and are marked by a sharp change in thermal conductivity at the completion of the reaction.

As in the magnesian anthophyllites, the peculiar phenomenon of heat evolution with rise in temperature takes place in the tremolite transformation. In addition, the reaction was not reversed thermographically possibly for the same reason that was applied to the orthorhombic species, namely, the rupturing of some bonds at temperatures slightly above 825° C. Quenching experiments failed to reveal the existence of any high form above 825° C. This, too, paralleled the results for the magnesian anthophyllites.

The high temperature optical examination revealed a contraction in the *c*-axis direction at 825° C. which was not reversed. A shrinkage of 0.65% was observed as indicated by the results shown below.

	Specimen	*Temp. °C.* (±10°)	*Length* (*c*)
	C	100	100.00
		300	100.00
		500	100.00
(Estimated accuracy)		775	100.00
(±15%)		825	99.35
		775	99.35
		825	99.35
		900	99.35
		1050	99.35

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[2] Wittels, M., The differential thermal analyzer as a microcalorimeter: *Am. Mineral.*, **36,** 615–521 (1951).

The base-line shift in the thermographic curves of tremolite at about 900° C. made precise calorimetric measurements indeterminate. However, by reversing the sequence of area measurement an approximate calorimetric determination was made possible. This was accomplished by extending the base-line at reaction completion to the lower temperature portion of the curve and employing the area thus obtained. The base-line shift also indicated that the measured area would be too small by a factor of about one-half. In order to obtain a more accurate heat of transformation the measured values were multiplied by 1.5. Both specimens evolved 2.76 calories per gram in the reaction as determined by this approximate method. It should be noted that this value is of the same order of magnitude as those obtained in the anthophyllite analysis.

RICHTERITE

At 700° C. richterite (Fig. 1, E) starts to undergo an exothermic transformation that approaches a peak about 825° C. This reaction is not rapid and evolves more heat than the corresponding reaction for tremolite. The reaction is thermographically irreversible even when the peak temperature is not exceeded.

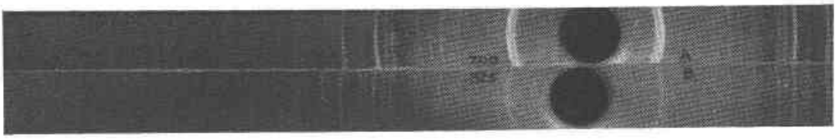

FIG. 2. Camera radius 114.6 mm., ($Cu_{K\alpha}$ radiation). Forward reflections only. A. Richterite quenched from 700° C. B. Richterite quenched from 825° C.

Quenching experiments established a structural change in the nature of a crystallographic contraction. *X*-ray powder diffraction patterns revealed a slight increase in the values for θ as seen in Fig. 2. In other words, the d spacings were slightly reduced. No new lines appeared nor were any of the original lines extinguished in the patterns of specimens quenched at 825° C. A decrease in the distances between interatomic planes in a crystal results in a volumetric contraction of the crystal structure which can be mathematically evaluated if the values for Δd are known and the various lines indexed. Shinoda[3] derived the equations for the changes in the lattice constants with respect to changes in d for all the crystal systems except monoclinic and triclinic by differentiation of the basic relations for each system. Differentiation of the formula for the monoclinic system

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[3] Shinoda, G., *X*-ray investigations on the thermal expansion of solids: *Mem. Coll. of Sci., Kyoto Imp. Univ. A*, **16**, 193 (1933).

$$d_{hkl} = \frac{1}{\sqrt{\dfrac{\dfrac{h^2}{a^2} + \dfrac{l^2}{c^2} - \dfrac{2hl\cos\beta}{ac}}{\sin^2\beta} + \dfrac{k^2}{b^2}}}$$

obviously results in a complex and unwieldy expression due to the presence of the radical and the β terms.

Since x-ray powder diffraction patterns do not give a high order of precision, an approximate method was employed in the determination of the changes in the lattice constants of richterite at 825° C. Although there are four constants in the monoclinic crystals, a, b, c, and β, only the axial changes were calculated. Two assumptions were made in this approximate method:

(1) Since the tables compiled by Strunz[4] do not include the cell constants for richterite, the constants for tremolite were substituted: $a_0 = 9.78$ Å, $b_0 = 17.8$ Å, $c_0 = 5.26$ Å, and $\beta = 106°2'$.

(2) The crystal was assumed to be orthorhombic because β approaches 90°.

The last assumption did not introduce any large error into the analysis and permitted the use of Shinoda's equation for the thermal expansion of orthorhombic crystals:

$$\frac{\Delta d}{d} = \frac{1}{\dfrac{h^2}{a^2} + \dfrac{k^2}{b^2} + \dfrac{l^2}{c^2}} \left[\frac{h^2\Delta a}{a^2 a} + \frac{k^2\Delta b}{b^2 b} + \frac{l^2\Delta c}{c^2 c}\right].$$

By using this formula and the assumptions above the following changes were derived:

(hkl)	$d_{700°\text{C.}}$	$d_{825°\text{C.}}$	Δd	$-\Delta a$	$-\Delta b$	$-\Delta c$
(300)	3.1367	3.1260	0.0107	0.033361	0.072548	0.028815
(550)	1.6548	1.6489	0.0059			
(003)	1.5882	1.5795	0.0087			

				Axial contractions in %		
	a_0	b_0	c_0	a_0	b_0	c_0
(Axes in Å)	9.78	17.8	5.26	0.33	0.44	0.55

The axial contractions are of the same order of magnitude as those for magnesian anthophyllite (0.45%) and tremolite (0.65%). The systematic and random errors of the analysis make the accuracy of the determination ±25%.

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[4] Strunz, H., Minerallen Tabellen, Leipzig, (1941).

Becker[5] gives the following expression for the average linear thermal coefficient of expansion of a solid by the x-ray powder diffraction method:

$$1 + \alpha(t_2 - t_1) = \frac{\sin \dfrac{\theta_1}{2}}{\sin \dfrac{\theta_2}{2}}$$

α is the average coefficient of linear thermal expansion between temperatures t_1 and t_2, θ_1 is the angle at t_1, and θ_2 is the angle at t_2. This equation is employed here for the determination of the average linear thermal coefficient of contraction.

(hkl)	700° C.		$\Delta\theta/2$	825° C.		$1+\alpha(t_2-t_1)$
	$\theta_1/2$	$\sin \theta_1/2$		$\theta_2/2$	$\sin \theta_2/2$	
(300)	7° 6.4′	0.12398	0°1.5′	7° 7.9′	0.12414	0.99871
(550)	13°52.1′	0.23969	0°3′	13°55.1′	0.24054	0.99646
(003)	14°30′	0.25038	0°5.3′	14°35.3′	0.25188	0.99402
Average						0.99639

Average coefficient of linear thermal contraction is

$$\alpha = \frac{0.99639 - 1.00000}{825 - 700} = 2.8 \times 10^{-5} \text{ per deg. C.}$$

The significance of this coefficient is more apparent when one realizes that the coefficient of linear thermal expansion is of the order of magnitude of 10^{-5} per degree Centigrade in many metals.

DISCUSSION

The similarities in the thermal behavior of these minerals are characteristic. The temperature range, the heat of transformation, and the degree of contraction, are the features which make this comparison striking. All of the transformations occur near 825° C. For two varieties the heat of reaction was of the order of 3 calories per gram. This heat determination may be compared with the heat of transformation in the $\alpha \rightarrow \beta$ quartz inversion, which is of the same order of magnitude. Calculated and observed values of linear thermal contraction were of the order of 0.50% for all three species.

Of equal interest is the fact that these minerals are of metamorphic origin and of comparable chemical composition. They are magnesian-type amphiboles that are sesquioxide-poor. However, it was seen that the

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[5] Becker, K., Eine röntgenographische Methode zur Bestimmung des Wärmeausdehnungskoeffizienten bei Hohen Temperaturen: *Z. Physik*, **40,** 37 (1926–7).

presence of considerable FeO (Spec. A, 8.71%) did not interfere with the transformation or prevent it from occurring. Also, other notable constituents did not hinder or prevent the changes from taking place. These are CaO, MnO, and Na_2O.

The transformations give an indication of being very closely related to the silicon-oxygen double-chains, since all the specimens are free, comparatively, from Al^{+++} substitution in those chains. What significance all this may have from a general mineralogic or geologic viewpoint is uncertain with the small amount of evidence on hand at present. The crystallization temperature of these minerals, below 825° C., only confirms information that is already well-known.

Three additional methods of analysis should help to clarify some of the problems encountered in this investigation. These are (1) high temperature *x*-ray studies, (2) investigation of optical properties at elevated temperatures, and (3) dilatometric tests at transition temperatures on good single crystals.

The results of this investigation indicate that perhaps many important thermal properties of the common rock-forming minerals have been overlooked through the absence of sensitive thermal apparatus.

ACKNOWLEDGMENTS

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