THERMAL EXPANSION OF CLAY MINERALS

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ABSTRACT

The thermal expansion coefficients of several clay minerals were measured by an x-ray technique in directions parallel and perpendicular to the layers in the structure. The coefficients lie in the range 18×10^{-6} for the perpendicular direction and in the range 5×10^{-6} for the parallel direction.

INTRODUCTION

Relatively little work has been done on the thermal expansion coefficients of layer lattice silicates, and the clay minerals themselves appear to never have been studied. Measurements on aggregate bodies give no information on differences in thermal expansion in different lattice directions.

Measurements on macroscopic single crystals of mica (Hidnert and Dickson, 1945; Ebert, 1935) have given an indication of the magnitude of the directional differences in expansion coefficients. X-ray measurements of thermal expansion coefficients have also been reported for mica (Megaw, 1933; Metsik and Zhidikhanov, 1958).

The x-ray method (Wooster, 1959; Partington, 1952) is ideally suited to the measurement of directional coefficients of thermal expansion, and is, moreover, the only method capable of giving the directional expansion in such fine-grained particles as are found in most clay minerals.

The reversible thermal expansion coefficient of a material is related to the structure energy and other thermodynamic parameters of a crystal, and could be used to gain further insight into the forces within a crystal. In the case of the clay minerals, it was hoped that correlations would be found between the thermal expansion and such variables as the dioctrahedral or trioctrahedral nature of the layers, and the extent of tetrahedral or octahedral ionic substitutions.

METHOD OF MEASUREMENT

The determination of thermal expansions by the x-ray method involves measuring the lattice spacings, d, at room temperature and at higher temperatures. The average coefficient over a temperature range is calculated from:

$$\bar{\alpha} = \frac{d_T - d_{T_0}}{d_{T_0}(T - T_0)}$$

where d_T is the spacing at temperature T, and d_{T_0} at room temperature

T_0. This is the average expansion coefficient in the direction perpendicular to the (hkl) plane specified. By measuring the expansion coefficients for several different planes, a least squares method can be devised for obtaining the direction and magnitude of the principal coefficients. However, for most layer-minerals, since the layer structures are almost hexagonal, it might be assumed that two coefficients of expansion would be adequate to describe the thermal behavior of the mineral, namely directions perpendicular to the basal spacing, 001, and perpendicular to the 010 plane, *i.e.*, in the direction of the plane of the layers.

Ideally, for these measurements, the diffraction peaks at the highest

TABLE 1. ESTIMATIONS OF ACCURACY ATTAINABLE IN DETERMINING $\bar{\alpha}$

Directions	Plane	2θ	"d"	Δd	$\Delta \bar{\alpha}$	% error in "d"	% error in $\bar{\alpha}$
perpendicular	006	37.8	2.40	± 0.0006	± 1.15	± 0.026	± 8.1
parallel	060	62.3	1.49	± 0.0003	± 0.5	± 0.014	± 10.3

possible Bragg angles (near $180°2\theta$) should be measured. This is not possible for clay minerals, since there are no discernible peaks beyond $90°2\theta$. The reflections actually measured were mainly in the angular region of $35°–60°2\theta$. The peak positions were measured from a diffractometer chart pattern obtained with a high angle Norelco diffractometer, using CuKα radiation (40 KV 15 ma), a nickel filter, 1° divergence slits and a 0.006″ detector slit. The scanning speed was $\frac{1}{4}°$/min., and the chart speed was 60″/hr. These speeds combine to give on the chart, a pattern with 4″ per degree 2θ. The center of the peak at half-height was used as the best compromise between a center of gravity measurement and an estimate of the peak maximum.

The angular position was read to the nearest 0.01″, but the reproducibility was found of the order $\pm 0.04″$, or $\pm 0.01°2\theta$. The precision of the measurements of "d" and $\bar{\alpha}$ is assessed in Table 1 for a temperature interval between 25° C. and 200° C. for expansion coefficients 18×10^{-6} and 5×10^{-6} which are, respectively, the orders of magnitude of the thermal expansion coefficients perpendicular to and parallel to the layers.

EXPERIMENTAL TECHNIQUE

The powdered samples were pressed into a rectangular depression $\frac{5}{8} \times \frac{1}{2} \times .03$ inches in a nickel plate. The front surface of the powder was made flush with the surface of the plate by means of a microscope glass slide, and then a few small flakes of a selected muscovite sample were

sprinkled onto the surface and pressed. This mica was used as a calibrant to allow for errors in the centering of the sample in the high temperature furnace.

The sample was placed on the silica sample support of the high temperature x-ray diffraction furnace. This consists essentially of two hemispherically-shaped platinum resistance heating elements with suitable insulation and a means for adjusting the position of the sample. The furnace is described elsewhere (McKinstry, 1965). Its principal merits lie in the low thermal gradients in the neighborhood of the sample and in the independent support of the sample with the accompanying alignment facilities. The front surface is aligned by adjusting the sample position until a narrow beam of x-rays, collimated by a fine slit, just grazes the surface. This brings the surface to within 0.01 inch of the center. To compensate for any remaining misalignment, the mica flakes sprinkled on the surface were used as an internal standard. The correct angular position of the mica diffraction peak was determined by calculations based on the experimental high angle 2θ measurements of a larger piece of the same mica flake. The angular corrections thus found were applied to the diffraction angles of the other clay minerals.

The base of the x-ray furnace is water-cooled to maintain the goniometer at constant temperature. The Norelco goniometer is set back two inches from its normal operating position and spacers were devised so that the diffractometer could be used normally when the furnace was removed. This made it possible to shift from normal to high temperature operation simply by replacing the normal sample holder and its rod with the furnace and its rod.

The furnace temperature was controlled by a West fully-proportioning controller, and the temperature was maintained $\pm 1°$ for several hours at any temperature up to 1000° C. Temperature homogeneity across the sample face is not worse than $\pm 3°$ at the highest temperature.

Description of Samples

Muscovite	Helen Beryl Mine, S. Dakota
	(courtesy Dr. M. L. Keith)
Phlogopite 2M	Unknown locality, large crystals
Kaolinite	High purity, No. BBCC/37/54
	(courtesy Dr. G. W. Brindley)
Dickite	(courtesy Dr. G. W. Brindley)
Halloysite	Kern County, California
	(courtesy Dr. C. S. Ross)
Serpentine	Unst, Scotland
	(courtesy Dr. G. W. Brindley)
Pyrophyllite	synthetic (contained some second phase)
	(courtesy Dr. R. Roy)

Talc   Manchuria
                              (courtesy Dr. G. W. Brindley)
Chlorite (magnesian)   Unknown locality
                              (courtesy Dr. G. W. Brindley)

EXPERIMENTAL RESULTS

The diffraction planes, diffraction angles, and "d" values used in the determination of the thermal expansion of the minerals measured, are listed in Table 2.

The several 00l planes for muscovite were used for the standard extrapolation technique for high precision measurements. Since the chief sys-

TABLE 2. LIST OF DIFFRACTION PLANES USED FOR THERMAL
EXPANSION MEASUREMENTS

	Planes	angles 2θ	"d"
Muscovite	00.12	133.6	0.8380
	00.11	114.9	0.9138
	00.10	100.0	1.006
	060	61.6	1.504
Phlogopite	006		
	060	60.2	1.535
Kaolinite	003	37.7	2.383
	060	62.2	1.492
Dickite	003	37.7	2.383
	060	62.2	1.492
Halloysite	002	24.5	3.633
	060	62.4	1.488
Serpentine	2.0.24	61.8	1.501
	0 6 0	60.2	1.535
Pyrophyllite	00.12	60.8	1.523
	0 6 0	62.6	1.484
Talc	006	59.9	1.543
	060	61.0	1.518
Chlorite	00.18	38.0	2.368
	0 6 0	60.2	1.535

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TABLE 3. REVERSIBLE THERMAL EXPANSION COEFFICIENTS OF CLAY MINERALS

Mineral	$\bar{\alpha}_1 \times 10^6$	$\bar{\alpha}_2 \times 10^6$	Temp. Range °C.
Muscovite	17.8±0.59	3.5±1.3	25–600
Phlogopite	17.8±1.4	14±3*	25–350
Kaolinite	18.6±1.3	5.2±1.7	25–400
Dickite	14.9±0.84	5.9±0.4	25–500
Halloysite	10.0±1.5	6.0±2	25–350
Serpentine	*10.2±0.9	6.9±1.7	25–500
Pyrophyllite	14.9±1.8	12.2±0.7*	25–400
Talc	16.3±2.4	3.7±1.4	25–700
Chlorite	9.0±2.3	11.1±1.4	25–500
	*2.0.24		

$\bar{\alpha}_1$ is the average coefficient of thermal expansion perpendicular to the layer.

$\bar{\alpha}_2$ is the average coefficient of thermal expansion within the layer.

The plus or minus number is the standard deviation of the measurements, assuming the coefficient to be independent of temperature.

* These values are suspected of being too high—see text.

tematic error was the displacement of the sample from the center of the goniometer, the extrapolation function, $\cos^2\theta/\sin\theta$, was used.

Since reflections at high angles were used and produced the most precise measurements in this study, the expansion of this mica was used as a calibrant for all other measurements. The expansion coefficient was found to be:

$$\bar{\alpha} = [16.8 + 0.004(T - T_0)] \times 10^{-6} \, (25° - 600° \, C.)$$

The expansion coefficients for all the minerals measured are reported in Table 3. These coefficients were derived from the measurement of one angle per temperature with the previously mentioned mica correction. The expansion coefficients are reported for the directions perpendicular to ($\bar{\alpha}_1$) and lying in the plane ($\bar{\alpha}_2$) of the layers. The standard deviations of the measurements are also given. These were estimated assuming the expansion coefficients to be independent of temperature. Several "d" *vs.* temperature plots are shown in Figs. 1–9.

DISCUSSION

The nature of the experimental measurements precludes a high precision. However, since the standard deviations are not much in excess of the estimate of the random error, it is concluded that these results are as good as can be achieved from medium angular range measurements.

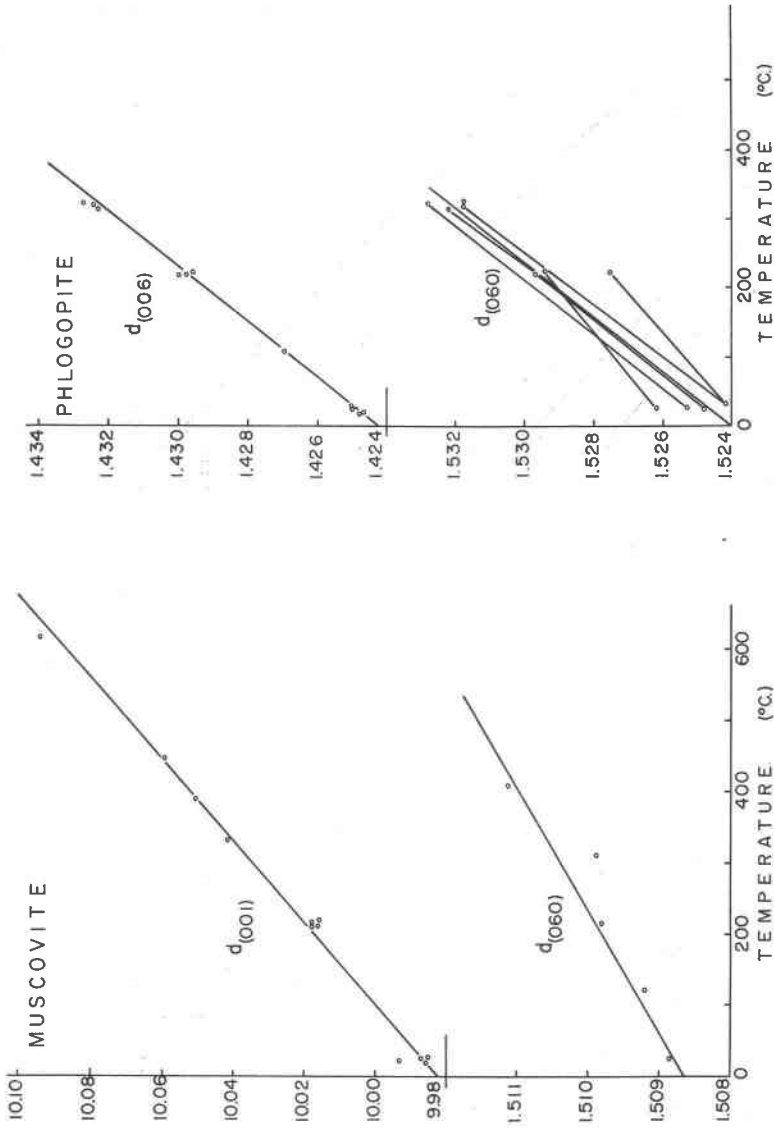It should be pointed out that the measurements reported are not con-

FIG. 1. The lattice spacings for mica as a temperature function of temperature.
Multiple points for one in dicote reproducibility.

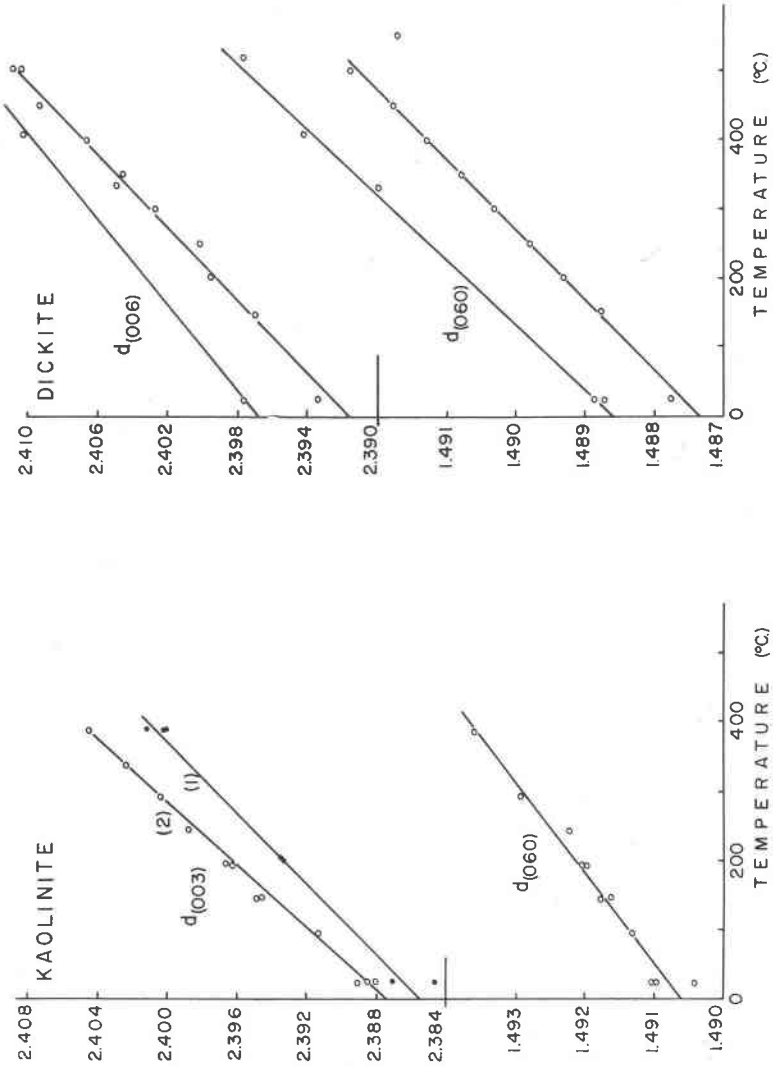FIG. 2. The lattice spacing for phlogopite as a function of temperature.

Fig. 3. The lattice spacing for kaolinite as a function of temperature.
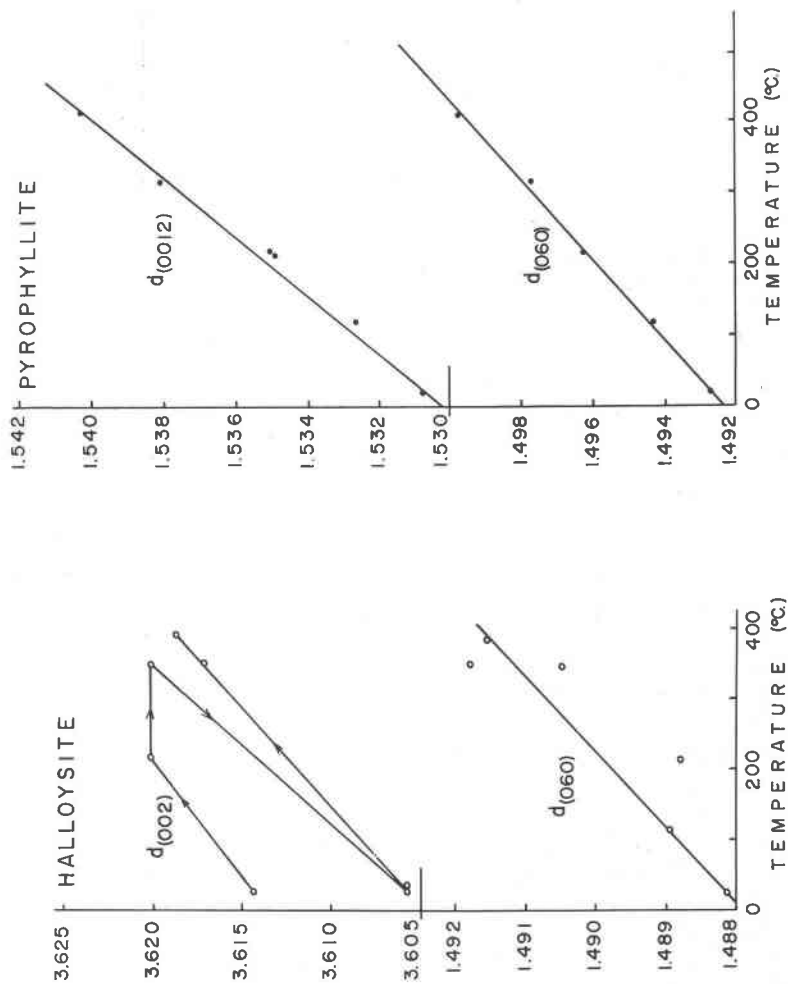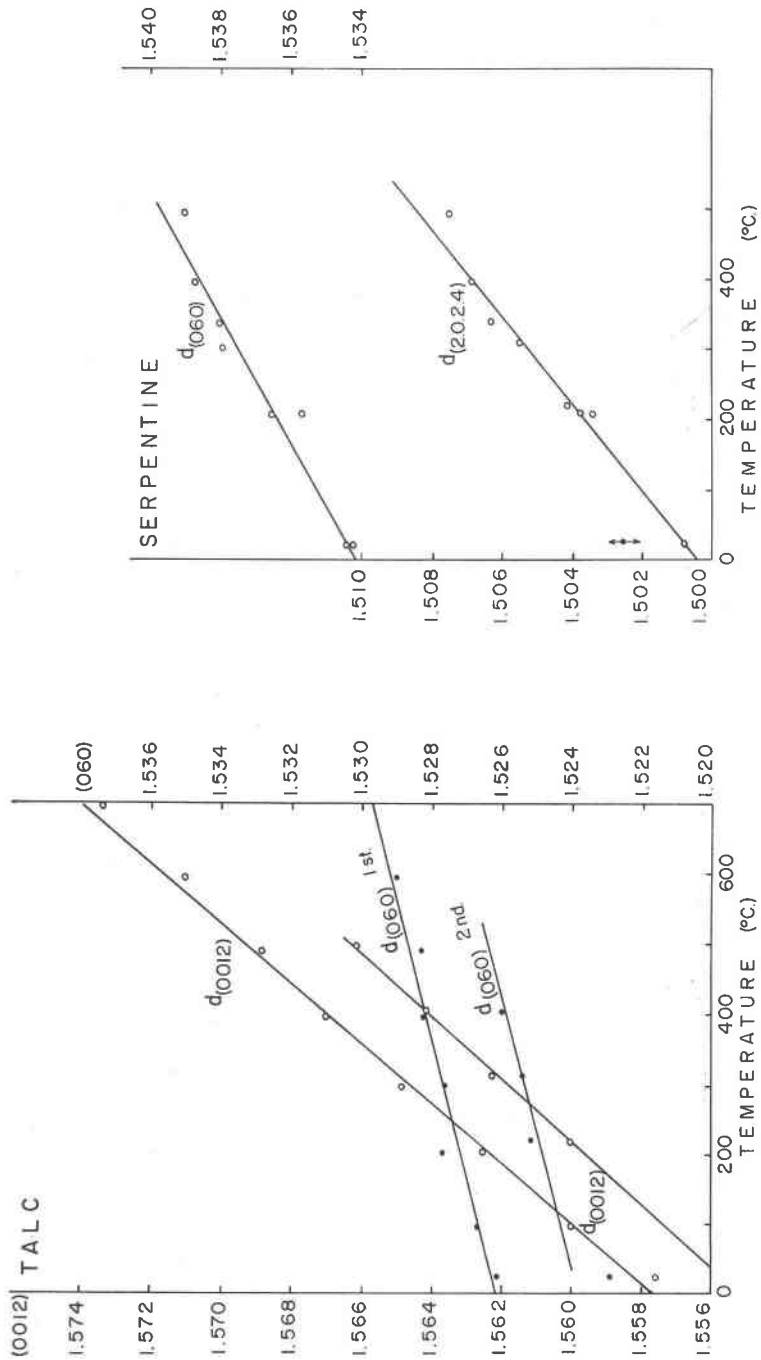Fig. 4. The lattice spacing for dickite as a function of temperature.

FIG. 5. The lattice spacing for halloysite as a function of temperature.
FIG. 6. The lattice spacing for pyrophyllite as a function of temperature.

FIG. 7. The lattice spacing for talc as a function of temperature.
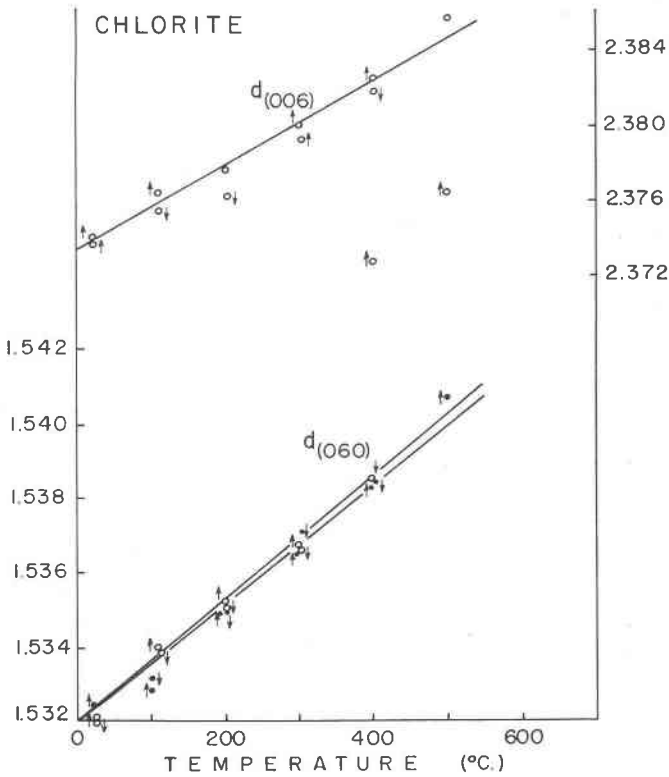FIG. 8. The lattice spacing for serpentine as a function of temperature.

FIG. 9. The lattice spacing for chlorite as a function of temperature.

nected in any way with any irreversible "expansion" due to change of relative amounts of expanding and non-expanding layers. Only the reversible expansion has been studied.

The measurements on halloysite, phlogopite and pyrophyllite were the least satisfactory. The halloysite measurement was poor because the 001 peak was measured at a relatively low angle, but no alternative was feasible.

The phlogopite had several overlapping peaks in the neighborhood of the 060 reflection which were not resolved because of their low intensity. The 006 peaks, however, were good. The pyrophyllite presented a similar problem to that of phlogopite, and in addition, a fairly substantial amount of a second component, probably hydralsite, was present in the sample; the possibility of overlap of unknown peaks from the second phase cannot be excluded.

The structure of the layer minerals suggests that the expansion co-efficient normal to the layers would be greater than that within the

layers. This anisotropy is found for muscovite, kaolinite, dickite halloysite, serpentine and talc. For phlogopite, pyrophyllite and chlorite, it does not appear so clear, defined. The problem of overlapping reflections may explain the large values of the $\bar{\alpha}_2$ coefficient measured for phlogopite and pyrophyllite, but does not seem to be the explanation in the chlorite measurement. Further work on these minerals seems desirable.

The dioctrahedral and trioctahedral structures appear to have essentially similar expansion coefficients, whereas one might expect that the "vacancy" in the dioctrahedral structures would produce significantly different expansions.

The similarity of the $\bar{\alpha}_1$ values for the kaolin minerals (kaolinite and dickite) and for the micas (muscovite and phlogopite) suggests that the difference in layer bonding, hydroxyl bonds in the first case, and ionic bonds in the second case, is less marked than might have been expected. Even for the essentially neutral layers in talc and pyrophyllite, the $\bar{\alpha}_1$ values are still not very different.

Conclusions

The thermal expansion for several of the layer minerals has been found to be anisotropic. However, there is no clear relationship between the thermal expansion of the minerals and the usual crystal chemistry parameters.

Acknowledgments

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