LINEAR THERMAL EXPANSION OF CALCITE, VAR. ICELAND SPAR, AND YULE MARBLE

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ABSTRACT

A new autographic dilatometer of high sensitivity for the measurement of linear thermal expansion is described. Results are given from 20° to 700° C. for calcite, var. Iceland spar, from Chihuahua, Mexico, and for Yule marble from Yule Creek, Colorado. The data for calcite is an approximate mean of previously published, low temperature values for orientations parallel and perpendicular to the *c* axis. Results for Yule marble indicate a possible correlation between linear thermal expansion and fabric analysis. The abnormal values for the marble are explained tentatively on the basis of recrystallization and residual strain.

INTRODUCTION

Since our program of mineral expansion studies was discontinued six years ago, a constant search has been made for newer equipment which would have greater sensitivity and be automatic in operation. Many devices were studied and several were built for test. As a result of the great strides in instrumentation in recent years, a combination of instruments has been adopted having all of the most desirable operational details for research in this field. This will permit the continuation of studies on mineral expansion and inversions, as well as associated studies on rocks.

EQUIPMENT

Furnace temperatures are controlled by a special Leeds & Northrup Micromax program controller. This is a versatile instrument in that the furnace may be heated and cooled at any predetermined rate, within the limits of the characteristics of the furnace. It has the further advantage of maintaining a preset temperature at the end of a heating cycle when this is desired before the cooling cycle begins. A continuous-line recorder is integral with the control unit and gives a temperature-time curve.

When changes occur which result in expansion variations, such as from inversions, a Leeds & Northrup Type K2 potentiometer is used to determine precise temperatures. In all cases, a platinum-platinum 10% rhodium thermocouple is used with a zero cold junction.

The recording dilatometer equipment was built for this research by the Baldwin Locomotive Works. It is quite unique in several respects, notably its sensitivity to length changes as small as three-millionths of an inch. Being constructed of invar, variations in room temperature produce very small changes which may be corrected for by conducting a blank determination. Line voltage variations may be disregarded

completely because the operation of the measuring equipment depends upon a self-balancing transformer bridge.

The assembly of the thermal control and dilatation units is shown in Fig. 1. The furnace, fused quartz dilatometer tube and rod, and the transmitting part of the recording dilatometer are suspended on a spring-supported platform to eliminate vibrations. Tests have shown that all building vibrations are completely absorbed by this suspension.

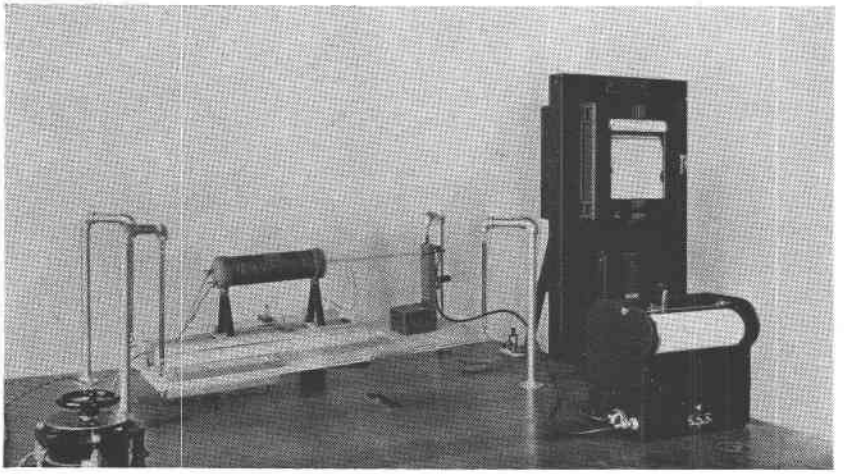

FIG. 1. Dilatometer assembly and thermal control unit.

The recording dilatometer consists of an expansion-follower assembly and an autographic recorder. In the latter, a silver wire stylus moves parallel to the axis of the recording drum at the rate of one inch per hour. The drum rotates in proportion to the length changes of the mineral or rock specimen in the dilatometer tube and will record a total length change as great as 0.02″. The recorder has three gear ratios so that magnifications of 500, 1,000 or 2,000 may be selected.

The follower assembly is shown in detail in Fig. 2. It consists of a heavy invar bar with a clamp to hold the sleeve A into which the fused quartz tube is cemented (not shown). The fused quartz rod, which is moved by length changes of the specimen in the quartz tube, makes contact with the adjustable fulcrum point *B* of the lever. The latter is supported on two knife edges at *C* and can be adjusted for contact by varying the tension on the small springs shown in the illustration. This insures that the minimum pressure will be applied which is necessary to maintain contact during expansion or contraction of the test specimen. As the lever is moved because of length changes in the test specimen, the

core of the microformer (transformer) *D* changes its position and thereby unbalances the electrical circuit.

The recorder contains a second, matched microformer. The unbalanced signal from the follower is amplified and drives a servo-motor which, in turn, rotates the recorder drum. At the same time, the core of the second

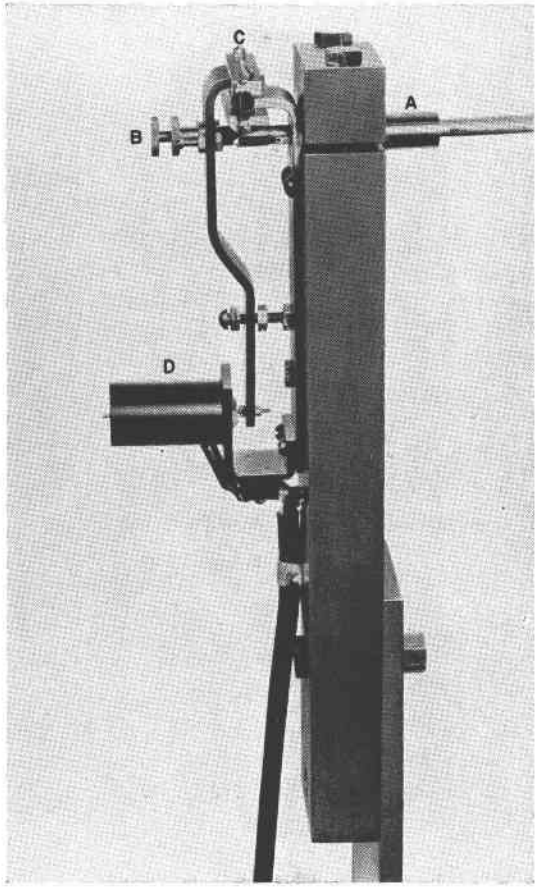

FIG. 2. Detail of the dilatation follower unit.

microformer is moved until it is brought to the position where its output balances that of the follower microformer. During this rotation the silver stylus draws a fine line on the chart paper so that an expansion-time curve is obtained. This curve is correlated with the temperature-time curve of the temperature recorder.

Two sizes of quartz tubes are used to allow for variations in specimen

sizes. These depend upon the nature of the samples and they are cut at the desired orientations to either 4×4×10 mm. or 8×8×10 mm.

Calcite, var. Iceland Spar

The specimens of calcite were cut from a large, clear cleavage from Chihuahua, Mexico. The cutting presented difficulties due to the ease of cleavage and it became necessary to develop a special saw for this purpose. Through the courtesy of the Bausch & Lomb Optical Company, information was received that a slowly reciprocating blade gave best results. To accomplish this, a device similar to a power hacksaw was built with a hard steel strip reciprocating at 48 R.P.M. The calcite was cemented to a hardwood block with glyptal and locked at the desired orientation in a universal vise. It was found that a slurry of *FF* carborundum gave best results; coarser grits resulted in cleavage.

Table 1. Mean Coefficients of Thermal Expansion of Calcite, var. Iceland Spar

20° C. to	Linear Expansion $\parallel c \times 10^{-6}$	Linear Expansion $\perp c \times 10^{-6}$	Volume Expansion $\times 10^{-6}$ calc.
100°	23.58	−5.22	13.14
200°	26.45	−5.31	15.83
300°	27.99	−5.01	17.97
400°	29.34	−4.61	20.12
500°	30.59	−4.23	22.13
600°	31.78	−3.86	24.06
700°	32.81	−3.69	25.43

The results of the expansion studies are given in Table 1. Values are not given above 700° because a large change in the rate of expansion was noted at 706 ± 1° which appears to be due to the initiation of dissociation of the calcite. Kôzu, Masuda and Ueda (1) found the same phenomenon but they did not indicate a specific temperature at which it occurred.

Austin, Saïni, Weigle and Pierce (2) have analyzed the data for the thermal expansion of calcite from their research and that reported by other observers. They have shown that significant differences may be attributed to variations in the samples. The results given in Table 1 are, coincidentally, an approximate mean of previously reported results to 100° (2) in which a variety of samples and instrumental methods were used. For the 20° to 700° range, there is a wide divergence between the values in Table 1 and those reported by Kôzu, Masuda and Ueda (1), especially for the orientation perpendicular to the optic axis.

Yule Marble

At the suggestion of Dr. Eleanora Bliss Knopf, the authors undertook expansion studies of Yule marble, from Yule Creek, Colorado. The test specimens, which were supplied by Dr. Knopf, were cut in north-south, east-west and vertical orientations, corresponding to the field orientation of the rock. These directions were chosen because they had been used in the analysis of the fabric of the marble.

The results obtained during the first heating-cooling cycle, given in Table 2, are considerably in excess of the maximum values for a single crystal of calcite. Furthermore, it was found that all specimens in all orientations acquired a permanent elongation after cooling to room temperature, this being a phenomenon which is common for marbles. It was then decided to subject all specimens to a second heating-cooling cycle and new values were obtained which are given in Table 3. Although no further length changes were observed at the end of the second cycle, measurements made several months later showed that further elongation had occurred at room temperature.

Table 2. Coefficients of Thermal Expansion of Yule Marble. First Heating-Cooling Cycle

20° C. to	N-S $\times 10^{-6}$	E-W $\times 10^{-6}$	Vertical $\times 10^{-6}$	Volume Coefficient $\times 10^{-6}$ calc.
100°	4.25	17.75	4.25	26.25
200°	10.56	29.33	9.67	49.56
300°	12.71	32.68	11.96	57.35
400°	13.34	33.76	13.71	60.81
500°	15.38	35.42	15.08	65.88
600°	16.29	36.72	16.26	69.27
700°	16.79	37.09	16.81	70.69
Elongation after cooling	0.50%	1.02%	0.71%	

Discussion of Results

The very high coefficients obtained in the cyclic heating of the Yule marble present several intriguing problems. The first to consider is a possible correlation between the results of fabric analysis and thermal expansion. In a personal communication, Dr. Knopf has indicated that, for the east-west orientation, 50 per cent of the optic axes are concentrated in 10 per cent of the total surface of the projection hemisphere and 15 per cent are in $1\frac{1}{2}$ per cent of the surface; furthermore, 45 per cent of the entire surface is unoccupied. These percentages are the result of

direct measurement but values may be computed from the coefficients of expansion.

Certain assumptions are of course necessary. In the first place, the results of the first heating-cooling cycle will not be used because, as will be discussed later, they are considered to be due in part to the relief of residual strain in the marble. Secondly, all grains are assumed to have their optic axes oriented either parallel or perpendicular to the axis of the expansion test specimen. Comparing the coefficients of expansion from

TABLE 3. COEFFICIENTS OF THERMAL EXPANSION OF YULE MARBLE. SECOND HEATING-COOLING CYCLE FOR ALL ORIENTATIONS

20° C. to	N-S $\times 10^{-6}$	E-W $\times 10^{-6}$	Vertical $\times 10^{-6}$	Volume Coefficient $\times 10^{-6}$ calc.
100°	−3.75	5.88	−2.62	− 0.49
200°	−2.44	8.61	−1.83	+ 4.34
300°	−1.43	11.04	−0.96	+ 8.65
400°	−0.63	11.05	−0.13	+10.29
500°	+0.85	13.02	+1.29	+15.16
600°	+2.93	16.64	+3.36	+22.93
700°	+4.71	18.44	+5.40	+28.55

20° to 100° of calcite with second cycle Yule marble, the following results are obtained:

East-West orientation	39% c concentration
North-South orientation	5% c concentration
Vertical orientation	9% c concentration

If calculations are based upon the 20° to 700° range, the E-W concentration is found to be 49% but the N-S is 13% and the vertical is 15%. There is, therefore, a good correlation between the measured and computed values in the E-W direction. The value for the N-S orientation should be zero on the basis of direct measurement. The fact that it is not zero by computation may be due either to the assumptions made in the calculations or, possibly, because of recrystallization during the first cycle with a consequent reorientation of a small number of grains; and the same reasoning applies to the other orientations.

There is one further point to consider in this connection. Fig. 3 shows the relationship between the coefficients of linear expansion from 20° to 100° for a single crystal of calcite and the angle between the c axis and any other direction. It is evident that appreciable changes may result from the displacement of the c axis. For example, for a 15° variation, the coefficient is reduced from 23.58 to 21.65×10^{-6}. In as much as

10 per cent of a hemispherical surface subtends a large angle, there is certainly added reason to expect appreciable variation between measured and calculated results. Studies now under way may make it possible to resolve the several factors mentioned and permit a revision in the method of correlation.

A second problem of considerable interest concerns the explanation for the large coefficients obtained, particularly from the first heating cycle. As shown in Tables 1 and 2, the values for Yule marble are extremely

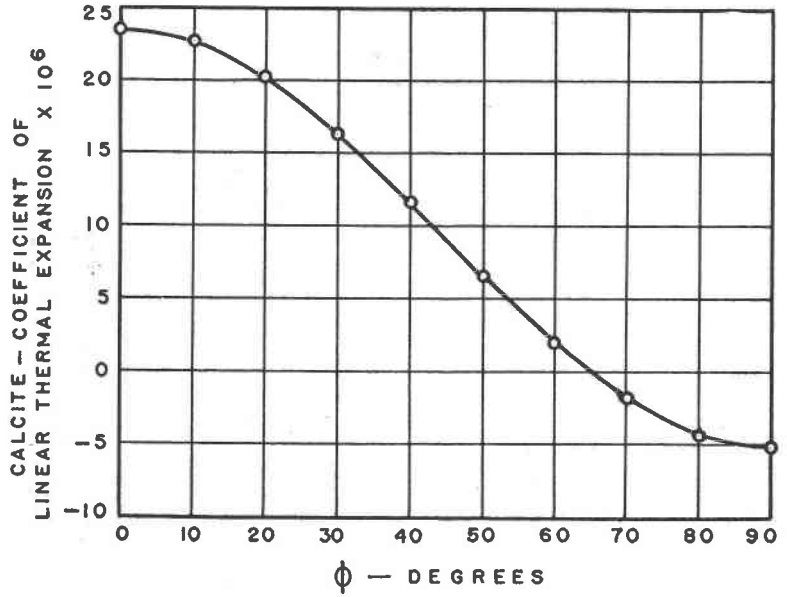

FIG. 3. ϕ is the angle between the c axis in a calcite crystal and any other direction.

high compared with the maximum for calcite. An apparent explanation, especially in view of the permanent elongation after cooling, is that part of the expansion is due to the relief of residual strain in the marble. Such strain may have a thermal or deformational origin, or both, but part of it may have been induced by the heating during the expansion measurements.

Boas and Honeycomb (3, 4) found that cyclic heating and cooling produces deformation in such metals as cadmium, zinc and tin, due to the anisotropy of their thermal expansion, and that there are other significant effects such as grain boundary migration and evidence of preferential deformation in the randomly oriented grains. There is a striking parallelism between the effects reported by Boas and Honeycomb

and those which may be inferred from thermal coefficients. The calculated volume coefficients of calcite and both cycles of Yule marble, plotted in Fig. 4, give the basis for the deductions which follow. It should be emphasized that, while the calculated values for calcite are correct,

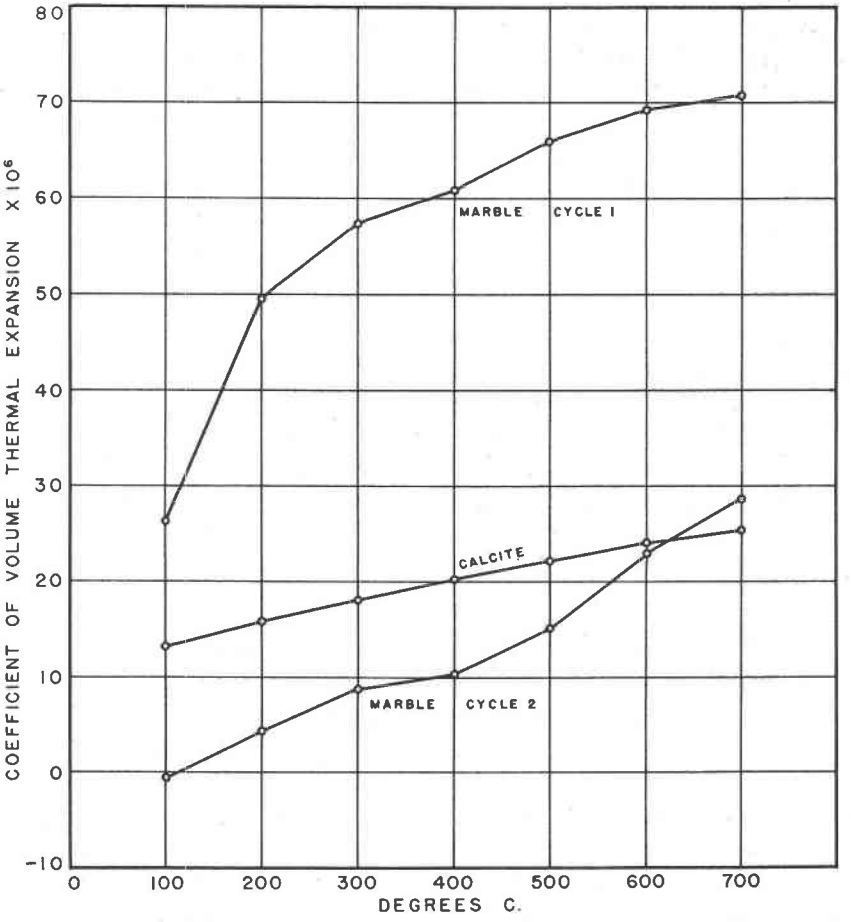

FIG. 4. Volume coefficients of expansion (calculated) for calcite and Yule marble.

those for the marble are not true volume coefficients since the orientations upon which they are based are more or less random in the N-S and vertical directions and, to a lesser extent, in the E-W direction.

SUMMARY

The Yule marble has a deformational history and, whether or not it was cyclic in character, residual strain remained which was relieved, for

the most part, during the early part of the first expansion cycle. The change in curvature in the 300° to 400° range is interpreted as the zone in which recrystallization began. Continued heating introduced new strain because of the anisotropy of thermal expansion of the individual calcite grains and it is probable that much of this strain was relieved during the cooling portion of the first cycle. The low coefficients in the early part of the second cycle tend to substantiate this inference. Further heating during the second cycle again caused recrystallization in the same temperature range as before, resulting in a volume change at 700° in excess of that for calcite.

The foregoing deductions are necessarily conjectural at this time but it is expected that at least some of the questions mentioned will be clarified by further studies.

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