

LINEAR THERMAL EXPANSION AND INVERSIONS OF QUARTZ, var. ROCK CRYSTAL

JOSEPH L. ROSENHOLTZ AND DUDLEY T. SMITH,
Rensselaer Polytechnic Institute, Troy, New York.

ABSTRACT

A new apparatus is described for the measurement of linear thermal expansion between 0° and 1000° C. and for the determination of inversion points. Results are given for expansion of Brazilian rock crystal perpendicular and parallel to the principal axis. The α - β inversion was found at $573.1 \pm 0.5^\circ$ C. A second change was observed at $872 \pm 1^\circ$ C. for sections cut perpendicular to the principal axis. This change, ascribed to the quartz-tridymite inversion, was observed on only one of four parallel sections. The remaining three showed a sudden acceleration in the rate of contraction at $830 \pm 2^\circ$ C.

INTRODUCTION

This is the first of a series of experimental studies of the linear thermal expansion of crystallographically oriented sections of rock-forming minerals at temperatures from 0° to 1000° C. The lack of such information, except for relatively few minerals, and its potential usefulness in geophysical studies has prompted this extended program. Despite the fact that reliable data is available for quartz, this mineral was selected because it would serve to test the accuracy of the special equipment devised for the expansion and inversion measurements herein described.

DESCRIPTION OF APPARATUS

The new apparatus is, in effect, a combination of a Chevenard type of differential dilatometer and a specially constructed capillary cell, a vertical section of which is shown in Fig. 1. The three principal parts are the capillary cell *A*, the advancing mechanism *B*, and the connecting block *C*, which also holds other measuring attachments. Except as will be indicated, all parts were machined from cold rolled steel. A circular recess *P* was turned in the front of the block. A circular, aluminum gasket *W* fits snugly into the face of *A* at the edge of this recess. The diaphragm *X*, made of 0.0035 in. shim steel, is held against the gasket by the restraining plate *N*. This plate is fastened to *A* by a series of closely-spaced bolts and is bored to receive the nut on the screw of part *O*. In order that the motion of expansion may be imparted to the diaphragm without twist, the bolt *O* has an extension which slides smoothly in *R*. The latter has several radial holes drilled through from the center to allow the mercury which fills the cell to flow freely without compression. The screw end of the bolt is cut to a sharp 90° cone to receive the ground point of the fused quartz rod *G*.

Two vertical holes are drilled into the cell block, one of them being shown at *S*. When pressure is applied to the diaphragm, mercury flows through *S* to the capillary tube. The latter is fastened to the cell by the collar *T* into which it is cemented. Tubing of various capillary bores may be used to register the displacement of mercury in the cell. For the range of displacement experienced during the expansion of quartz, it was found that a bore of 0.75 mm. gave excellent results. Regardless of bore size, it

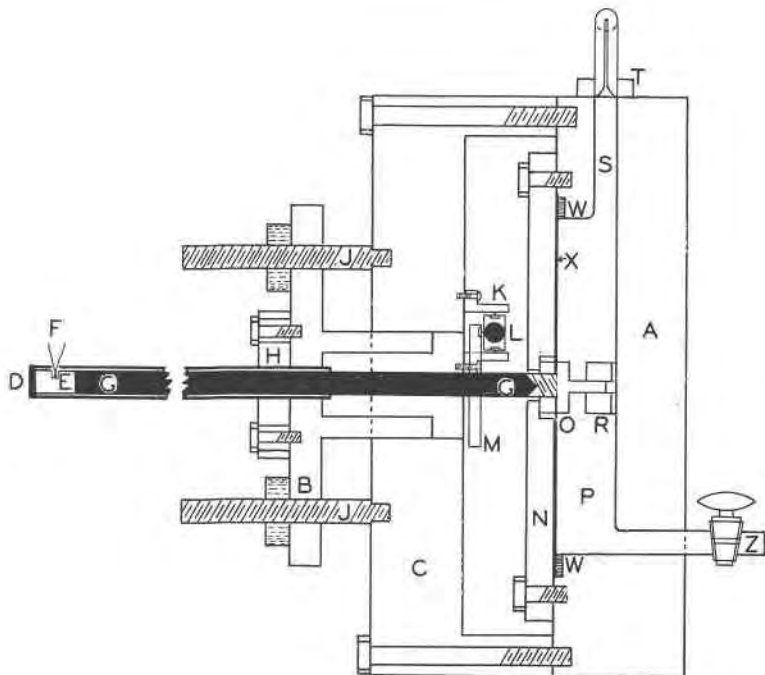


FIG. 1. Vertical section of capillary cell apparatus.

is important that the tubing be carefully selected for uniformity. The tube extends about one meter in a direction away from the reader. A Beckmann differential thermometer is cemented into the second hole (not shown in Fig. 1) with the bulb totally immersed in the mercury. The cell is filled through the glass stopcock *Z* which was specially ground to insure against leakage.

The advancing mechanism *B* holds the fused quartz tube *D*, the sample *E*, and the fused quartz rod *G*. The end of the tube was closed by fusing on a flat. All fused quartz is transparent vitreosil. The inside end of the tube and the corresponding end of the rod are ground flat. A thermocouple *F* is made from *B. & S. No. 30* platinum and platinum-10% rhodium wires obtained from Baker and Company. This is brought

through a hole drilled in *D* into the depression drilled in the sample. The thermocouple was frequently calibrated against similar thermoelements certified by the Bureau of Standards. The tube is cemented into the plate *H* which is bolted to *B* in such a manner that its orientation may be varied in order to center *G* with respect to the cone in *O*. The entire unit *B* is advanced toward the diaphragm on the fine-threaded studs *J*. Block *C* is bolted to *A* so that a rigid unit is obtained.

A circular ring *M*, cemented to *G*, imparts the advance motion to the lever mechanism *K*. The lever rod *L* is made of fused quartz and is mounted in jewel bearings. The end of the lever opposite from the reader makes contact with an Ames indicator which is rigidly attached to *C*. This indicator has ten-thousandth inch divisions and was made with a friction of only 5 grams. Its sensitivity is 0.00001" and it is precise to less than ± 0.000025 ".

The complete cell assembly and projecting capillary tube are enclosed in a large air bath built of double-walled celotex. The air temperature is controlled by a mercury thermoregulator and relay and the air circulation is maintained by a blower which is separately and externally supported. Vibration is eliminated by a sheet of Foam Sponge rubber under the air bath. The fused quartz tube projects through the front wall of the bath and a tubular electric furnace slides over it to a predetermined position such that the hot junction of the thermocouple is at the hot spot of the furnace. This arrangement insures a uniform temperature over the length of the quartz sample.

Movement of the mercury in the capillary tube is observed through a double-walled plate glass window and is measured by a horizontal cathetometer which reads to 0.02 mm. Temperatures are measured with a Leeds & Northrup Type K_2 potentiometer and Weston cell.

It seems advisable at this point to explain the necessity for certain parts of the cell apparatus. The restraining plate prevents the diaphragm from bulging and also permits its restoration to approximately the same point. If absolute restoration were possible—and such was not found to be the case—direct calibration of a particular diaphragm and capillary tube could be accomplished. The minute variations in diaphragm restoration from one determination to the next is a possible source of error. Many trials established that this error was too great to permit reliable values to be obtained. While the variations would be of minor consequence where reasonably large movements (over 0.05 mm.) were involved, the expansion of a 10 mm. parallel section for a temperature interval of 25° is only approximately 0.002 mm. It was concluded, therefore, that the most certain method should include a calibration to be obtained coincidentally with the expansion of each test section. The lever

and indicator arrangement makes this a possibility. Their calibration was obtained interferometrically. An obvious question is, "Why not use the indicator and lever alone and eliminate the complications of the capillary cell?" The answer is that, for small expansions, such as the amounts obtained up to a few hundred degrees, the indicator and lever arrangement alone is not adequate. Higher indicator values can be used with full confidence and these, in conjunction with the cathetometer readings, permit the true values for small expansions to be computed.

PREPARATION OF TEST SPECIMENS

The sample selected was clear rock crystal from Minas Geraes, Brazil. Its density was $d_{20}=2.649$. Polished plates were used for the determination of refractive indices on an Abbe refractometer using sodium light, the results being $\omega=1.5444$ and $\epsilon=1.5532$. By means of a diamond saw, plates approximately 4 mm. thick were cut parallel and perpendicular to the principal axis. These plates were then cut into prisms 4 mm. square and 10 mm. long. They will be referred to hereafter as sections rather than prisms in order to avoid confusion with the crystallographic nomenclature. It would have been possible to cut sections much longer than 10 mm. This was not done because it was desired to develop a technique which would apply to minerals from which long sections could not be obtained. The ends of each section were ground flat and a small depression for the thermocouple was drilled in the center of one face. Optical examination showed that some of the plates as cut deviated slightly from the desired orientations. A special grinding machine was constructed to correct these deviations by modifying a transit theodolite to hold the quartz plates. The transit is mounted on a lathe compound so that a plate may be brought up to an FF carborundum wheel mounted on the shaft of a high speed motor. The horizontal and vertical circles of the transit permit a freedom of adjustment which corresponds to that obtained on a two-circle goniometer.

TECHNIQUE

A prepared quartz section, the length of which is measured with a micrometer caliper, is placed in the fused quartz tube, the rod is inserted, and the advancing mechanism is adjusted until the mercury in the capillary tube begins to move. The thermocouple is then connected to the potentiometer through a 0° C. cold junction, and the hot junction is inserted into the depression in the sample. It is important that the couple wires be cemented into the tube in order to avoid temperature irregularities. The air bath is maintained above room temperature and the temperature within the cell is measured on the Beckmann thermometer.

Because of the large mass of steel and the large air volume, the temperature variation within the cell is not greater than 0.1° C. during the course of a complete determination. Even so small an amount is important and corrections must be applied for any variations.

In order to obtain expansion data beginning at 0° C., rather than at room temperature, the furnace tube is packed with granules of solid carbon dioxide and is allowed to remain so for one-half hour. The furnace is then emptied and is slid in place over the fused quartz tube as explained previously. Both ends of the furnace are then packed with asbestos. By this procedure the quartz sample is chilled much below 0° C. and, because of the furnace insulation, it warms quite slowly. As soon as 0° C. is reached, readings are begun and are continued at regular intervals up to 1000° C. Readings are taken on the potentiometer, cathetometer, Ames indicator, and Beckmann thermometer. Furnace temperatures are controlled by a Variac adjustable transformer which has been calibrated, thus making it possible to regulate the rate of heating very closely. All determinations were made only during heating and the rate was such that no sections were cracked when finally cooled to room temperature.

RESULTS

We shall first consider the results obtained with sections cut perpendicular to the c -axis. Since there is a distinct difference in piezoelectric properties in equatorial sections cut parallel to the first and second order crystallographic directions, it was thought that a variation might be found in their linear thermal expansions. As a consequence, three sections were studied for each of these equatorial orientations. Because all results were found to be the same, within the range of experimental error, they were cast as a single equatorial mean, the values being given in Table I. The last column lists the most probable values for the perpendicular orientation as presented by Sosman.¹ His data is the result of a most careful analysis of all previously published work on quartz and is more reliable for comparison than the results of any individual investigator. With the exception of the coefficients at 573° and 1000° , there is a remarkably good agreement. Since there is a large personal element involved in determining when the rate of expansion changes at the inversion point, it is easily conceivable that a substantial difference might occur here. It should be said, however, that it is not difficult to observe the change with the equipment described, and that the α - β change is very sharply defined. Sosman's data above 573° is not derived from many linear determinations, as contrasted with numerous values in the lower temperature range. Still another consideration is the variation which is found in different quartz samples.

¹ Sosman, R. B., *The Properties of Silica* (1927, New York), p. 370.

Four sections were studied in the direction parallel to the principal axis. The results are given in Table 2, together with Sosman's² corresponding values. A comparison of both columns reveals a close agreement

TABLE 1. EQUATORIAL MEAN COEFFICIENT OF LINEAR THERMAL EXPANSION FOR QUARTZ.

| 0° C. to | R. & S. $10^6\delta_{m\perp}$ | Sosman $10^6\delta_{m\perp}$ |
|----------|----------------------------------|---------------------------------|
| 100° | 14.37 | 14.45 |
| 200° | 15.62 | 15.61 |
| 300° | 16.81 | 16.89 |
| 400° | 18.37 | 18.50 |
| 500° | 21.04 | 20.91 |
| 550° | 23.58 | 23.40 |
| 573° | 26.17 | 25.15 |
| { Before | | |
| { After | 30.48 | 31.02 |
| 600° | 29.53 | 29.71 |
| 700° | 25.22 | |
| 800° | 22.18 | 22.18 |
| 900° | 19.64 | |
| 1000° | 17.69 | 16.97 |

up to 500° but divergence above that temperature, except where the inversion begins. It is to be noted that in both orientations the maximum observed values are lower than those previously reported.

TABLE 2. AXIAL MEAN COEFFICIENT OF LINEAR THERMAL EXPANSION FOR QUARTZ.

| 0° C. to | R. & S. $10^6\delta_{m\parallel}$ | Sosman $10^6\delta_{m\parallel}$ |
|----------|--------------------------------------|-------------------------------------|
| 100° | 7.82 | 7.97 |
| 200° | 8.64 | 8.75 |
| 300° | 9.52 | 9.60 |
| 400° | 10.53 | 10.65 |
| 500° | 12.02 | 12.22 |
| 550° | 13.43 | 13.81 |
| 573° | 15.00 | 15.00 |
| { Before | | |
| { After | 17.03 | 17.98 |
| 600° | 16.60 | 17.08 |
| 700° | 14.15 | |
| 800° | 12.41 | 12.02 |
| 900° | 10.88 | |
| 1000° | 9.45 | 8.83 |

² *Ibid.*

The critical point for the α - β inversion was determined on 14 different specimens, all cut from the same crystal, and was found at $573.1 \pm 0.5^\circ \text{C}$. This is in excellent agreement with the very carefully determined values of Bates and Phelps³ who reported the limits 573.2° and 573.4°C .

A second change was found in all perpendicular sections at $872 \pm 1^\circ \text{C}$. The change was observed simultaneously on the mercury cell and the indicator as an abrupt, though small, increase in the rate of contraction. The amount of contraction at this point is approximately 0.1 per cent. If this is contrasted with the large expansion at 573° , it is obvious that there is no appreciable difference in the value of the mean coefficient at 872° before and after the change. It appears most likely that this represents the quartz-tridymite inversion which was reported at $870 \pm 10^\circ \text{C}$. by Fenner.⁴ This change was observed at 871.5° for only one of the four parallel sections. The remaining three showed a marked acceleration in the previous uniform rate of contraction at 828.2° , 831° and 830° , the mean being $830 \pm 2^\circ$. It is possible that, due to this acceleration, the 872° point was obscured. Since the quartz-tridymite inversion is extremely sluggish in the temperature range where the change was observed, except in the presence of fluxes—and no fluxes were used in this work—no apparent explanation is at hand for the uniformity of perpendicular sections and the lack of uniformity of the others.

SUMMARY

The results of this research indicate the validity of the new apparatus as an instrument for the precise determination of both linear thermal expansion and inversion points. Since the source of the quartz used by previous investigators is not reported, an exact comparison with their work is impossible. It is to be noted that the quartz-tridymite inversion had not been observed previously in any similar investigations.

ACKNOWLEDGMENTS

It is with deep appreciation that the authors express their gratitude to the Carnegie Corporation of New York, whose grant-in-aid made it possible to obtain the precision instruments for measurement and calibration which were necessary for this research program. They are indebted to W. & L. E. Gurley, Troy, New York, for their cooperation in the development of the transit grinding equipment. It is also a pleasure to acknowledge the helpfulness of Professors George Howard Carragan and Harold A. Wilson of the Rensselaer Polytechnic Institute.

³ Bates, F., and Phelps, F. P., The new fixed point on the thermometric scale: *Physical Rev.* (2) **18**, 115-116 (1921).

⁴ Fenner, C. N., The stability relations of the silica minerals: *Am. Journ. Sci.*, **36**, 331-384 (1913).