

A THERMAL INCREMENT DIFFRACTOMETER

WILLIAM A. BASSETT AND DAVIS M. LAPHAM, *Columbia University,
New York, N.Y.*

ABSTRACT

A furnace has been designed to fit the Philips x -ray diffractometer. The temperature may be raised at a uniform rate or maintained at a controlled level from 0° C. to 1000° C. Powdered crystalline materials are placed on a Pt-Rh plate which rests on a heating element near the center of the furnace. The temperature is recorded by a Pt, Pt-Rh thermocouple connected to a Brown recorder. Variations in intensity and angle of reflection for oscillations or scans are charted on a second Brown recorder synchronized with the temperature recorder. The back of the furnace contains a water jacket for cooling while the front assembly is enclosed by an inconel cover. The insertion of a beryllium window permits controlled atmosphere experiments. Arkansas quartz has been used to ascertain the temperature characteristics of the furnace and to obtain data on the alpha-beta lattice expansion with its accompanying intensity changes.

INSTRUMENT DESIGN

Introduction

Investigation of the structural characteristics of minerals at elevated temperatures is an important part of mineralogical procedure. A method designed to aid such investigation utilizing the x -ray diffraction of powders at high temperatures has been described by Weiss and Rowland (1956) and by Birks and Friedman (1947). An instrument of this type may be used in conjunction with a goniometric scanning unit and may be easily substituted for the normal diffractometer arrangement.

This paper describes a high temperature diffraction unit capable of observations over the range 0° C.– 1000° C. It has been constructed under the direction and with the assistance of Professor Paul F. Kerr of Columbia University. The writers are also indebted to Dr. Richards A. Rowland, Shell Research Laboratory, for suggestions for the design of this instrument, and to Dr. John Thompson of the International Nickel Company for providing specially cast inconel blocks of adequate size for furnace construction.

Furnace and Sample Placement

The heating unit was built by Professor Robert L. Stone, Department of Ceramics, University of Texas. It consists of 0.1 mm. Pt-13% Rh wire set in a ceramic block $1" \times 1" \times \frac{1}{4}"$ thick and is capable of an internal temperature of 1400° C. A powdered sample may be either deposited from suspension on a flat Pt-Rh plate 0.1 mm. thick which then rests on the surface of the heating element (Fig. 1) or pressed into a flat rectangular Pt-Rh receptacle with sides 1.0 mm. high. The former arrangement

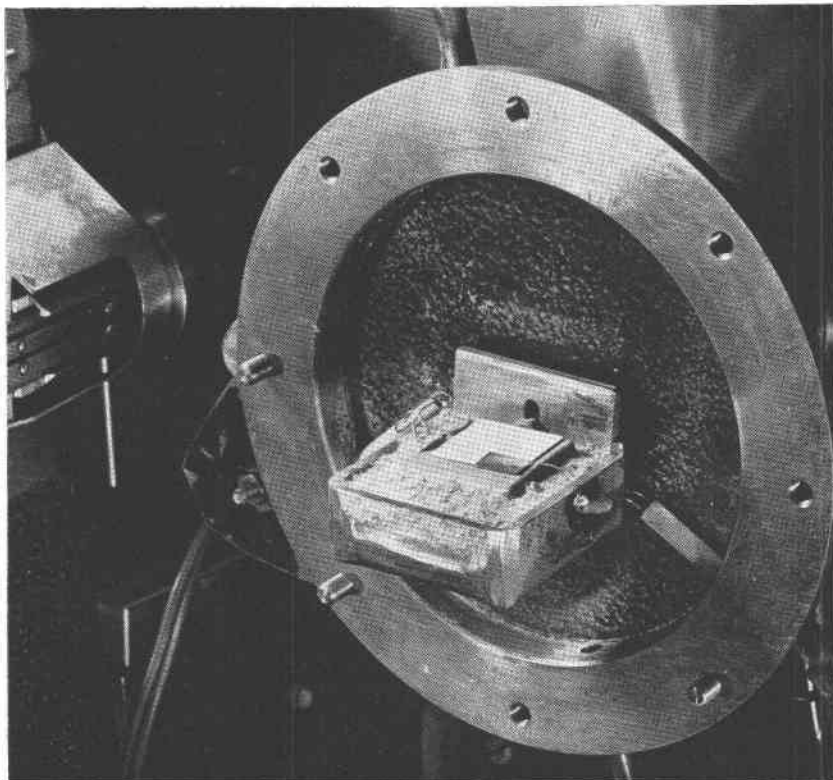


FIG. 1. Sample, thermocouple, heating element and furnace mount of the thermal increment diffractometer.

yields basal orientation for micas and clays and allows for expansion without surface buckling. The receptacle may be used for orientations other than basal spacings if the sample surface remains planar during heating. The receptacle also furnishes a smooth, regular surface which assists in quantitative interpretations of diffraction intensities.

Temperature Recording and Calibration

The mineral sample temperature is determined by use of a Pt, Pt-13% Rh thermocouple on a Pt-Rh plate adjacent to the sample and connected to a cold junction thermocouple. The potential from the thermocouples is recorded directly on a Brown recorder. Temperatures may be read by calibration of the recorder millivolt scale. This calibration was accomplished with inorganic compounds having a range of melting points between 200° C. and 900° C. The calibration curve corresponds to values

listed in the Handbook of Chemistry and Physics (1955). Since the sample surface is at a slightly lower temperature than the hot junction thermocouple due to sample thickness and different heat reflectivity, the millivolt scale was recalibrated by means of the known linear expansion of Pt-Rh for temperatures between 0° C. and 1000° C. The formula used is:

$$l_t = l_o(1 + \alpha t + \beta t^2),$$

where

l_t = the total linear expansion at t temperature,

l_o = the initial length

$\alpha = 0.08668 \times 10^{-4}$ and

$\beta = 0.013 \times 10^{-7}$.

This correction amounts to about 30° C. at 600° C. and decreases at lower temperatures.

Cassette Construction

The heating element is embedded in asbestos within an inconel tray and attached to a circular inconel plate. This plate separates the furnace from a water cooling chamber and is seated by a rubber "o" ring. The plate is drawn tight against the "o" ring by means of three Allen head stainless steel screws which enter the back of the plate through the cassette back and water chamber. Two welded monel tubes near the back of the cassette provide a water inlet and outlet. The water exits from the top of the water chamber to eliminate the collection of air. A Hays flow switch is connected to an alarm to indicate when the flow has fallen below $\frac{1}{2}$ gal./min.

Two additional monel tubes are welded to the cassette in front of the separating plate to permit either immersion of the sample in an inert atmosphere or attachment of a vacuum line. A Ni heat radiation barrier is attached to the cassette front by three threaded ceramic stand-off insulators. Two rectangular slots in the barrier covered by thin Ni foil cemented with ceramic cement allow the x-rays to impinge upon the sample and to be reflected to the Geiger tube. An inconel cover outside the radiation barrier is flange-bolted to the cassette back. It also contains slits which may be covered by a thin Be sheet for inert atmosphere or vacuum runs.

Holes in the cassette back allow entry of the power leads to the furnace and exit of the Pt, Pt-13% Rh thermocouple. The power leads are connected to a double variac-synchronous motor controller system. A variac driven by a synchronous motor controls the power to the heating element. The desired heating rate is obtained by regulating the applied

voltage with a second variac. A heating rate of about 10° C./min. up to 1000° C. has been found to be satisfactory. By shifting the motor from one side of the gear reduction system to the other, the variac may be reversed so that the furnace is cooled at a controlled rate. Two micro-switches have been installed on this variac so that both lower and upper power supply limits can be set automatically.

CALIBRATION

Introduction

Finely powdered quartz from Hot Springs, Arkansas was used both to check the accuracy of the temperature readings and to illustrate the application of the thermal increment diffractometer. Both the structure of quartz and its inversion temperatures have been studied by many workers, some of the latest using a diffraction goniometer furnace in conjunction with other methods of study (Keith and Tuttle, 1952). Available data indicate that the alpha-beta transition takes place over a considerable range which may vary with crystallographic direction as well as with composition and is complete at about 574° C. The tridymite transition is so slow, however, that a scan at 910° C. after heating for two hours produced no significant differences in the pattern from the beta quartz pattern at 625° C.

Results and Interpretations

A comparison of the diffraction pattern data for alpha and beta Arkansas quartz is shown in Table 1. The calculated "*d*" values and intensities for the two polymorphic forms are compared with quartz data by Swanson and Fuyat (1953). A general shift of about 0.4° 2θ may be observed for the low angle planes in which *h* is 1 and *k* is 0 or 1. Where *h* is 2 and *k* is 0 or 1, the shift is doubled to 0.8° 2θ . The majority of reflections show no significant change in intensity from alpha to beta quartz, but (100), (101), and (112) increase while (110), (102), (202), and (211) decrease. Presumably an increase in intensity represents a greater degree of order while a decrease represents a less ordered condition. The latter also show increased peak broadening which could be expected as the degree of disorder increases. Since beta quartz commonly has less well developed prism faces than alpha quartz, the lower intensity and decrease in sharpness of (110) substantiates this morphologic feature.

A modification of the graphical method of successive approximations was used to calculate the a_0 and c_0 values for alpha and beta quartz. They are compared below with values given by Donnay and Nowacki (1954).

TABLE 1. ALPHA—BETA ARKANSAS QUARTZ COMPARISONS

(hkl)	Alpha Quartz		Beta Quartz		Swanson and Fuyat (alpha)	
	$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.	$d(\text{\AA})$	Int.
100	4.264	20.6	4.340	22.8	4.26	35
101	3.348	100.0	3.399	109.4	3.343	100
110	2.456	4.4	2.500	2.3	2.458	12
102	2.248	6.4(?)	2.310	1.9	2.282	12
111					2.237	6
200	2.131	4.5	2.166	3.2	2.128	9
201	1.982	4.4	2.013	3.9	1.980	6
112	1.819	8.5	1.837	10.3	1.817	17
003	1.801	1.5			1.801	1
202	1.673	5.5	1.696	1.8	1.672	7
103	1.659	2.6	1.673	1.9	1.659	3
210	1.605	1.4	1.624	1.8	1.608	1
211	1.541	6.9	1.566	3.6	1.541	15
113	1.453	3.1	1.477	1.0	1.453	3
300	1.415	1.3	1.433	1.3	1.418	1
212					1.382	7
203					1.375	11
301					1.372	9
104	1.288	1.5	1.347(?)	1.3	1.288	3
302	1.2553	1.6	1.276	1.8	1.256	4
220	1.228	1.6	1.2495	1.9	1.228	2
213	1.1997	1.5	1.2162	1.8	1.1997	5
221					1.1973	2
114					1.1838	4
310					1.1802	4
311					1.1530	2
204					1.1408	1
303	1.126	4.7(?)	1.172(?)	1.5	1.1144	1

	<i>Arkansas Quartz</i>	<i>Donnay and Nowacki</i>
alpha	a_0 4.910 \AA	4.910 \AA
	c_0 5.390 \AA	5.39 \AA
beta	a_0 5.002 \AA	5.01 \AA
	c_0 5.454 \AA	5.47 \AA

The linear expansions for (100) and (101) in 2θ values plotted against temperature are shown in Figs. 2*b* and 2*c*, respectively. Bond reorganization signalling the beginning of the alpha-beta transition appears to begin earlier for the (101) plane and takes place over a wider temperature range of the order of 60° C. or 70° C. while the (100) transition occurs more suddenly. The transition expansion reaches a maximum at 573° C. for (100) and at 574° C. for (101). Beyond this point there is generally a

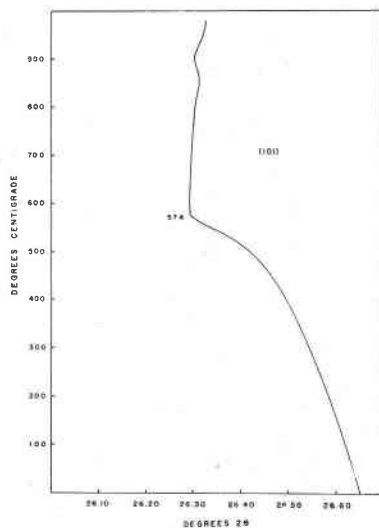
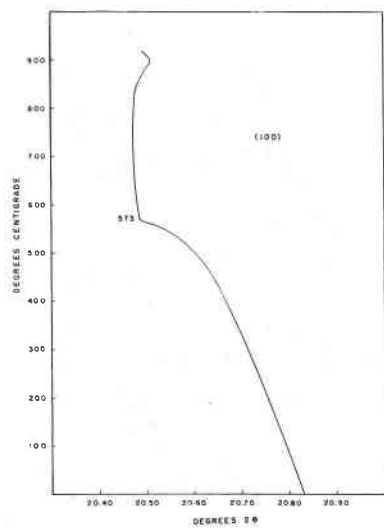
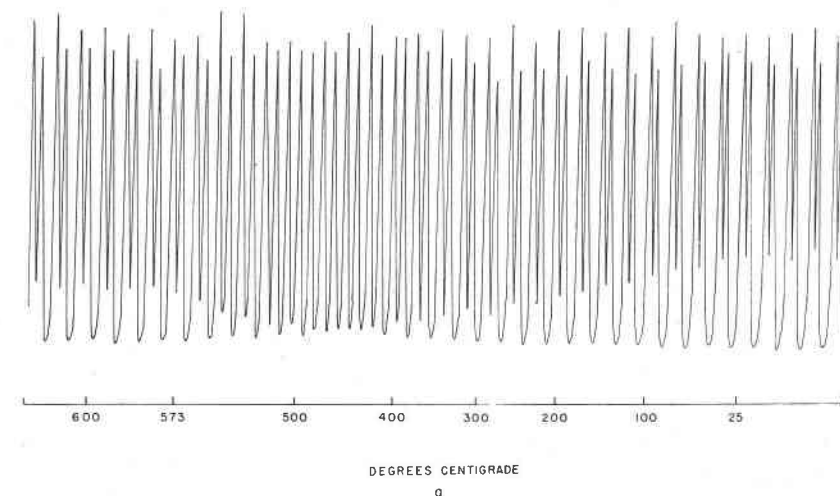


FIG. 2. Heating-oscillation and expansion curves of Arkansas quartz.

- (a) Heating-oscillation chart for (101). Changes in separation of forward and reverse scan peaks signify quartz expansion.
- (b) Plot of 2θ against temperature demonstrating the expansion of Arkansas quartz normal to (100).
- (c) Expansion similar to (b) for (101). The inversion takes place at 573°C .– 574°C . in each case.

slight contraction of the lattice as has been noted by Jay (1933). At about 900° C. there is a slight contraction for (100), and a slight expansion for (101). Since this is in the tridymite region, these changes may be related to a further change in symmetry. The tridymite transition is extremely sluggish, however, and it is doubtful that significant reorganization to the tridymite form occurs over the span of a few hours.

Keith and Tuttle (1952) and others have noted that reflections from all planes become hazy and divide into multiple reflections at the inversion temperature, but rejoin to form sharp reflections after inversion. These results were secured from larger crystal fragments than the fine grained powder used here. Since inversion triggers are supplied by surface irregularities and are dependent upon grain size, fine powder should yield sharp reflections at the inversion point. Inspection of the oscillation diagram for (101) and (100) shows that the peaks are quite sharp at the inversion point (Fig. 2*a*). A similar oscillation was carried out under equilibrium conditions from 555° C. to 610° C. All peaks were sharp at

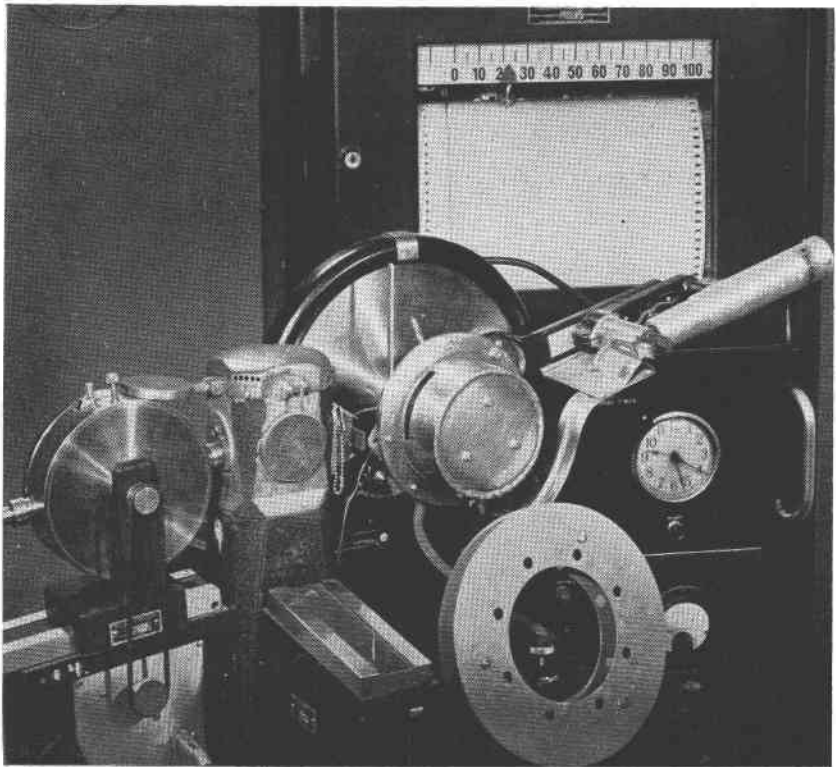


FIG. 3. Thermal increment diffractometer installed on the Philips x-ray apparatus.

the inversion temperature and the shape of the expansion curve remained unchanged for the 10° C./min. heating rate used in the illustrated curves (Fig. 2b, 2c).

Accuracy of Data

Temperatures were read from the millivolt-temperature graph plotted initially on a theoretical basis and checked against the fusion point of ZnCl₂ (262° C.), Zn (419° C.), Al (659.5° C.) and CaCl₂ (772° C.). The control curve was then recalibrated for the thermocouple position during quartz runs using the known thermal coefficients of expansion for the Pt-Rh plate upon which the sample was deposited. The same sample was used for all runs and several runs were made for each scan and each oscillation. Reproducibility lies within the limit of error of the Philips-Brown recorder system which is about $\pm 0.03^\circ 2\theta$ and ± 0.7 intensity units on a scale of 100 units. Temperatures are considered to be accurate to $\pm 4^\circ$ C. between 0° C. and 800° C. and to be about $\pm 8^\circ$ C. at higher temperatures.

CONCLUSIONS

Arkansas quartz has an inversion temperature close to 573° C. which is the temperature for 70% of natural quartz specimens (Keith and Tuttle, 1952). Inversion is believed to begin from 50° C. to 70° C. below the transition temperature. A slight contraction of the lattice gradually occurs above the inversion temperature and continues to at least 900° C. There is an irregularity in the expansion for the (101) and (100) planes at about 900° C. In the alpha-beta transition low angle reflection planes expand as much as 0.076 Å while planes having a smaller $d(\text{Å})$ show a correspondingly smaller change. Certain planes such as the (101) have a more orderly atomic arrangement in the beta form while others such as the (211) are less ordered.

REFERENCES

- BIRKS, L. S., AND FRIEDMAN, H. A. (1947), A high temperature diffraction apparatus: *Rev. Sci. Instruments*, **18**, 578-580.
- BRAGG, W. L. (1937), *Atomic Structure of Minerals*: Cornell Univ. Press, 83-90.
- DONNAY, J. H., AND NOWACKI, W. (1954), *Crystal Data*: Geol. Soc. Am., Mem. **60**, p. 413.
- Handbook of Chemistry and Physics (1955), ed. by Hodgman, C. D., Weast, R. C., and Selby, S. M.: Chem. Rubber Pub. Co., Cleveland, Ohio, p. 2065.
- JAY, A. H. (1933), *Proc. Roy. Soc.*, **A142**, p. 237.
- KEITH, M. L., AND TUTTLE, O. F. (1952), Significance of variation in the high-low inversion of quartz: *Am. Jour. Sci.*, **Bowen Volume**, 203-280.
- SWANSON, H. E., AND FUYAT, R. K. (1953), N.B.S. Circular 539, III.
- WEISS, E. J., AND ROWLAND, R. (1956), Oscillating-heating x-ray diffractometer studies of clay mineral dehydroxylation: *Am. Mineral.*, **41**, 117-126.