

## MINERALOGICAL NOTES

A NEW HEATING STAGE FOR THE X-RAY DIFFRACTOMETER<sup>1</sup>

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A heating stage for an *x*-ray diffractometer is a valuable aid, and sometimes an essential tool, for investigations of the high temperature *x*-ray powder-diffraction properties of solids.

We have designed a simple and convenient stage which can be easily aligned in the *x*-ray beam and which will hold the alignment at all operating temperatures. The stage can be conveniently used to 1400° C., with a temperature control of  $\pm 1^\circ$  C. up to 1000° C. and  $\pm 5^\circ$  C. or better up to 1400° C. Maximum thermal gradients of 2° C./cm at 1000° C. occur across the surface of the sample. Temperatures can be changed and stabilized rapidly and are accurately measured at the center of the irradiated specimen.

X-ray measurements are performed rapidly and to the same accuracy and resolution as standard *x*-ray diffractometer measurements performed at room temperature. The stage can be operated in a vacuum or in a noncorrosive gas atmosphere.

## DESCRIPTION

Details of the instrument are readily apparent from Fig. 1, and the dimensions of the component parts from Fig. 2 and 3. The heating stage is designed for operation on a Norelco *x*-ray diffractometer.

A 7-inch diameter brass base plate (A) is centrally mounted on a steel drive shaft (B); the drive shaft is identical in outside diameter to the regular drive shaft of the diffractometer and uses the same adjustable positioning collar (C). The drive shaft is hollow to allow the entrance of the coolant, water.

Mounted directly on the base plate is a flanged mullite cylinder (M), made to our design by a commercial refractory company, attached by stainless steel screws through four parallel slots (D) in the flanged base (E), the slots being perpendicular to the irradiated specimen surface. The mullite cylinder contains the heating elements and positions the specimen holder. Two slots  $\frac{1}{2}$  inch wide (Fig. 3) permit passage of *x*-rays through the cylinder. The removable mullite specimen holder (F) is positioned by shoulders (G) cut in the slots so that the surface of the plate contains the axis of rotation of the instrument. The sample surface is heated by two, flat, parallel radiant heaters normal to the sample sur-

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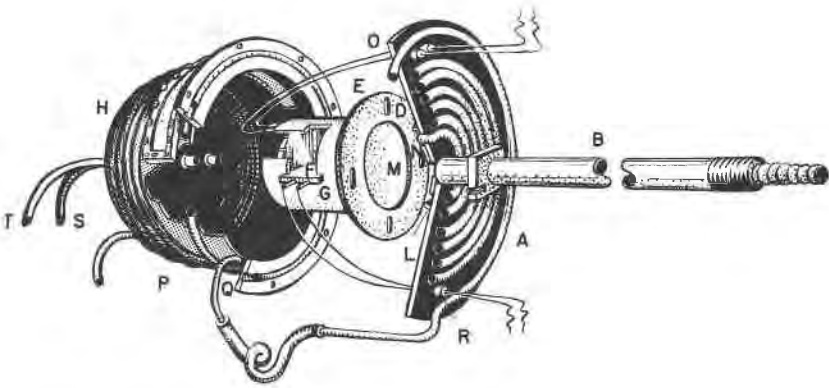


FIG. 1. Diagrammatic sketch of heating stage for  $x$ -ray diffractometer, showing cap (H), heating cylinder and heaters, base plate (A) and mounting shaft (B). Parts designated by letters are specifically referred to in the text.

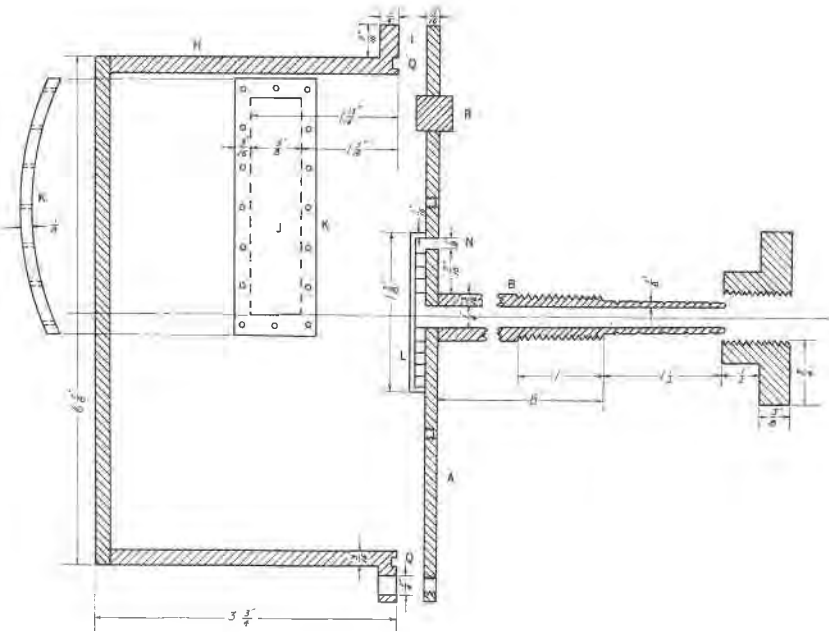


FIG. 2. Diagram of cap (H), base plate (A), and mounting shaft (B) of the heating stage. Cooling coils, shown on Fig. 1, have been omitted to avoid confusion. Parts designated by letters are specifically referred to in the text.

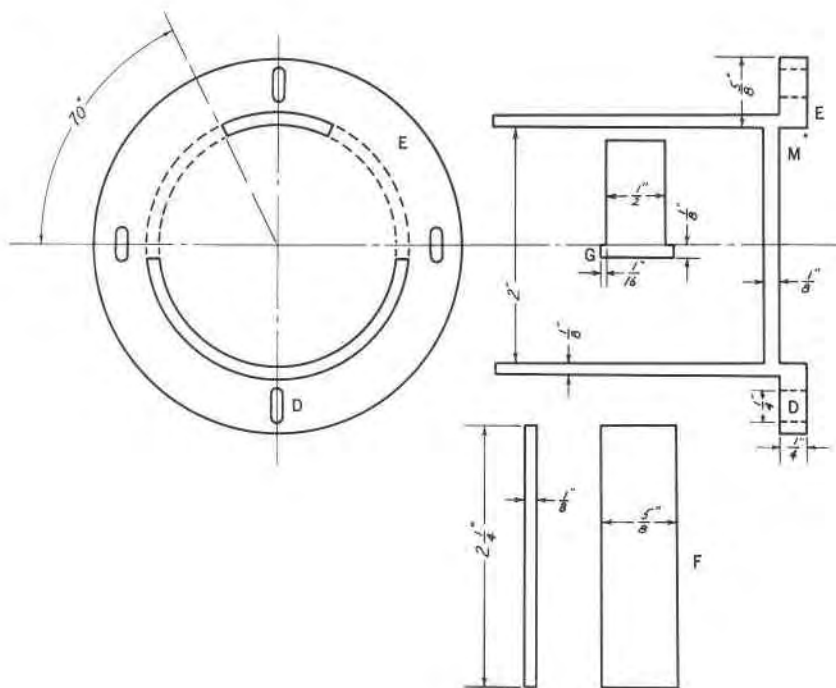


FIG. 3. Diagram of mullite heating cylinder and sample holder (F). Heating elements, shown on Fig. 1, are not shown. Features designated by letters are specifically referred to in the text.

face and parallel to the base plate. The heaters extend both above and below the sample surface and do not touch the sample holder. The heaters are made of 0.031-inch diameter platinum wire wound vertically on two grooved circular discs of sintered alundum, and are connected in series. The resistance of the cold heating circuit is approximately 1 ohm. A 2000 watt variable transformer is used to supply power to the heaters. An unregulated power supply is satisfactory for the short intervals of time required for most measurements, but a temperature controller is necessary to compensate for voltage fluctuations during long experiments and to compensate for temperature changes induced by variations in coolant pressure. We use the resistance of the heating elements as the variable arm of a balancing bridge circuit; any unbalance in the circuit is compensated by a reversible motor-driven variable transformer. Temperature control to  $\pm 5^\circ$  C. at  $600^\circ$  C. has been maintained for several days; for periods of several hours, temperature control to  $\pm 1^\circ$  C. up to  $1000^\circ$  C. has been attained.

The heating system is covered by a flanged brass cap (H), 7 inches in diameter, which is attached to the base plate by eight screws through the flange (I). Windows (J), 5/8 inch wide, cut in the brass cap correspond to the slots in the mullite cylinder and allow  $x$ -rays to traverse the heating chamber. Vacuum-tight covers seal the windows. Brass collars (K) screwed to the cap have been successfully used to hold 0.001-inch nickel foil, 0.002-inch aluminum foil, and thin Mylar films in place as covers. Because uniform support is provided by the brass collars, even the thin foils used will successfully hold a vacuum inside the chamber.

An important feature of any heating stage is the cooling system, which must prevent any part of the diffractometer from becoming heated. In our design, water enters the hollow drive shaft (B), and passes through a series of helical baffles in a cooling chamber (L) which projects into the space inside the recessed base of the mullite cylinder (M). This cooling chamber reduces stresses developing around the metal screws holding the mullite cylinder to the base plate. From the cooling chamber, water passes through a small hole in the base plate (N) to a spiral of 3/16-inch diameter copper tubing (O), soldered to the back of the base plate. The water then passes, via a removable rubber hose, to a copper cooling coil (P) soldered to the surface of the brass cap, and thence to the drain. A water flow rate of 500 cc per minute is adequate to cool the camera body when the furnace temperature is 1300° C.

To prevent heat loss by convection and to reduce thermal gradients, the heating stage is normally operated in a vacuum. The vacuum seal between the cap and the base plate is a static neoprene O-ring, positioned in a recess in the flange of the cover (Q). Leads to the heating system and thermocouple are taken through Kovar seals (R) soldered into the base plate. The system is evacuated through a tube soldered into the end of the cap (S). If it is desired to work with a gas other than air, the gas is introduced through a gas inlet tube (T).

The sample holder is a flat mullite slab, prepared from the same ceramic material as the mullite cylinder. It is important that the same ceramic material be used in both cases in order to prevent misalignments from differential thermal expansion. The sample holder is ground to fit exactly the positioning shoulders in the cylinder (Fig. 3). By careful grinding, using diamond abrasives, both the sample holder and positioning shoulders can be precisely shaped until the positioning shoulders and the sample holder surface lie in the same plane as the axis of the instrument. Specimen alignment is performed by setting the diffractometer at 0°  $2\theta$ , placing a flat metal bar on the sample surface, and moving the cylinder to bring the lower edge of the metal bar into alignment with the centers of the collimating and receiving slits of the diffractometer.

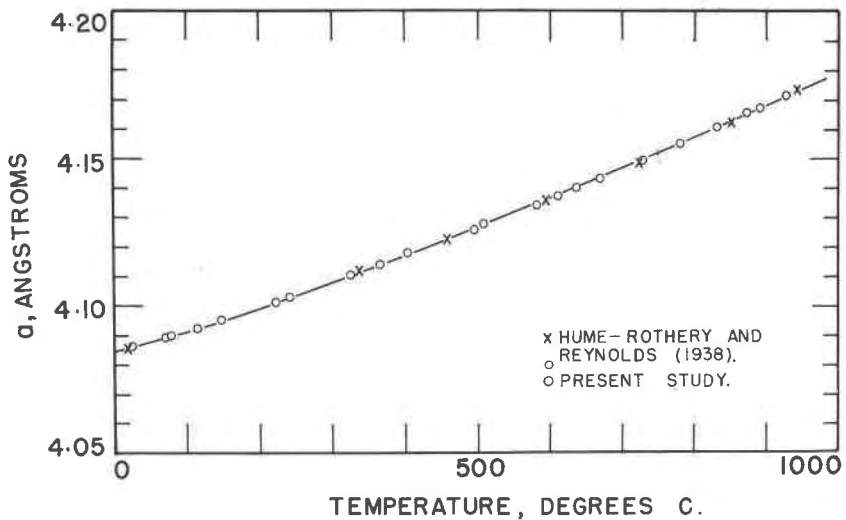


FIG. 4. Plot of cell edge ( $a$ ) of pure silver against temperature, showing agreement between present measurements and those of Hume-Rothery and Reynolds (1938).

Adjustments are made with the screws holding the cylinder and the positioning collar on the drive shaft. Repeated tests, using substances of known thermal expansion, have shown that the assembly remains aligned up to at least 1300° C.

The temperature is measured by a platinum to platinum-10-per cent-rhodium thermocouple cemented in a small hole in the center of the sample holder. The thermocouple bead is cemented in the hole with alundum cement so that most of the bead projects above the upper surface of the sample holder. The bead is then ground down until it is flush with the surface. It is important that the bead be very thin after grinding, so that the temperature measured is the surface temperature of the sample holder. Thermocouple leads are taken from the heating chamber by cementing them in two slots cut in the base of the sample holder. If the substance being irradiated on the sample holder is corrosive to the thermocouple, care must be taken to keep the actual surface of the bead clean.

#### OPERATION AND CALIBRATION OF INSTRUMENT

The finely ground specimen to be irradiated is spread on the mullite plate in the same manner that standard glass slide mounts are prepared, and should be as thin as possible. Normally neither intense background radiation nor objectionable line interference from the mullite occurs.

By cementing several thermocouples into a single sample holder we have measured a maximum thermal gradient across the sample surface of  $2^{\circ}$  C./cm at  $1000^{\circ}$  C. We have further established that no correction need ordinarily be applied to temperature readings. The measured thermal expansion of pure silver powder (Fig. 4) agrees exceedingly well with the careful measurements by Hume-Rothery and Reynolds (1938). The  $\alpha$ - $\beta$  inversion in a sample of quartz from Lake Toxaway was measured at  $575^{\circ} \pm 2^{\circ}$  C. The most sensitive test, however, was the measurement of the melting point of silver ( $960.8^{\circ}$  C., Stimson, 1949). The mullite plate was completely covered with very fine silver powder. At  $959.5^{\circ}$  C., no silver had melted. At  $961.7^{\circ}$  C., silver had melted over an area twice as large as the maximum area irradiated, indicating that the temperature measurement was accurate and that thermal gradients over the irradiated area were negligible.

#### USES OF THE HEATING STAGE

The heating stage described has been successfully used for a variety of x-ray powder diffraction studies. Chao *et al.*, (1961) used it to study the complex crystallographic inversions in neighborite ( $\text{NaMgF}_3$ ); Skinner *et al.* (1961) measured the thermal expansions of andalusite, kyanite and sillimanite from room temperature to  $1050^{\circ}$  C.; Roseboom (1960) successfully studied unquenchable phase relations in the sub-solidus region of the system Cu-S between chalcocite ( $\text{Cu}_2\text{S}$ ) and digenite ( $\text{Cu}_9\text{S}_5$ ); Schreyer and Schairer (1960) studied the inversion in metastable low-quartz structure-type compounds found in the system  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ , and Fournier (1961) studied water losses at various temperatures from a regular, mixed-layer, vermiculite-chlorite mineral.

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