

fore indicates the apparent temperature of decomposition of malachite with different heating rate, but it does not establish the minimum decomposition temperature of malachite. It does show, however, that if the decomposition of malachite is to be tested at, for example, 200° C., the heating rate can be no more than approximately 0.001° C. per minute.

To test whether decomposition of malachite proceeds at 200° C., samples were held at a constant temperature for 20 days. During this period of time there was more than 3 per cent weight loss with the products being CuO and malachite (Fig. 3). It would require about 200 days for the reaction to go to completion. Azurite was tested in a similar manner and found to decompose at 190° C. losing 2.76 per cent weight in 45 days. The temperature of decomposition of azurite and malachite is therefore less than 200° C.

In conclusion, the reported decomposition temperatures of azurite and malachite are largely explainable by the different heating rates used by the investigators. And further, the minimum possible heating rate should always be used for determinations of decomposition temperatures of any material.

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QUARTZ GLASS PRESSURE VESSELS FOR HYDROTHERMAL STUDIES

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INTRODUCTION

Sealed quartz glass tubes have proved useful as pressure vessels in low PT hydrothermal experiments in silica-saturated systems. These tubes provide an inexpensive means for making simultaneous runs along an

isotherm with varying bulk composition, pH, partial gas pressure, etc. within a single heater. The arrangement is well adapted to very long runs which are often necessary to attain equilibrium at low temperatures. Each tube forms an isolated system and can be completely enclosed by a furnace so that temperature gradients in the reaction vessel are lower than those in cold seal controlled-pressure bombs.

Our hydrothermal studies with quartz glass tubes are in the system plagioclase—NaCl—Na₂CO₃—H₂O with emphasis on synthesis and decomposition of sodic scapolites. These vessels appear to be useful in experiments with silica-saturated zeolites, clays, and chlorites as well as sulfides, carbonates, and other non-silicates.

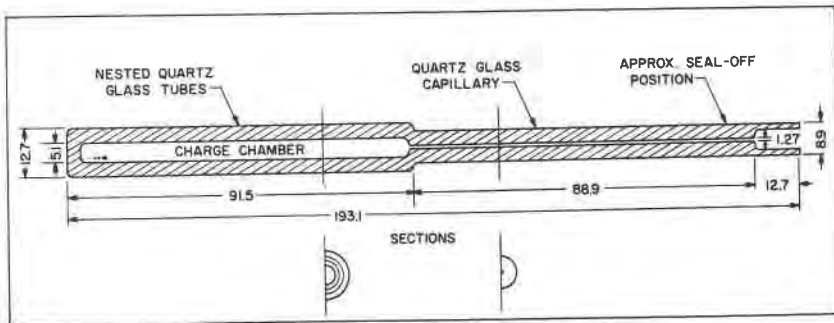


FIG. 1. Cross sections of quartz glass tube. Dimensions in mm.

QUARTZ GLASS TUBES

The geometry of the tubes used in our experiments is shown in Fig. 1. The tubes were prepared in the following way. The lower half or charge chamber is made by nesting three close-fitting quartz glass tubes of 1.25 mm wall thickness and appropriate internal diameters and fusing the tubes together in vacuum. The chamber diameter is sufficiently large that the charge would not be unduly elongate in the vertical dimension, and the effective wall thickness is increased by a factor of 3 over that of a single tube. The base of the chamber is sealed, and a thick-walled capillary is fused onto the other end. The diameter of the capillary is sufficient for insertion of a long syringe to place liquid in the charge chamber, but it is small enough that errors in the position of tube seal-off affect the tube volume by less than 0.8%. A wide diameter tube is attached to the upper end of the capillary for ease of loading solids into the vessel.

After loading, the tubes are sealed below the top of the capillary with a hydrogen flame. It is helpful to immerse the tube and ingredients in

liquid air before the seal is made. This procedure and the large distance from charge chamber to the seal point precludes bulging in the melted SiO_2 by increases in internal gas pressure during sealing.

Table 1 gives experimental data on temperatures and internal pressures at which quartz vessels failed. The pressure in tubes 1, 2 and 3 is a vapor pressure in equilibrium with a saturated liquid phase and is a function only of temperature (Keevil, 1942, for NaBr; Sourirajan and Kennedy, 1962, for NaCl). These pressures are not significantly affected by the presence of SiO_2 as indicated by measurements of NaCl- H_2O saturation vapor pressures with SiO_2 gel in controlled-pressure bombs; the measured pressures agreed with pure NaCl- H_2O saturation pressures of Sourirajan and Kennedy (1962) at the same temperature within the uncertainty of the pressure reading. That SiO_2 probably does not

TABLE 1. TEMPERATURES AND INTERNAL PRESSURES OF QUARTZ GLASS TUBE FAILURE

Tube	Charge	Temp. ($^{\circ}$ C.)	Pressure (Bars)
1	Saturated NaBr Solution	543 ± 7	146 ± 4
2	Saturated NaCl Solution	511 ± 13	345 ± 13
3	Saturated NaCl Solution	493 ± 13	323 ± 12
4	H_2O	474 ± 5	414 ± 11

react with these fluids is further indicated by very high Gibbs free energies (>200 K cal.) in the temperature range of Table 1 for reactions of the form $4\text{NaCl}(\text{Br}) + \text{SiO}_2 \rightleftharpoons \text{SiCl}_4(\text{Br})_4 + 2\text{Na}_2\text{O}$. The pressure in tube 4 was calculated from the degree of filling by the perfect gas equation and fugacity coefficients given by Holser (1954). Kennedy (1952) has shown that the solubility of SiO_2 in pure H_2O in the PT range of interest here is very low and that the vapor pressure of the solutions is not measurably different from that of pure water under the same conditions.

Quartz glass is the most suitable composition for these vessels because of its strength at high temperatures, low coefficient of thermal expansion, and absence of possibly reactive components. Vycor and pyrex both contain 3% or more B_2O_3 in addition to significant quantities of Al_2O_3 and the alkalis; pyrex softens at about 600° C.

PRESSURE

The gas pressure in these tubes cannot be directly controlled or measured after seal-off, and desired pressures must be obtained by other means. Subcritical systems, in which the pressure of vapor in equilibrium with a liquid is known as a function of temperature and composition,

provide accurate knowledge of the pressure. Pressures in supercritical systems may be approximated from the mass of the fluid and sealed tube internal volume together with appropriate fugacity coefficients. An error of 1 cm in the seal position leads to an error of 0.65% in an intended internal volume of 2 cc. The quantity of liquid inserted can be controlled to about .01 cc/cc with a pipette or syringe. The mass of liquid added, however, can be found by weighing to an accuracy of 0.0005 g/cc. The volume increase of the chamber by thermal expansion from 0 to 500° C. is about 0.1%. Coupled with a temperature error of 3° C., these errors produce an uncertainty in a perfect gas pressure of about 1.3%. This error in actual pressure is probably small compared to errors caused by deviations from perfect gas pressure in many systems for which experimental PVT data are not available.

FURNACE

Our furnace is designed with the view toward creating a large isothermal chamber which could house ten or more tubes simultaneously. Figure 2 outlines the furnace configuration. The heater is a nichrome resistance-type direct radiating cylindrical element which is capable of sustained temperature of 1000° C. The element is inserted in a stainless steel cylinder of 3.2 mm sheet with one removable end plate. Between the element and the cylinder walls is 11.55 cm of insulation. The basal, top, and midring layers of insulation are castable ceramic and provide support for the element. The rest of the insulation is ceramic fiber. A plug is cut into the upper ceramic layer to allow access to the furnace interior.

Stainless steel cylinders, 1.92 cm diameter, into which the quartz vessels are placed, are welded in a ring around a larger steel tube of diameter such that each of the smaller steel cylinders touches the adjacent cylinders; temperature differences between the quartz vessels are thus minimized. This steel cylinder assembly is placed in the central part of the furnace as shown in Fig. 2. The use of a separate steel jacket for each quartz tube protects the tube from shock created by failure of an adjacent tube.

Power regulation to the heating element is supplied by a W30G2BB Variac Autotransformer. Thermocouples are placed at various positions in the furnace for temperature monitoring. Pt—10% Rh thermocouples in the positions shown in Fig. 2 give readings consistently within 1° C. By setting the Variac at maximum power, the furnace was brought from 25 to 500° C. in six hours. The time interval to reach run temperature in the glass tubes could be reduced if the furnace were preheated before emplacement of the steel tube assembly.

The problem of rapid cooling of the glass vessels, however, is severe

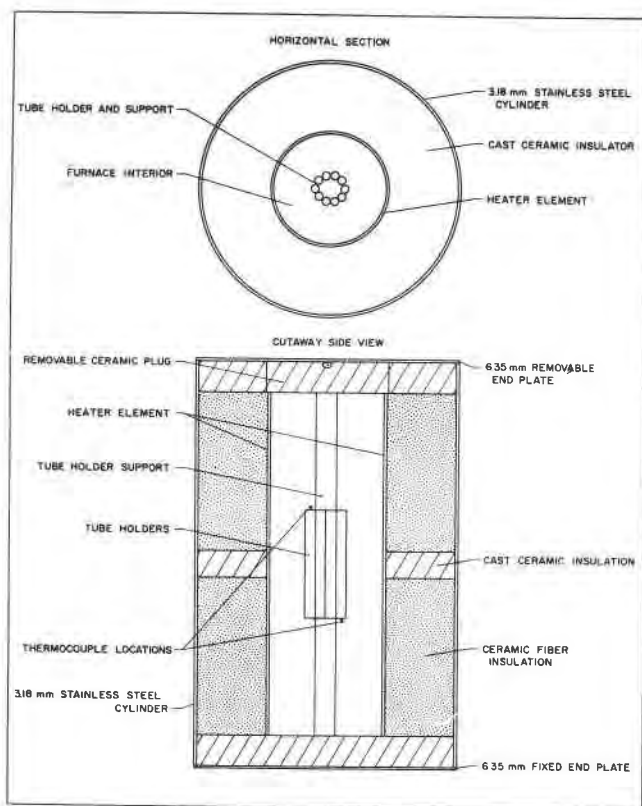


FIG. 2. Vertical and horizontal sections of furnace. Scale approximately 1:20.

because strong tensile stresses are introduced along the tube exterior during chilling. Quartz glass plates of 3.2 mm thickness at about 1250° C. do not shatter when plunged into water at 1° C. (Corning Glass Co. Bulletin #83, 1957). These tubes would probably shatter at a lower temperature difference, however, because of their geometry and internal pressure. Rapid quenching has not been investigated experimentally; our cooling method is to remove the steel tube assembly after power shut down and to place it under an air stream. Because forward reaction rates are generally slow in systems for which this apparatus is well suited, reverse rates will probably also be slow and metastable equilibrium will be retained over the cooling period.

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NOTES ON SOME BLACK HILLS PHOSPHATES

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A recent collecting trip to the Etta pegmatite, Keystone, South Dakota revealed many interesting phosphate pods, widely and abundantly distributed throughout the quarry dumps.

The parent material appears to be triphylite. Blocks of triphylite, more or less oxidized, are common on the dumps and the alteration products are mainly iron phosphates. Landes (1928) gave an account of the stages of mineralization of the Keystone pegmatites and assigned triphylite to the "magmatic" period of crystallization. Since triphylite appears to be ubiquitous throughout the dumps, it probably originated between the wall zone and the core of the pegmatite which represents by far the greatest volume of the body. Specifically, the Fe-Mn phosphates usually occur between the wall zone and the part of the intermediate zone in which amblygonite begins to appear (Page *et al.*, 1953).

One large nodule, markedly altered, displays many of the oxidation-alkali leaching-hydration products of the primary triphylite. The specimen consists of reddish-brown radiating blades of frondelite-rockbridgeite (identified from x-ray powder data), implanted upon mitridatite, which, in turn, rests upon pulverulent manganese and iron oxides. Several other unidentified phosphates occur as tiny crystals throughout the mass.

Fracture surfaces in the mitridatite display white coatings and tiny glistening colorless spherical radiating laths up to 1 mm across. Careful handpicking resulted in only 2 mg of material for investigation. A powder pattern of the material shows no relationship to any substance in the Powder Data File, 1962. Emission spectrography shows Mg, Ca, Al and P as major constituents, with minor Fe, Mn, Si. Two single crystals studied by means of the Weissenberg technique showed them to be identical with montgomeryite (Table I), a rare hydrated Ca, Al phosphate occurring in variscite nodules at Fairfield, Utah (Larsen, 1940). This apparently represents the first reported occurrence of montgomeryite from a pegmatite.