

pressure vessel, and also reduces the power required to reach high temperatures. The winding is about 3 inches long and is insulated by a closely fitting sleeve of massive pyrophyllite, marketed by the American Lava Corp. under the name "Lava".

Considerable difficulty is encountered with thermal gradients in these small furnaces. One of the main sources of trouble is convection of nitrogen through the furnace, which is mounted in a vertical position. Gradients due to the flow of nitrogen are markedly reduced by making the metal furnace sleeve gas-tight at the top, and by filling all open spaces within the furnace and between the furnace and the Lava sleeve with refractory material.

Near the ends of the furnace winding, gradients of the order of $1000^{\circ}\text{C}/\text{inch}$ are inevitable, and the region of essentially uniform temperature in the center of the furnace is extremely short. The windings are more closely spaced near the ends of the furnace than opposite the charges, but steep gradients near the central part of the furnace have persisted. The gradient is reduced to about ten degrees in the length of the charge by placing the capsules in a heavy block of metal. The number of capsules is reduced when the metal block is used, but the more uniform temperature compensates for this sacrifice.

Five insulated leads, accommodating the various electrical circuits, are let into the pressure vessel through the plug at its bottom. The stem of the bottom plug is necessarily rather large, and its seal has not been wholly satisfactory. Leaks at this point terminated many of the runs. An unsupported area packing with five insulated leads has been tried recently; it has eliminated difficulties at pressures up to 20,000 bars.

Temperature is measured with platinum-platinum 10 percent rhodium thermocouples placed at each end of the capsules containing the charges. The cold junction of the thermocouples is in an ice bath outside the pressure vessel. Each thermocouple lead consists entirely of thermocouple wire except for a distance of three-sixteenth inches, which is in a hardened steel cone forming the pressure-tight seal. The mean thermal gradient in the bottom plug is measured by thermocouples at each end. It has never exceeded $15^{\circ}\text{C}/\text{inch}$, and hence the error introduced by the cones can hardly exceed 3°C . This small correction and the correction for the effect of pressure on the emf of the thermocouples have been neglected in the results.

Pressure is measured with a manganin coil calibrated against the freezing point of mercury at 0°C . The coil has a resistance of about 51 ohms, and its change of resistance is measured on a Carey-Foster bridge with a precision equivalent to about 20 bars. The coil is mounted on the bottom plug, between leads of thermocouple wire. Measurement of the thermal emf in this circuit gives the mean temperature of the coil. In this position its mean temperature has never exceeded 50°C ; the correction to the measured pressure is less than 100 bars at this temperature (Robertson et al., 1957).

In making a run, the pressure is first raised to about 2,000 bars below the desired value, and the furnace is then heated to the desired temperature. The temperature is raised relatively slowly (about 100°C per minute) to reduce thermal shock in the apparatus and to guard against the development of

local hot spots in the furnace winding. After the furnace has reached temperature, the pressure is adjusted if necessary.

The charges are quenched by turning off the power to the furnace. The temperature drops below 300°C in 30 seconds and reaches about 100°C in one minute. The pressure is then released.

In the early stages of this work, the duration of runs was limited to about three hours by persistent small leaks and burning out of furnaces. Many of these difficulties have gradually been eliminated, and considerably longer runs are now feasible.

Starting materials tried in the synthesis of kyanite and sillimanite were kyanite from Gorham, Me., sillimanite from near Mt. Monadnock, N. H., andalusite from Laws, Calif., kaolinite from Murfreesboro, Ark., and synthetic gibbsite from the Norton Co. Capsules containing the charges were left unsealed, so that any water present could escape freely. In most of the successful runs the starting material was andalusite, kaolinite, or a mixture of kaolinite and gibbsite. Analyses of the andalusite and kaolinite are given in table 1.

TABLE 1
Chemical Analyses of Andalusite and Kaolinite

	J. Ito, Analyst	
	(1)	(2)
SiO ₂	34.92	44.56
TiO ₂	0.63	0.49
Al ₂ O ₃	59.61	39.40
Total Fe as Fe ₂ O ₃	0.66	0.47
MnO	0.00	0.00
MgO	0.00	0.10
CaO	0.28	0.73
Na ₂ O	0.10	0.09
K ₂ O	0.13	0.10
H ₂ O	3.71	14.47
	<u>100.04</u>	<u>100.41</u>
	Traces of	Traces of
	Ga, Cu, Au.	Ga, Cu, Zr.
Mole fractions		
SiO ₂	582	743
Al ₂ O ₃	584	386

(1) Andalusite, White Mts., near Laws, Calif. Harvard Museum #95769.

(2) Kaolinite, Murfreesboro, Ark. Harvard Museum #102649.

In some of the runs, kaolinite and gibbsite were mixed to give a 1:1 ratio of Al₂O₃ and SiO₂, but it was thought that dehydration of the gibbsite favored nucleation of corundum and was partially responsible for the appearance of metastable quartz plus corundum. In later runs, kaolinite alone was used as a starting material; it reacts to form an aluminosilicate plus quartz, but since both kyanite and sillimanite are stable with quartz, this has no effect on the equilibrium curve.