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DIFFERENTIAL THERMAL ANALYSIS IN CLOSED SYSTEMS
AT HIGH HYDROSTATIC PRESSURES

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Investigations of phase transitions at elevated pressures in various systems can often be conveniently carried out by quenching techniques when the phases on either side of the transition can be preserved and identified by subsequent *x*-ray and/or optical examination. Many sub-solidus enantiotropic transitions, and melting relations (where the liquid phase cannot be quenched as a glass) have to be detected by indirect evidence such as the presence or absence of twinning, a meniscus, or bubbles. The accuracy of such methods is often somewhat low and sometimes quite misleading (Wyllie and Tuttle, 1963).

During an investigation of the liquidus in the systems $\text{Ca}(\text{OH})_2\text{-Ca}_2\text{SiO}_4$ and $\text{Ca}(\text{OH})_2\text{-Ca}_2\text{SiO}_4\text{-CaO}$ by quench techniques, the need arose for more direct data in support of the petrographic and *x*-ray evidence. In systems such as these, dehydration has to be prevented by the application of elevated pressures and the proportions of the components have to be maintained, by completely enclosing the sample in sealed malleable noble-metal capsules, for example, to which the desired pressure is applied externally.

Conventional differential thermal analysis techniques at low pressures are not applicable to such closed systems, but it was found possible to pick up the latent heat effects on both melting and freezing by a rather simple device. This consisted of folding the base of a noble-metal capsule

around the bead of a chromel-alumel thermocouple. This assembly was placed in a Tem-Pres pressurized micro-reactor and the thermocouple leads were brought out through a packing gland.

For calcium hydroxide, the heating and cooling curves were run at 5,000 and 15,000 psi and the results were very similar at both pressures (Figs 1, 2). The shapes of the curves obtained by this rather crude method are as might be expected for freezing and melting transitions, with an indicated melting and freezing temperature (with at least 5° C. of supercooling) of 775 to 780° C. This may be compared with 830° C. for the equivalent melting point "determined" by the quench method (Harker *et al.*, 1962).

By modification of the apparatus for DTA-it was possible to magnify the heat effects and to eliminate any possible errors due to thermocouple contamination. A schematic diagram of the apparatus is shown in Fig. 3. The sample under investigation and an inert standard, in this case calcined MgO, were sealed in platinum capsules. To the base of each capsule was welded a platinum-13% rhodium wire. These wires were led from the micro-reactor through pressure packing to a microvolt pre-amplifier. To complete the differential couple, the capsules in the micro-reactor were joined by a fine, platinum wire. The junctions of the differential couple were thus formed where the Pt-13Rh wire joined the base of the capsule.

In addition to the differential couple, a platinum-platinum 10% rhodium thermocouple was also placed in the pressure vessel to measure the temperature. The leads from this thermocouple were also passed through the pressure packing.

Before the apparatus was completely assembled, the capsules and the thermocouple were wrapped in glass cloth to insulate the capsules and the thermocouple from each other and also to insulate them from the walls of the pressure vessel.

The desired pressure was supplied by nitrogen gas, although argon is to be preferred since nitrogen causes severe embrittlement of the platinum alloys. The EMF of the differential couple was amplified by a Leeds and Northrup Model 9835 Microvolt Amplifier. This amplified signal and the EMF from the temperature-measuring thermocouple were recorded on a multipoint recorder.

With this apparatus, several melting points in the CaO-Ca(OH)₂-Ca₂SiO₄ system at 15,000 psi. were obtained. The heating curves from three typical compositions studied are shown in Fig. 4. The upper curve is for calcium hydroxide heated at 12° C./minute and the larger endotherm to the right represents the melting of Ca(OH)₂ at 15,000 psi. The indicated melting temperature of 770° C. is in good agreement with the

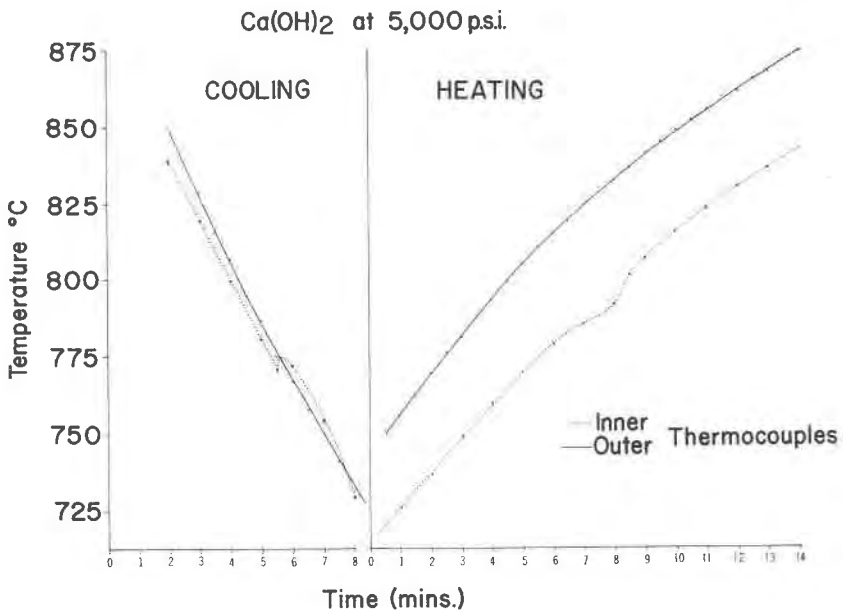


FIG. 1. Cooling and heating curves for Ca(OH)₂ at 5000 psi showing latent heat effects on freezing and melting.

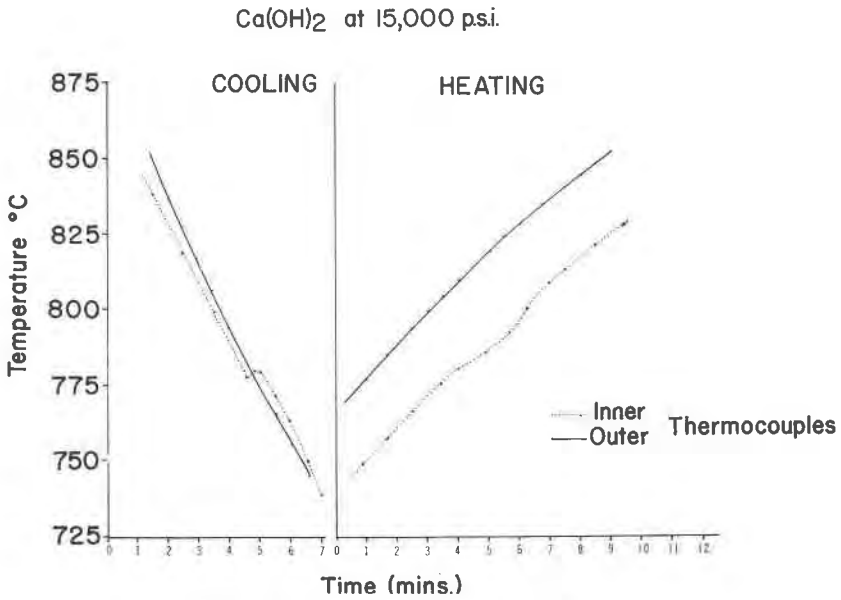


FIG. 2. Cooling and heating curves for Ca(OH)₂ at 15,000 psi showing latent heat effects on freezing and melting.

simple heating and cooling curves shown in Fig. 2 but is much lower than the melting point "observed" by the quenching/optical technique. The smaller endotherm at 630° C. was unexpected in this system. It is probably caused by a small amount of ternary liquid forming at the $\text{CaCO}_3\text{-Ca(OH)}_2\text{-H}_2\text{O}$ eutectic. This eutectic is at 675° C. according to Wyllie

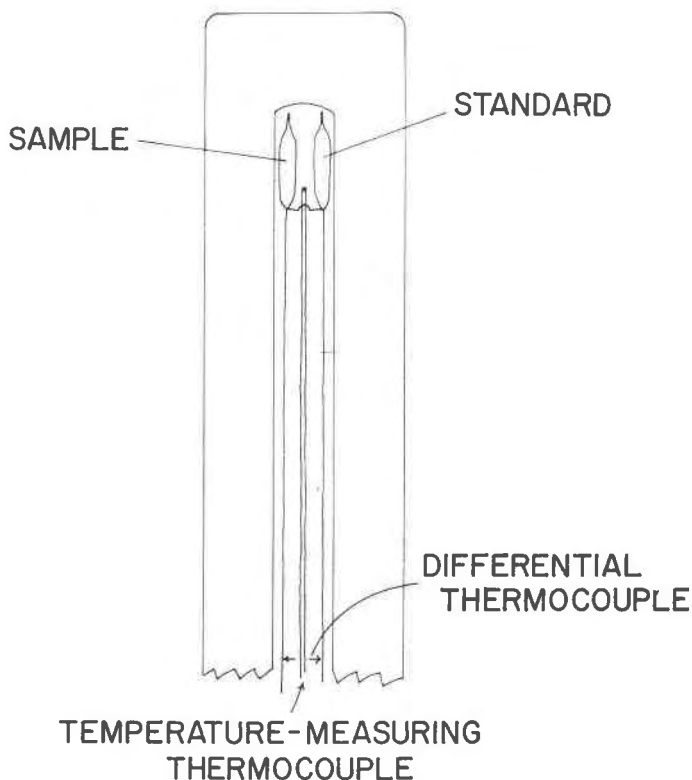


FIG. 3. Schematic diagram showing longitudinal cross-section of pressure vessel and the arrangement of capsules and thermocouples for runs up to 1000° C. and 15,000 psi.

and Tuttle (1960) who used the quench/optical method for its determination.

In the binary system, for a composition 85% Ca(OH)_2 and 15% Ca_2SiO_4 , melting apparently commences at approximately 725° C. and the small lower temperature endotherm occurs at 608° C. The temperature of 725° C. is almost 100° C. lower than that "observed" for the eutectic by Harker *et al.* (1962).

The beginning of melting in the ternary system for a composition of

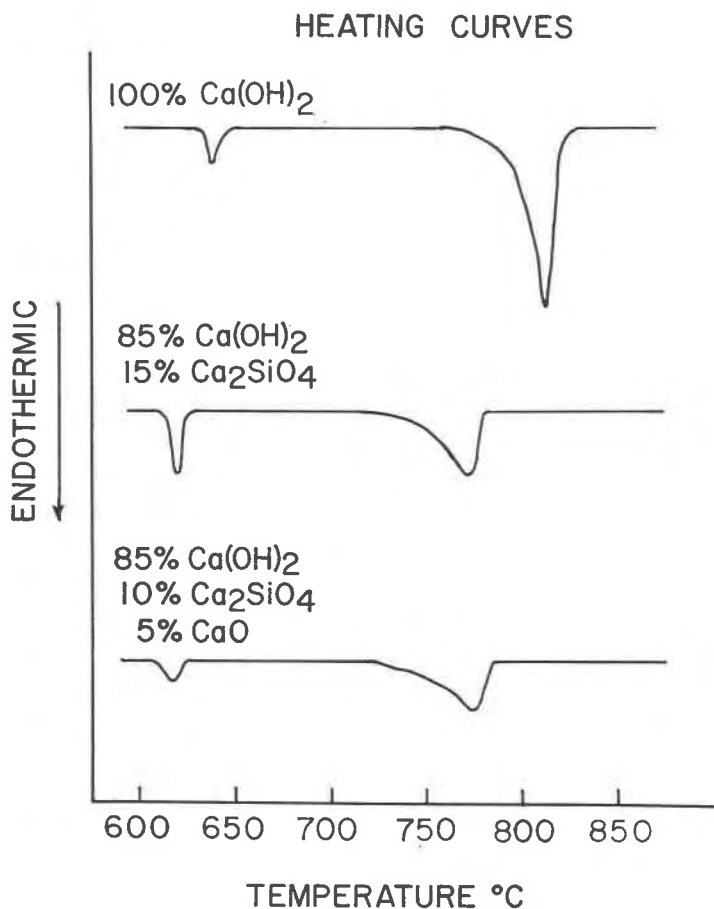


FIG. 4. Differential thermal analysis heating curves for compositions as indicated at 15,000 psi.

85% Ca(OH)_2 , 10% Ca_2SiO_4 and 5% CaO was detected at 720° C. which may be compared with about 800° C. from the quench method. The small lower temperature endotherm occurs at 605° C. indicating that extra CaO has little if any effect on it.

Cooling curves for these same compositions are shown in Fig. 5. In all cases it must be noted that for the main peaks freezing commences at a slightly higher temperature than melting. This is contrary to normal behavior for simple congruently melting compounds and suggests that Ca(OH)_2 melts incongruently up to at least 15,000 psi. It may also be noted that in the ternary system there is a double exotherm on cooling

which may be related to a degree of supercooling in the subliquidus field above an incongruent melting point.

Considerably more runs are needed in order to explain all the phenomena taking place in this system. However, this relatively simple technique for differential thermal analysis in closed systems containing volatile components at elevated pressures should be applied to a wide variety of systems to eliminate some of the errors inherent in the indirect methods frequently used to study such systems.

The writer wishes to acknowledge the cooperation of Dr. James P. Leineweber in those stages of the work which were carried out at the Johns-Manville Research Center, Manville, New Jersey.

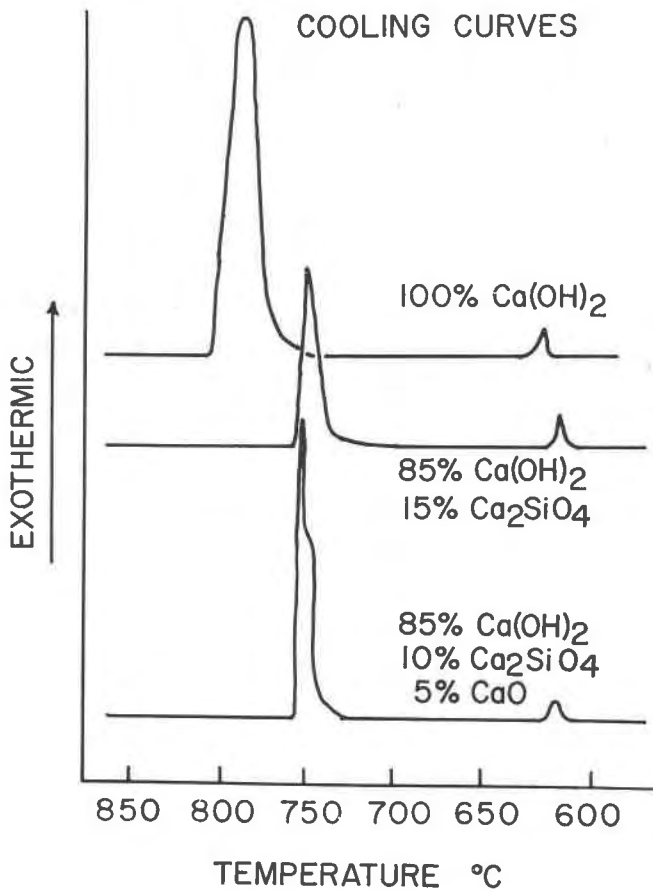


Fig. 5. Differential thermal analysis cooling curves for compositions as indicated at 15,000 psi.

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ALLANITE IN THE TAN-Y-GRISIAU MICROGRANITE,
MERIONETHSHIRE, NORTH WALES

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INTRODUCTION

The occurrence of allanite in veins and cavities in the northern margin of the Tan-y-Grisiau microgranite, N. Merionethshire, was noted by Fearnside (1910). During a recent investigation of the microgranite the author has found that the mineral is not confined to such veins and cavities but occurs in reasonable abundance in accessory amounts throughout the microgranite. It has been encountered in about 50% of thin sections examined and has been found in all heavy mineral concentrates.

The physical and optical properties of the allanite are extremely variable. Much of it is partly metamict and some of that occurring in veins is altered to a number of unidentified secondary minerals, one of which strongly resembles the yellow isotropic mineral described by Silver and Grunfelder (1957) from the Elberton granites of Georgia. The physical and chemical properties of the allanite will be described later when more work has been completed but the textural relationships of the mineral are constant and of sufficient importance to warrant separate consideration.

MODES OF OCCURRENCE OF THE ALLANITE

Allanite in the Tan-y-Grisiau Microgranite has two major modes of occurrence.

1. Allanite occurs with quartz, chlorite, calcite and locally epidote and ore minerals, in narrow veins (up to 1 inch across) and cavities (up to 1 foot across) in and adjacent to the northern margin of the intrusion. The vein and cavity fillings have a drusy texture. Individual crystals of