

Effect of pressure on reversible solid–solid transitions in nepheline and carnegieite

LEWIS H. COHEN¹ AND WILLIAM KLEMENT, *Jr.*²

SUMMARY. Differential thermal analysis of a rapidly reversible transition in carnegieite to 7 kbar shows the transition temperature increases from $\approx 707^\circ\text{C}$ (on heating) at 1 bar with initial slope ≈ 8.0 deg kbar⁻¹ and anomalous curvature ($d^2T/dp^2 > 0$), with hysteresis between heating and cooling signals that decreases with pressure. DTA of rapidly reversible transitions in nepheline shows the very subtle transition near 185°C (on heating) at 1 bar decreases with pressure to $\approx 170^\circ\text{C}$ near 2–3 kbar and hardly varies in temperature up to 6 kbar; and the higher temperature transition increases from $\approx 872^\circ\text{C}$ (on heating) at 1 bar with slope ≈ 25 deg kbar⁻¹, to 5 kbar, with the hysteretic interval remaining essentially unchanged in the investigated range.

AT 1 bar, nepheline is the stable low-temperature polymorph of $\text{NaAlSi}_3\text{O}_8$ and carnegieite the stable high-temperature polymorph. The transition between the two is sluggish (Bowen and Greig, 1925) and the 1-bar equilibrium transition temperature is taken as $\approx 1252^\circ\text{C}$ (Kelley *et al.*, 1953). At lower temperatures, each polymorph shows rapidly reversible transitions—one in carnegieite, known (Bowen and Greig, 1925; Kelley *et al.*, 1953) to be first-order, and two in nepheline, which may not (Kelley *et al.*, 1953) be first-order. This investigation of the transitions by differential thermal analysis (DTA) reports the variations of transition temperatures with pressure, quantities that are always useful in sorting out the thermodynamics of phase transitions.

Experimental details specific to each polymorph are given below, whereas common procedures are indicated here. Small amounts of synthetic powdered samples, kindly provided by Dr. E. G. King from the same lots of materials as used in the calorimetric investigation (Kelley *et al.*, 1953), were loaded in 1.59 mm o.d. Pt tubes, of 0.13 mm wall thickness, sealed at one end. Measuring thermocouples of 0.13 mm diam. chromel and alumel wires were lashed against the sample capsule with 0.13 mm diam. chromel wire. The reference junction was in contact with mullite thermocouple tubing and within < 2 mm of the measuring junction. Arrangement of sample capsule, thermocouples and the hydrostatic pressure apparatus using argon are described elsewhere (Cohen and Klement, 1974). In these DTA runs, sensitivities in recording temperature and differential temperature were 0.2 mV cm^{-1} and as much as 4 μV cm^{-1} , respectively, on the 2-pen recorder. Pressures were read to ± 5 bar on a Heise bourdon pressure gauge. Previous *in situ* calibrations (Cohen and Klement, 1973, 1974) of thermocouples made from the same reels of wire have been used in correcting temperatures

¹ Department of Earth Sciences, University of California, Riverside 92502.

² School of Engineering and Applied Science, University of California, Los Angeles 90024. Now on leave at National Physical Research Laboratory, Pretoria, Republic of South Africa.

reported here. No attempts were made to correct for the effects of pressure upon thermocouple emf.

Carnegieite. In the first run, using a 3.8 mg sample, signals were readily observed over the range of heating/cooling rates of ≈ 30 to 115 deg min^{-1} , using a sensitivity of $8 \mu\text{V cm}^{-1}$ for differential temperature. Peaks of the differential temperature vs. time traces were taken for the transition temperatures and were reproducible to within

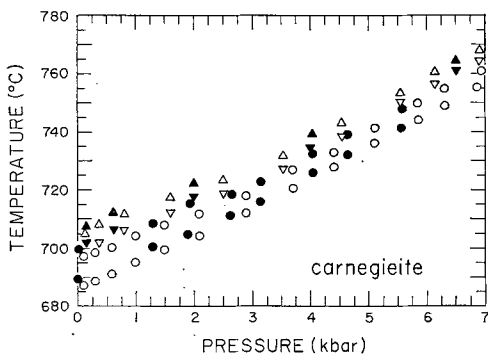


FIG. 1. Data for transition temperatures in *carnegieite*. Low \rightarrow high data lie higher in temperature at the same pressure than high \rightarrow low. Open circles (○) denote data from the first run on increasing pressure; shaded circles (●) denote data obtained on subsequent decrease of pressure. Open triangles (△) denote data from the fourth run on increasing pressure; shaded triangles (▲) denote data obtained on subsequent decrease of pressure.

1° in the two or more cycles made at each pressure. The transition temperatures on cooling were several degrees below those on heating. Temperatures for onsets of transitions typically were $\approx 3^\circ$ – 6° lower than peak temperatures on heating and similarly higher on cooling. Since peak temperatures were more accurately determinable and since the onset temperatures on cooling were often higher than those on heating at a given pressure, data are reported only for the peak temperatures (fig. 1). The results from this first run were not satisfactorily reproducible. On the initial, stepwise increase of pressure, the heating and cooling points yielded, respectively, trajectories with slight positive curvature ($d^2T/dp^2 > 0$), which is rare among phase boundaries. On decreasing pressure

stepwise from the maximum pressure, transition temperatures fell slightly above the data obtained on increasing pressure, until, near 1 bar, there was $\approx 2^\circ$ – 4° difference. Data obtained on subsequent increase and then decrease of pressure revealed further systematic upward movement of transition temperatures, small but beyond the criteria for reproducibility.

In the second run, using a 1.9 mg sample, similar procedures as in the first run were used and similar results were obtained, viz., the systematic increase in transition temperatures.

In the third run, using a 0.9 mg sample, ten cycles were initially made through the transition (over the range $\approx 673^\circ$ – 711°) near 0.11 kbar with no detectable change in the transition temperatures for heating/cooling rates ≈ 65 – 85 deg min^{-1} . Then, a 1-hour anneal near 690°C and 0.11 kbar yielded $\approx 1^\circ$ increase in transition temperatures. Next, an 0.5 hour anneal near 680° and 4.7–5.2 kbar increased the transition temperatures near 0.16 kbar only $\approx 1^\circ$. A final anneal for 1.3 hour near 745°C and 0.16 kbar increased the transition temperatures $\approx 2^\circ$. The temperature–pressure–time dependence of the upward drift in transition temperatures was clarified, in this run, only to the extent that low-pressure anneals both above and below the transition and a high-pressure anneal all had approximately similar effects.

For the fourth run, the sample from the third run was annealed in the Pt capsule at $\approx 780^\circ\text{C}$ in air for 113 hrs. The data obtained from this run, using procedures similar to those used in the first and second runs, are also shown in fig. 1. Although the transition temperatures are displaced upwards by $\approx 7^\circ\text{--}9^\circ$ for the fourth run as compared with the first run, the over-all shapes of the curves are somewhat similar.

Kelley *et al.* (1953) give 707°C as the 1-bar transition temperature in this lot of carnegieite, which is very close to the 1-bar transition temperature on heating obtained here for the most extensively annealed and cycled sample. Earlier, Bowen and Greig (1925) had found the transition on heating at 692°C and, on cooling, 687°C by DTA at very low heating/cooling rates ($< 1/2$ deg hr^{-1}), thus establishing a definite hysteresis for their specimens. They also used peaks of the differential vs. time curves as indicative of the transition temperatures. Roy and Roy (1971) report sample-dependent ranges of transition temperatures and hystereses which, if reinterpreted using peaks of the differential signals, are consonant with values found here and found by Bowen and Greig.

Independent of the drift of transition temperatures, the hysteresis decreases with increasing pressure; for the first run (fig. 1), there is $\approx 10^\circ$ hysteresis at the lower pressures and $\approx 6^\circ$ at the higher and, for the fourth run, $\approx 6^\circ$ at the lower and $\approx 4^\circ$ at the higher. The absolute magnitude of the hysteresis depends somewhat (Klement and Cohen, 1975; Cohen *et al.*, 1974) on sample size, placement of thermocouple relative to sample, etc. Considering the data taken sequentially at the lowest pressures for increasing and decreasing pressure, the initial slope for the transition for both runs (fig. 1), is ≈ 7.7 deg kbar^{-1} on heating and ≈ 8.2 deg kbar^{-1} on cooling, within ± 0.5 deg kbar^{-1} . At the highest pressures (fig. 1), the slope is $\approx 10\text{--}11$ deg kbar^{-1} . If the drift in transition temperature during a run up to maximum pressure and back is distributed uniformly among the data in the run, the curvature $d^2T/dp^2 > 0$ is also quite apparent.

There are few thermodynamic data for this transition but the volume change at the transition may be estimated via the Clausius–Clapeyron equation, $dT/dp = \Delta V/\Delta S$. For $\Delta S = 2.08$ (Kelley *et al.*, 1953) or $\approx 2.2_2$ (Bowen and Greig, 1925) cal mole^{-1} deg^{-1} and $dT/dp \approx 8.0 \pm 0.8$ deg kbar^{-1} , $\Delta V \approx 0.7$ cm^3 mole^{-1} , possibly within $\pm 10\%$. The volume for high-carnegieite (high-cristobalite analog (Bowen and Greig, 1925)) is known (Barth and Posnjak, 1932) near 750°C but the structure of low-carnegieite is not known nor are there any dilatometric data.

$$\text{Since} \quad \frac{d^2T}{dp^2} = (\Delta S)^{-1} \left\{ \left(\frac{\partial \Delta V}{\partial p} \right)_T + 2 \frac{dT}{dp} \left(\frac{\partial \Delta V}{\partial T} \right)_p - \left(\frac{dT}{dp} \right)^2 \left(\frac{\partial \Delta S}{\partial T} \right)_p \right\}$$

and $(\partial \Delta S / \partial T)_p$ appears to be very small, the curvature requires

$$\left(\frac{\partial \Delta V}{\partial p} \right)_T + 2 \left(\frac{dT}{dp} \right) \left(\frac{\partial \Delta V}{\partial T} \right)_p > 0.$$

If the $(\partial \Delta V / \partial p)_T$ term is dominant, as is usual, the isothermal compressibility must be greater for low- than for high-carnegieite; otherwise, the thermal expansion of high- must be much greater than for low-carnegieite. It has recently (Cohen and

Klement, 1975) been inferred that the compressibility of low-cristobalite is greater than that for high-cristobalite near the inversion and this phenomenon may be common among these structures.

Nepheline. In the first run, using ≈ 4 mg of sample, signals for the lower transition were hardly discernible, even with $4 \mu\text{V cm}^{-1}$ sensitivity for differential temperature. Silver paint was also used in these runs to enhance thermal contact between measuring thermocouple and capsule. For the second run, the sample from the initial run was annealed in the Pt capsule at $\approx 780^\circ\text{C}$ in air for 113 hr. Using heating rates of ≈ 100 deg min^{-1} and the maximum possible cooling rates of ≈ 60 – 70 deg min^{-1} , it was possible to obtain discernible, albeit quite broad signals for the transition. Taking the peak temperature for the transition temperature, very little variation was observed in the transition temperatures over the range ≈ 3 to 6 kbar. On heating, the observed transition temperature is $\approx 168 \pm 4^\circ\text{C}$ and, on cooling, $\approx 143 \pm 4^\circ\text{C}$. In the third run, 8 mg of sample taken from the original lot was used. Over the ≈ 3 – 6 kbar range, the observed transition temperature on heating is $\approx 169 \pm 3^\circ\text{C}$, whereas it is $\approx 145 \pm 3^\circ\text{C}$ on cooling. Up to 2–3 kbar, cooling signals were very poor and signals on heating suggested a decrease in transition temperature from $\approx 185 \pm 5^\circ\text{C}$ near 1 bar toward $\approx 170^\circ\text{C}$ at 2–3 kbar. Conceivably there may be a triple point near $\approx 170^\circ\text{C}$ and 2–3 kbar, which would involve a hitherto unknown phase. No conspicuous differences were observed in the heating signals below and above this possible triple point, although the cooling signals were more discernible above than below. The signals were poor, so that undue confidence should not be invested in these data. Kelley *et al.* (1953) gave 194°C for the 1-bar lower transition temperature in this material but their calorimetric technique is also limited in establishing the location of this subtle transition. This transition was not observed by Roy and Roy (1971) with DTA at 1 bar; a transition that they found at $120 \pm 20^\circ\text{C}$ by X-ray diffraction is too distant from the temperature found here for the two to be correlated.

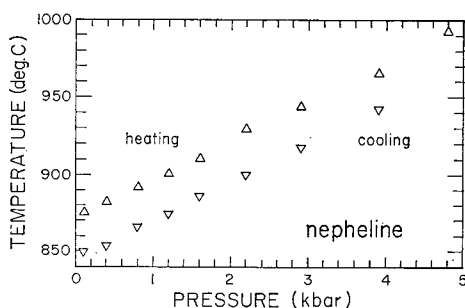


FIG. 2. Data for upper transition temperatures in nepheline. Low \rightarrow high data lie higher in temperature at the same pressure than high \rightarrow low. See text for further discussion.

The upper nepheline transition was more readily observed, using the 8 mg sample from the third run discussed above. Signals could again only be discerned at higher heating/cooling rates and reproducibility was only within $\pm 2^\circ$. The peak temperatures obtained on heating and cooling are shown in fig. 2, for data taken with monotonically increasing pressures. On decrease of pressure, corroboration was obtained for cooling signals whereas the heating signal appeared to be a couple of degrees higher than the transition temperature from the initial part of the run; there was no further pursuit of this possible upward drift in temperature or of its course. The data shown in fig. 2 are consistent with a linear fit of slope ≈ 25 deg kbar^{-1} and 1-bar intercepts of $872 \pm 3^\circ\text{C}$

on heating and 845 ± 3 °C on cooling. Kelley *et al.* (1953) give an equilibrium transition temperature of 907 °C for this material. Tuttle and Smith (1958) preferred ≈ 850 °C for the transition temperature, as obtained by DTA in their nepheline sample, over the less accurate determination of ≈ 900 °C from X-ray work. Roy and Roy (1971) were unable to locate the transition by DTA but found a possible small structural change in their sample, by X-ray techniques, at 900 ± 25 °C. Donnay *et al.* (1959) suggested that a discontinuity in the slopes of volume vs. temperature near 810 ± 50 °C indicated the transition. The absence of any discontinuity in volume is compatible with the trajectory of the phase boundary and with the lack of detection (Kelley *et al.*, 1953) of any isothermal heat for the transition.

Thus the thermodynamic data allow the hypothesis that the transitions in nepheline are not first-order. On the other hand, the present work shows appreciable hystereses for both upper and lower transitions. These are not due to sample and thermocouple geometry since the same experimental arrangement was employed in recent work (Cohen and Klement, 1975) with some alkali carbonate transitions, almost certainly not first-order, and did not encounter such hystereses. Possibly the hystereses and transition temperature are more interrelated with the complex orderings and domain rearrangements known for this mineral rather than with volume changes, as in transitions in simpler crystals. Unfortunately, precise DTA work at high pressures cannot presently contribute enough to the resolution of those problems.

Further high pressure investigation of these NaAlSiO₄ polymorphs is probably useful. Pressurization well beyond the range available here may further order or disorder the carnegieite polymorphs; an effect of this sort on the transition temperatures could not be established in these experiments. Study of analogous transitions in structurally similar minerals often show common behaviour. For instance, the high–low transition in AlPO₄ (berlinite) (Cohen and Klement, 1973) is very similar, under pressure, to the high–low quartz inversion. The high–low cristobalite inversions (Cohen and Klement, 1975) and the high–low carnegieite transition studied here show similar greater compressibilities of low- compared to high-. Perhaps useful analogies can be proposed for nepheline, with its tridymite-like structure, when rapidly reversible transitions in tridymite are investigated at high pressures.

Acknowledgement. Equipment used in this investigation was maintained under NSF Grant GA-27618. Aid from the Committee on Research, University of California, Riverside is gratefully acknowledged.

REFERENCES

- BARTH (T. F. W.) and POSNJAK (E.), 1932. *Zeits. Krist.* **81**, 135.
BOWEN (N. L.) and GREIG (J. W.), 1925. *Amer. Journ. Sci.* **210**, 204.
COHEN (L. H.) and KLEMENT (W.), 1973. *Amer. Min.* **58**, 796.
———, 1974. *Journ. Chem. Eng. Data*, **19**, 210.
———, 1975. *Journ. Amer. Ceram. Soc.* **58**, 206.
——— and ADAMS (H. G.), 1974. *Amer. Min.* **59**, 1099.
DONNAY (G.), SCHAIRER (J. F.), and DONNAY (J. D. H.), 1959. *Min. Mag.* **32**, 93.
KELLEY (K. K.), TODD (S. S.), ORR (R. L.), KING (E. G.), and BONNICKSON (K. R.), 1953. *U.S. Bureau of Mines Report 4955*, 21 pp.

KLEMENT (W.) and COHEN (L. H.), 1975. *Ber. Bunsenges. physikal Chem.* **79**, 327-34.

ROY (D. M.) and ROY (R.), 1971. *Indian Min.* **10**, 16.

TUTTLE (O. F.) and SMITH (J. V.), 1958. *Amer. Journ. Sci.* **256**, 571.

[*Manuscript received 3 February 1975, revised 21 April 1975*]