

nitrate scapolite was determined, its absence could be ascribed to the nucleation difficulty. As will be seen, however, it is more likely that scapolite is unstable relative to the albite and NaNO_3 in at least some of the relatively low-pressure rod-bomb runs.

The well-formed euhedral crystals (from run #14) have typical scapolite morphology; tetragonal, prismatic, with pyramidal terminations. They produce sharp single-crystal diffraction spots with tetragonal $I4/m$ symmetry; the pattern is that of the scapolite structure. The unit cell constants $a = 12.1643 \pm 0.0008 \text{ \AA}$, $c = 7.5297 \pm 0.0011 \text{ \AA}$ were obtained by 2 cycles of computer least-square refinement (Burnham, 1962) taken from X-ray powder diffractometer data. The unit cell volume is $1114.166 \pm 0.177 \text{ \AA}^3$. The density, measured by a sink-float method, is 2.618 ± 0.010 , slightly greater than that calculated from the cell constants, 2.598. This may reflect slight deviation from the assumed ideal formula.

The measured refractive indices are $\epsilon = 1.522 \pm 0.002$, and $\omega = 1.540 \pm 0.002$. A Gladstone-Dale calculation (Larson and Berman, 1934), using the ideal formulation as the basis for the specific refractive energies, gives a refractive index of 1.541, compared to the observed mean index of 1.534.

Several electron microprobe analyses were made on different crystals, pressed into indium metal. The analyses were carried out on the unpolished original crystal faces. The results in wt percent are:

	Na_2O	K_2O	Al_2O_3	SiO_2	N_2O_5
Ideal composition	14.22	0	17.55	62.03	6.20
As analyzed	11.02	0.06	18.00	53.99	—

The analyzed crystals were also from run #14, and thus crystallized from a melt containing potassium. There appears to be little if any potassium in the scapolite, although the surrounding indium metal may have interfered somewhat with the K analysis. Indeed, the low sum of the elements recorded may also be due to beam overlap onto indium. The low Na can be explained by Na volatile loss, for the NaNO_3 -containing scapolite is quite Na-rich. The slight excess of Al_2O_3 and the deficiency in SiO_2 compared to the ideal ($3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$) composition may be real.

An IR absorption spectrogram shows a strong maximum at 7.15μ which is uniquely assignable to the asymmetric stretching vibration of the nitrate groups.

Cancrinite

In a number of runs in which scapolite was formed several extraneous X-ray diffraction lines were observed. This additional phase appeared more abundantly in some of the higher temperature runs, particularly in the absence of scapolite. Perusal of the ASTM Index to the X-ray Powder Data File for a reasonable composition with the appropriate lines revealed a reference to the synthetic compound $3\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$, called natrodavyne by Edgar and Burley (1963). Edgar and Burley found that this composition crystallized with a cancrinite structure at temperatures below approximately 600°C in the pressure range of 10,000–30,000 psi, but as a high temperature modification that they considered to be cubic (nosean structure) above approximately 600°C . Synthesis from a starting mixture of NaAlSiO_4 and NaNO_3 (run 42, Table 1) indicates that the phase encountered here is a cancrinite-like compound, most probably of the composition $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$. Cancrinite was observed in some of the rod-bomb runs.

An X-ray diffractometer scan was made of the product of run #42, using Cu radiation with KBrO_3 as an internal standard, at $1/8$ degree per minute. An attempt to index the pattern on a hexagonal lattice indicated that the sample was in fact a mixture or intergrowth of hexagonal cancrinite and a related cubic substance. It is likely that these substances are polymorphic modifications (with many coincident X-ray reflections) of $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$, namely, a lower-temperature cancrinite form and a high-temperature cubic modification which are analogous to the natrodavyne-nosean pair discussed by Edgar and Burley (1963). We have not pursued the examination of this relationship, but it is possible that cancrinite forms during cooling of the run.

The fairly strong 111 and 400 reflections of the hexagonal cancrinite structure are not coincident with any reflections of the cubic phase, and yield lattice constants for the cancrinite of $a = 12.76_0$, and $c = 5.19_8$. In addition, the 310 reflection of the nosean structure is uniquely resolvable and gives $a = 9.05_1$.

Phase Relations on the Join $\text{NaAlSi}_3\text{O}_8$ - NaNO_3

The appearance of cancrinite in some of the runs made over much of the P - T range in this system requires an interpretation not immediately evident in the raw data. With this reservation the pertinent data from Table 1 are plotted in Figure 1, which

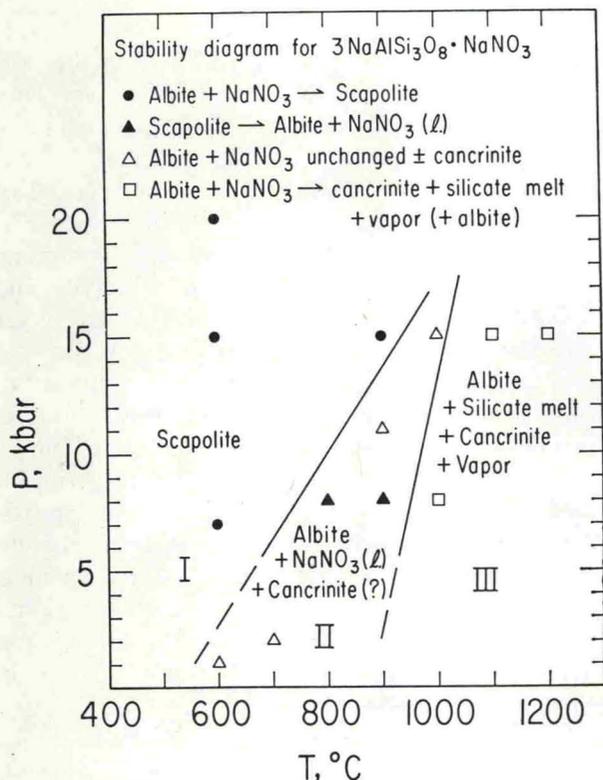


Fig. 1. P - T relations for the composition $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$.

is a P - T stability diagram for the join $\text{NaAlSi}_3\text{O}_8$ - NaNO_3 .

Three fields may be delineated for a bulk composition corresponding to the scapolite formula, $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$. Field I contains scapolite, field II contains the thermal decomposition products of scapolite, namely albite and nitrate melt (+ cancrinite?), and field III contains albite + silicate melt + vapor + cancrinite. There is some doubt about the stability of cancrinite, particularly in field II. If, however, there is considerably more NaNO_3 in the system than necessary to make scapolite, as was true in many of our runs, nitrate melt will be present in all three fields and will replace albite in field III.

The boundary between fields I and II is univariant and has been reversed (nos. 35a, 35b, 40, 41a, Table 1) at 8 kbar. In shorter runs (nos. 43a, 43b, Table 1) cancrinite appeared in field II. Because the silica content of cancrinite is lower than that of scapolite, it is obvious that a complementary amount of silica must have been stored elsewhere in the assemblage. No evidence for an additional silica-rich phase was found. Although the

most likely explanation is that it was dissolved in the nitrate melt, no evidence of high solubility was seen in the quenched charge of a run made with a mixture of quartz and NaNO_3 (no. 45b, Table 1). Likewise, in the somewhat analogous system $\text{NaAlSi}_3\text{O}_8$ - Na_2CO_3 at 1 kbar, the solubility of albite in molten Na_2CO_3 is very small (Koster van Groos and Wyllie, 1966). Longer runs on albite plus NaNO_3 at 15 kbar showed no cancrinite. The cancrinite formed in field II in shorter runs or at lower temperatures in rod bombs (nos. 17, 20, 21, 34, Table 1) would therefore appear to be a metastable phase possibly attended by metastably high solubility of SiO_2 . If so, the phase boundary between fields I and II can be considered to be doubly degenerate in the system Na_2O - Al_2O_3 - SiO_2 - N_2O_5 , being essentially the univariant dissociation of scapolite to albite plus molten NaNO_3 .

Cancrinite was found in the runs made below 1200°C in field III, and metastability is less likely at the higher temperatures of this field than in field II. If the cancrinite is stable in field III, the five phases along the II-III boundary satisfy univariacy in the four-component system. The siliceous melt was produced at temperatures as low as 1000°C . This strongly suggests that a considerable amount of Na_2O is added from the breakdown of nitrate. Further evidence for the enrichment of the silicate melt in Na_2O relative to albite comes from the refractive index (~ 1.52) of the glass from run no. 36 at 1200°C . The isofrac data from the system Na_2O - Al_2O_3 - SiO_2 (Schairer and Bowen, 1956) although uncorrected for the effects of temperature and pressure, would indicate a composition substantially enriched in Na_2O . The nitrogen liberated by the breakdown of NaNO_3 forms a vapor of the bulk composition N_2O_5 . The fact that a puffed capsule was always found in conjunction with identifiable siliceous glass is consistent with this picture.

The runs defining the field boundaries are widely spaced, and only the scapolite field boundary has been reversed, and only at one pressure. Therefore there is considerable uncertainty in the slope of the boundaries. It may be easily demonstrated that the experimental slope of the scapolite decomposition is essentially correct, however. Thus, if we take the density of the scapolite as 2.60 gm/cc , the molar volume is 335 cc/mole . The molar volume of molten NaNO_3 is the volume of the solid, 37.6 cc/mole (Robie and Waldbaum, 1968) plus the ΔV of fusion, which can be gotten from the entropy of fusion of