

6.4 e.u. (Robie and Waldbaum, 1968) and the initial dP/dT melting slope of about 70 bars/ $^{\circ}\text{C}$ (Klement and Jayaraman, 1966, p. 347). Ignoring thermal expansion corrections and using 100.2 cc/mole for albite, we get 7 cc/mole for the volume change of scapolite breakdown. The entropy change will be given as a first approximation by the heat of fusion of NaNO_3 . Thus $dP/dT \sim 6.4 \times 41.8/7 = 38$ bars/ $^{\circ}\text{C}$. The entropy change will be slightly larger than this because of the relatively large molar volume of the assemblage albite + NaNO_3 (Fyfe, Turner, and Verhoogen, 1958), which will increase the dP/dT slope by a small amount. If we used the physically measured density of 2.62 gm/cc for scapolite we would get a smaller slope. The slight solubility of albite in the nitrate melt is still another factor which has not been considered. Nevertheless, the general validity of the experimental slope is evident.

It is established that the nitrate scapolite is quite a refractory phase at high pressures. At still higher pressures, beyond the experimental range of this investigation, albite will be replaced as a scapolite decomposition product by jadeite plus quartz. The effect of albite breakdown on the scapolite stability is easily calculated. The boundary separating jadeite + quartz + nitrate melt from scapolite will be very nearly coincident with the albite to jadeite + quartz curve. This is a consequence of the fact that the ΔV of scapolite breakdown changes from small and positive to large and negative when jadeite + quartz becomes stable. This will be the case regardless of whether the I-II and II-III boundaries intersect before albite becomes unstable. Thus the field of stability of the scapolite will be essentially confined to the region where albite is stable.

The cancrinite appears to be thermally very stable. The present evidence indicates that it is absorbed into the siliceous melt between 1100 $^{\circ}\text{C}$ and 1200 $^{\circ}\text{C}$ at 15 kbar. Cancrinite by itself will be yet more thermally stable. Albite will also be progressively absorbed into the silicate melt as temperature is increased in field III.

Some Crystal-Chemical and Petrologic Considerations

At first glance one might discount the possible role of nitrate groups as significant elements in the structure of silicates. The structural similarity between crystalline NaNO_3 and CaCO_3 is well known,

however; NaNO_3 is basically the calcite structure type (Wyckoff, 1920), and the effective ionic radii are similar. The nitrate scapolite can be viewed as a NO_3 -containing marialite. It has a large field of stability, and can be appropriately considered a high-pressure phase. In fact, if the unusual compositional requirements could be met in the earth, this phase could exist as a mineral in the upper mantle. We have not investigated the stability relations of nitrate or nitrate-containing scapolites or cancrinites (or sodalite-nosean minerals) in chemical environments approaching rocks of the deep crust or upper mantle. However, it is unlikely that conditions in the deep earth are sufficiently oxidizing to make nitrates stable; aside from the essential range of stability with respect to P and T , the tendency for nitrate to be reduced is very great. Only locally and under rather unusual oxidizing conditions might nitrate minerals be stable.

We have not attempted the synthesis of any other mineral species in which NO_3 might replace CO_3 , nor have we attempted to replace some rather than all of the CO_3 with NO_3 in scapolite. This matter could be of importance in consideration of CO_2 and possibly N_2 stored in or derived from the mantle or deep crust. There is no information in the literature on analyses for nitrogen in scapolite or related minerals. Wlotzka (1961) reports N as NH_3 in a variety of rocks, but found no NO_3 -nitrogen in crustal rocks except for minute amounts (5-20 g/ton) in surface sediments, some saline clays, and limestones.

Shaw (1960b) points out that although scapolite is typically a metamorphic mineral, it coexists with a wide variety of common minerals and in a large number of rock types that probably formed over a large range of P and T conditions. That it is not an even more common mineral is probably because of compositional factors: the requisite anions usually are sparingly present in quartzo-feldspathic rocks, and any water present would probably form zoisite or mica at the expense of scapolite under most crustal conditions. The large P - T field of stability of the nitrate scapolite is less surprising in light of the cosmopolitan character of the natural scapolites. It was inferred from the present work on the nitrate scapolite that its upper pressure limit is nearly coincident with the upper pressure stability limit of albite. It may well be found that this upper pressure stability limit of natural scapolites will approximate that of the feldspars. Work on the upper pressure

limits of marialite and meionite is currently under way in this laboratory.

Similarly, the nitrate cancrinite is a very refractory phase, and it is probable that the typical carbonate cancrinites are more so. Edgar (1964) states, "The stability data indicate that the common varieties of cancrinite, namely the calcium carbonate and the sodium carbonate end members, are moderately high temperature minerals. The calcium carbonate and potassium carbonate varieties are reaction products of nepheline and the appropriate carbonate." As in scapolite, the availability of anions or anionic groups may restrict the occurrence of cancrinite; otherwise it might be more common, particularly in high-temperature metamorphic rocks.

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References

- BARKER, D. S. (1964) Ammonium in alkali feldspars. *Am. Mineral.* **49**, 851-858.
- BURNHAM, C. W. (1962) Lattice constant refinement. Carnegie Inst. Wash. Year Book, **61**, 132-135.
- EDGAR, A. D. (1964) Studies on cancrinites: II—Stability fields and cell dimensions of calcium and potassium-rich cancrinites. *Can. Mineral.* **8**, 53-67.
- , AND B. J. BURLEY (1963) Studies on cancrinites: I—Polymorphism in sodium carbonate rich cancrinite-natrodavynite. *Can. Mineral.* **7**, 631-642.
- ERD, R. C., D. E. WHITE, J. J. FAHEY, AND D. E. LEE (1964) Buddingtonite, an ammonium feldspar with zeolitic water. *Am. Mineral.* **49**, 831-850.
- EUGSTER, H. P., AND J. MUNOZ (1966) Ammonium micas: possible sources of atmospheric ammonia and nitrogen. *Science*, **151**, 683-686.
- EVANS, B. W., D. M. SHAW, AND D. W. HAUGHTON (1969) Scapolite stoichiometry. *Contrib. Mineral. Petrol.* **24**, 293-305.
- FYFE, W. S., F. J. TURNER, AND J. VERHOOGEN (1958) Metamorphic reactions and metamorphic facies. *Geol. Soc. Am. Mem.* **73**, 259 p.
- GOLDSMITH, J. R., AND R. C. NEWTON (1969) P-T-X relations in the system CaCO₃-MgCO₃ at high temperatures and pressures. *Am. J. Sci., Schairer Volume*, **267-A**, 160-190.
- JOHANNES, W., AND D. PUHAN (1971) The calcite-aragonite transition, reinvestigated. *Contrib. Mineral. Petrol.* **31**, 28-38.
- KLEMENT, W., JR., AND A. JAYARAMAN (1966) Phase relations and structures of solids at high pressures. In *Progress in Solid State Chemistry*, Vol. 3, Pergamon Press, N. Y., p. 289-376.
- KOSTER VAN GROOS, A. F., AND P. J. WYLLIE (1966) Liquid immiscibility in the system Na₂O-Al₂O₃-SiO₂-CO₂ at pressures to 1 kilobar. *Am. J. Sci.* **264**, 234-255.
- LARSEN, E. S., AND H. BERMAN (1934) The microscopic determination of the nonopaque minerals. *U. S. Geol. Surv. Bull.* **848**, Washington, D. C.
- LEVIN, E. M., C. R. ROBBINS, AND H. F. MCMURDIE, Editors (1969) *Phase Diagrams for Ceramists. 1969 Supplement*. American Ceramic Society, Columbus, Ohio.
- ROBIE, R. A., AND D. R. WALDBAUM (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 bars) pressure at higher temperatures. *U. S. Geol. Surv. Bull.* **1259**, Washington, D. C.
- SCHAIERER, J. F., AND N. L. BOWEN (1956) The system Na₂O-Al₂O₃-SiO₂. *Am. J. Sci.* **254**, 129-195.
- SHAW, D. M. (1960a) The geochemistry of scapolite. Part I. Previous work and general mineralogy. *J. Petrol.* **1**, 218-260.
- (1960b) The geochemistry of scapolite. Part II. Trace elements, petrology, and general geochemistry. *J. Petrol.* **1**, 261-285.
- WLOTZKA, F. (1961) Untersuchungen zur Geochemie des Stickstoffs. *Geochim. Cosmochim. Acta.* **24**, 106-154.
- WYCKOFF, R. W. G. (1920) The crystal structure of sodium nitrate. *Phys. Rev.* **16**, 149.

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