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Silicate-Nitrate Compounds: High-Pressure Synthesis and Stability of a Nitrate Scapolite

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Abstract

The compound $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$ has been prepared from crystalline albite and molten NaNO_3 in the temperature range $600^\circ\text{--}900^\circ\text{C}$ and at pressures above 7 kbar. Well formed crystals giving sharp single-crystal diffraction spots are tetragonal, $I4/m$, have the scapolite structure, and unit cell constants $a = 12.1643 \pm 0.0008 \text{ \AA}$, $c = 7.5297 \pm 0.0011 \text{ \AA}$. Density measured by a sink-float method is 2.618 ± 0.010 , slightly greater than that calculated from the cell constants, 2.598. An IR absorption spectrogram shows a strong maximum at 7.15μ uniquely assignable to the asymmetric stretching vibration of the nitrate groups.

Some of the relevant P - T relations in a portion of the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-N}_2\text{O}_5$ were explored. At higher temperatures or at lower pressures the nitrate scapolite breaks down to albite plus nitrate melt, and at still higher temperatures the compound $3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$ (nitrate cancrinite) is formed along with a silicate melt and vapor produced by the decomposition of NaNO_3 . The cancrinite is quite refractory, persisting to temperatures near 1200°C at 15 kbar.

Although the P - T conditions for nitrate scapolite and cancrinite are such that stability in the deep crust and upper mantle is reasonable, it is unlikely that the requirement of an adequately oxidizing environment for the stability of any nitrate could be met.

Introduction

The minerals of the scapolite and the cancrinite groups are related in that they contain anionic radicals such as CO_3^{2-} , SO_4^{2-} , Cl^- in alkali and alkaline-earth aluminosilicate framework structures. For example, the idealized end-member compositions for scapolite are usually represented by $3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaCl}$ [marialite] and $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{CaCO}_3$ [meionite] (Shaw, 1960a, 1960b; Evans, Shaw, and Haughton, 1969). An idealized end-member cancrinite can be written as $3\text{NaAlSiO}_4 \cdot \text{CaCO}_3$ (Edgar, 1964). We have found no references in the literature to any aluminosilicates containing nitrate groups. The only nitrogen-containing silicates that we are aware of are ammonium-bearing feldspar (Erd *et al.*, 1964; Barker, 1964), and ammonium-bearing mica (Eugster and Munoz, 1966) in which NH_4^+ ion replaces K^+ in the structures. Little if any work on combined silicate-nitrate systems has been done, possibly because of the problem of decomposition of nitrates at moderate to high temperatures at atmospheric pressure. The 1969 supplement of the compilation of phase dia-

grams (Levin, Robbins, and McMurdie, editors) contains no references to such systems.

We have synthesized a nitrate scapolite ($3\text{NaAlSi}_3\text{O}_8 \cdot \text{NaNO}_3$) and a nitrate cancrinite ($3\text{NaAlSiO}_4 \cdot \text{NaNO}_3$) at high pressures and temperatures and have explored some of the relevant P - T relations in a portion of the system $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-N}_2\text{O}_5$.

Experimental Methods and Procedure

The starting materials for most of the runs were: (a) synthetic albite, crystallized hydrothermally at 700°C and 1 kbar H_2O pressure from a gel of the albite composition; (b) albite from Amelia Courthouse, Virginia; (c) a syngenetic K-feldspar (sanidine) from St. Peter Sandstone, Wisconsin; (d) reagent grade NaNO_3 and KNO_3 .

In several runs carnegite was used, crystallized dry at 1270°C from a gel of the composition NaAlSiO_4 .

Mixtures of the feldspars and nitrates were sealed in platinum or gold capsules, generally in the ratio of one part silicate to one part nitrate by weight.