Synthesis of Scapolite under Magmatic Conditions

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Abstract

Scapolite was synthesized from a calcite-bearing nepheline syenite in the presence of H₂O-rich and CO₂-rich aqueous vapor phases in the melting interval at pressures between 3 and 6 kbar. Electronmicroprobe analysis of a scapolite formed at about 6 kbar and 900°C in the presence of a CO₂-rich aqueous vapor phase gives a structural formula of NaCa₃Al₃Si₇O₂₄(CO₃) (CO₃ assigned arbitrarily). This formula is equivalent to 3 plagioclase (An₆₇) + 1 calcite.

A reconnaissance study of phase relations in the melting interval of a calcite-bearing nepheline syenite was carried out in conjunction with a study of melting relations of a simple nepheline syenite with H_2O and $H_2O + CO_2$ vapor phases (Millhollen, 1970, 1971). In the process of this reconnaissance study, scapolite was synthesized at relatively high temperatures and pressures in the melting interval of the calcite-bearing nepheline syenite. Other minerals synthesized in this study include cancrinite, garnet, clinopyroxene, and amphibole.

The chemical composition and norm of the calcitebearing nepheline syenite is given in Table 1. This rock is from the York River area near Bancroft, Ontario, Canada (Tilley, 1958). The mode contains albite, microcline, nepheline, biotite, minor magnetite, and considerable calcite (15.4 wt percent in the norm).

Experimental runs were made from 0.5 to 6 kbar in cold-seal and internally-heated pressure vessels. Sealed capsules (PdAg or Au) initially contained distilled water or oxalic acid, together with powdered crystalline nepheline syenite. Oxalic acid produces a vapor phase consisting of $H_2O:CO_2 = 50:50$ mole ratio under these conditions (Holloway, Burnham, and Millhollen, 1968), but some runs in this study were made with slightly dried oxalic acid that produced a vapor phase of $H_2O:CO_2 = 48:52$ mole ratio. During runs above the solidus, some calcite dissociated and some water was dissolved in the melt, so the vapor composition varied from H₂O-rich in runs with distilled water to relatively CO₂-rich in runs with oxalic acid. The solubility of CO₂ in nepheline syenite melts under these conditions is believed to be low (Millhollen, 1971).

Figure 1 shows the approximate lower limits of synthesis for scapolite in runs with a H₂O-rich vapor phase (curve c) and with a relatively CO₂-rich aqueous vapor phase (curve d). Because of the variable ratio of H₂O:CO₂ in the vapor for runs above the solidus, these curves in P-T projection compare results obtained under variable conditions and are therefore purely descriptive. Scapolite is present at temperatures and pressures above these curves, but the upper synthesis limits were not determined. Curves c and d could not be located exactly because of the difficulty in distinguishing scapolite in small amounts from calcite, which was invariably present. Therefore, scapolite may be present to somewhat lower temperatures than indicated by the dashed curves. No scapolite was identified in runs below 3 kbar.

Also shown in Figure 1 are solidus curves for the Blue Mountain nepheline syenite with nearly pure H_2O (curve a) and with $H_2O:CO_2 = 50:50$ mole ratio (curve b) (Millhollen, 1971). The solidus curves of the calcite-bearing nepheline syenite could not be located readily, but apparently lie very close to the solidus curves shown (Millhollen, 1970). Comparisons of curve a with curve c and of curve b with curve d indicate that in the presence of both H_2O -rich and CO_2 -rich aqueous vapor phases, respectively, scapolite is stable within the melting interval at relatively high pressures in this system.

An electron-microprobe analysis of scapolite formed at 900° and 6 kbar with a CO_2 -rich vapor phase (from slightly dry oxalic acid) is given in Table 1. In thin section the scapolite in this charge forms large euhedral crystals with moderate birefringence. In addition to about 7 percent scapolite, this charge

contains clinopyroxene, amphibole, calcite, and more than 50 percent glass (melt). Although some chlorine is present in the bulk rock (Table 1), the scapolite was formed in a CO₂-rich environment, so the deficiency in the scapolite analysis in Table 1 (about 3.7 percent) is probably mostly due to CO2. This analysis gives a structural formula of NaCa₃Al₅Si₇O₂₄(CO₃), with CO₃ being assigned arbitrarily. This is consistent with the conclusions of Orville (in preparation) and Evans, Shaw, and Haughton (1969) that at Ca/(Na + Ca) =0.75 substitution of CO_3 for Cl is complete. This formula is equivalent to $2(CaAl_2Si_2O_8) \cdot (NaAlSi_3O_8) \cdot$ $(CaCO_3)$ or 3 plagioclase $(An_{67}) + 1$ calcite. Orville (in preparation) indicates that natural scapolites of this composition (also called mizzonites) are very common.

It is difficult to determine the actual reaction by which scapolite is formed here. Since the plagioclase has a relatively low anorthite content (An_{13} in the norm), the reaction probably is more complex than simply plagioclase + calcite = scapolite. Also, since the scapolite is formed within the melting interval, the melt phase probably participates in the reaction. Possible reactions are

 TABLE 1. Compositions of Calcite-Bearing Nepheline Syenite

 and of Scapolite

	Chemical Analyses Nepheline			
	Syenite*	Scapolite**		rm*** of e Syenite
Si02	45.00	46.7	Or	18.73
A1203	20.58	27.8	Ab	27.62
Ti02	0.13	0.03	An Ne	4.09 26.78
Fe203	1.02	nd		
			01	2.00
FeO	0.84	0.31	Fo	(1.48)
MnO	0.10	nd	Fa	(0.52)
MgO	0.85	0.13	- 1	
CaO	9.45	17.8	11	0.25
			C	0.67
Na20	9.22	3.43	Mt	1.48
K20	3.17	0.14	H1	0.21
cī	0.13	nd	Cc	15.40
co,	6.77	nď		
6-			Total	97.23
(+)	0.81	nđ		
^H 2 ⁰ (-)	0.03	nd		
Total	98.10	96.34		

*Analysis by spectrometry and flame photometry, I.A. Kilinc, analyst; except CO_2 , H_2O^+ and H_2O^- determined by J.B. Bodkin. Iron oxides calculated using the Fe₂O₃/FeO ratio of Nockolds' (1954) average nepheline syenite.

**Electron microprobe analysis of scapolite from run (D250) at 6.0 - 6.2 kbar and 900°C with a CO₂-rich aqueous vapor phase (see text). All iron as FeO; nd = not determined.

***Weight percent.

6-(Jug4) 3-(Jug4) 3-1-0 600 700 800 900 1000 TEMPERATURE (°C)

FIG. 1. Lower synthesis limit of scapolite. Filled circles indicate scapolite present in runs with H_2O ; filled squares indicate scapolite present in runs with oxalic acid; open circles indicate scapolite absent in runs with oxalic acid. Curves a and b are solidus curves of Blue Mountain nepheline syntie with H_2O and with $H_2O + CO_2$, respectively (Millhollen, 1971). Curves c and d are approximate lower synthesis limits of scapolite in calcite-bearing nepheline synthesis limits of scapolite in cCO₂-rich aqueous vapor phases, respectively.

$$4 \operatorname{NaAlSiO}_{a \text{ hepheline}} + \operatorname{NaAlSi}_{a \text{ lbite}} O_8 + 3 \operatorname{CaCO}_{a \text{ calcite}}$$
$$= \operatorname{NaCa}_3 A_{15} \operatorname{Si}_7 O_{24} (CO_3) + 2 \operatorname{Na}_2 O_7 + 2 \operatorname{CO}_2,$$
$$\operatorname{scapolite}_{\text{scapolite}} O_8 + 3 \operatorname{CaCO}_3 = \operatorname{NaCa}_3 A_{15} \operatorname{Si}_7 O_{24} (CO_3)$$
$$\operatorname{scapolite}_{\text{scapolite}} O_8 + 3 \operatorname{CaCO}_3 = \operatorname{NaCa}_3 A_{15} \operatorname{Si}_7 O_{24} (CO_3)$$

$$+ 2 \operatorname{Na_2O}_{\text{melt}} + 8 \operatorname{SiO_2}_{\text{melt}} + 2 \operatorname{CO}_{\text{vapor}}$$

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References

- EVANS, B. W., D. M. SHAW, AND D. R. HAUGHTON (1969) Scapolite stoichiometry. *Contrib. Mineral. Petrol.* 24, 293–305.
- HOLLOWAY, J. R., C. W. BURNHAM, AND G. L. MILLHOLLEN (1968) Generation of H₂O-CO₂ mixtures for use in hydrothermal experimentation. J. Geophys. Res. 73, 6598-6600.
- MILLHOLLEN, G. L. (1970) Melting and Phase Relations in Nepheline Syenites with H_*O and $H_*O + CO_*$. Ph.D. thesis, Pennsylvania State University, University Park, Pennsylvania.

(1971) Melting of nepheline syenite with H_2O and $H_2O + CO_2$, and the effect of dilution of the aqueous phase on the beginning of melting. *Am. J. Sci.* 270, 244-254.

- NOCKOLDS, S. R. (1954) Average chemical compositions of some igneous rocks. *Geol. Soc. Am. Bull.* **65**, 1007– 1032.
- TILLEY, C. E. (1958) Problems of alkali rock genesis. Quart. J. Geol. Soc. London, 113, 323-360.
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