# Compressibility of sodalite and scapolite

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## Abstract

Equation-of-state parameters of sodalite ($Na_4Al_3Si_3O_{12}Cl$) and a meionitic scapolite (approximately $Ca_4Al_6Si_6O_{24}CO_3$) have been calculated from pressure-volume data obtained by single-crystal X-ray diffraction techniques. Linear compressibility of cubic sodalite is $6.4 \times 10^{-4}$ kbar$^{-1}$, corresponding to a bulk modulus of $0.52 \pm 0.08$ Mbar (assuming $K' = 4$). The pressure response of tetragonal scapolite is almost isotropic with compressibilities parallel and perpendicular to the $c$ axis of $3.5 \times 10^{-4}$ and $3.7 \times 10^{-4}$ kbar$^{-1}$, respectively; the bulk modulus is $0.90 \pm 0.12$ Mbar. Sodalite and scapolite compress principally by deformation of the Al-Si tetrahedral framework coupled with Na–O and Ca–O bond compression, respectively. The greater compressibility of sodalite compared to scapolite is primarily a Coulombic effect, arising from the difference in bond strength of $Na^+$–O versus $Ca^{2+}$–O bonds.

## Introduction

Sodalite and scapolite are open framework silicates that contain halides or carbonates of Na or Ca. NaCl is an essential component of sodalite ($Na_4Al_3Si_3O_{12}Cl$), whereas coupled NaCl-CaCO$_3$ and NaSi-CaAl substitutions relate end members of the scapolite solid-solution series between marialite ($Na_4Al_3Si_9O_{24}Cl$) and meionite ($Ca_4Al_6Si_6O_{24}CO_3$). The unusual "stuffed" open framework structures are of interest to crystal chemists, and the presence of NaCl and CaCO$_3$ as essential components in these silicates makes them important for petrology and geochemistry.

Sodalite exists as a primary phase in undersaturated syenites and phonolites (e.g., Deer et al., 1963). The activity of NaCl in sodalite-bearing rocks can be calculated if the thermodynamic properties of sodalite and sodalite-related phases are known (Wellman, 1970; Helffrich et al., 1986). These data could also be used to evaluate the cooling histories of sodalite-bearing meteorites (Grossman and Steele, 1976; Lumpkin, 1980) and to limit NaCl activities in sodalite-free undersaturated rocks.

Scapolite forms in a wide range of metamorphic environments (e.g., Deer et al., 1963). The CO$_3$ content of scapolite generally increases with increasing metamorphic grade. A number of scapolite-bearing assemblages found in high-grade rocks buffer CO$_2$ activities, and, as with sodalite, the lack of scapolite in certain lithologies places an upper limit on the activity of CO$_2$ in those terranes (Moecher and Essene, 1985). With accurate phase equilibria for scapolite and related minerals, petrologists can place limits on fluid compositions and evaluate processes such as CO$_2$ flooding in the lower crust (e.g., Newton et al., 1980).

The thermochemical and thermophysical properties enthalpy, low- and high-temperature heat capacity, and volume at elevated temperatures have been measured for both sodalite (N. Komada, E. F. Westrum, Jr., B. S. Hemingway, M. Y. Zolotov, Y. V. Semenov, I. L. Khodakovsky, and L. M. Anovitz, in prep.; Taylor, 1968) and scapolite (N. Komada, D. P. Moecher, E. F. Westrum, Jr., B. S. Hemingway, Y. V. Semenov, and I. L. Khodakovsky, in prep.; Graziani and Lucchesi, 1981). In this study we have made compressibility measurements for these two minerals to complete the thermodynamic database, to search for possible high-pressure phase transformations, and to evaluate inverse relationships of compressibility and expansivity for these open framework structures.

## Experimental details

**Sample description.** Sodalite was collected from a pegmatitic vein in a nepheline syenite from Mont St. Hilaire, Quebec. The sodalite crystals are milky-white dodecahedrons up to 1 cm in diameter. Composition was determined using an automated CAMECA electron microprobe at the University of Michigan operating at 10-kV accelerating voltage with a defocused beam to avoid volatilization of either Na or Cl. The composition of the sodalite is $(Na_{7.99}K_{0.01})(Al_{5.98}Fe^{3+}_{0.04}Si_{5.98})O_{23.99}(Cl_{1.96}(SO_4)_{0.02})$ (Helffrich et al., 1986).

The scapolite sample, 88 mol% meionite, was supplied by D. P. Moecher at the University of Michigan. It was found in an ejected block within a tuff from Monte Somma, Italy. The crystals are translucent, white grains less than 1 mm in diameter. The composition, determined by Moecher using the University of Michigan CAMECA electron microprobe, is $(Na_{0.34}K_{0.13}Ca_{3.48}Fe_{0.01})(Si_{6.47}Al_{5.53})O_{24.01}(Cl_{0.06}(CO_3)_{0.91}(SO_4)_{0.02})$.

**High-pressure X-ray diffraction.** Rectangular single crystals of sodalite and scapolite, approximately $60 \times 60 \times 40$ $\mu$m on edge, were selected for study in a gasketed diamond-anvil cell for X-ray diffraction. Both crystals were included in the same high-pressure mount—a procedure that facilitates comparison of bulk moduli of different materials because pressure is identical for both samples. A 4:1 methanol:ethanol mixture was used as the hydrostatic pressure medium and 10-$\mu$m chips of ruby were in-

TABLE 1. Sodalite unit-cell parameters versus pressure

| P (kbar) | a (Å) | V (Å³) | V/V₀ |
|---|---|---|---|
| 0.001 | 8.878(2)* | 699.7(4) | 1.0000 |
| 5 | 8.8509(6) | 693.4(1) | 0.9910 |
| 11 | 8.8228(6) | 686.8(1) | 0.9816 |
| 22 | 8.761(1) | 672.5(3) | 0.9611 |
| 26 | 8.7425(6) | 668.2(1) | 0.9550 |

*Note:* Numbers in parentheses represent esd's.

TABLE 2. Scapolite unit-cell parameters versus pressure

| P (kbar) | a (Å) | c (Å) | V (Å³) | V/V₀ | C/a |
|---|---|---|---|---|---|
| 0.001 | 12.191(2) | 7.575(5) | 1125.8(5) | 1.0013 | 0.6214 |
| <1* | 12.186(1) | 7.572(1) | 1124.3(3) | 1.0000 | 0.6213 |
| 5 | 12.172(1) | 7.563(1) | 1120.5(2) | 0.9966 | 0.6213 |
| 9.5 | 12.144(2) | 7.550(1) | 1113.3(3) | 0.9902 | 0.6217 |
| 11 | 12.141(1) | 7.546(1) | 1112.3(3) | 0.9893 | 0.6215 |
| 11 | 12.141(2) | 7.545(2) | 1112.1(4) | 0.9891 | 0.6215 |
| 17 | 12.113(1) | 7.530(1) | 1104.8(3) | 0.9827 | 0.6217 |
| 22 | 12.087(1) | 7.516(1) | 1098.1(3) | 0.9767 | 0.6218 |
| 25 | 12.076(2) | 7.510(3) | 1095.2(6) | 0.9741 | 0.6219 |
| 26 | 12.072(1) | 7.506(1) | 1093.9(3) | 0.9730 | 0.6218 |
| 30 | 12.060(4) | 7.498(6) | 1090.6(10) | 0.9700 | 0.6217 |
| 41 | 12.013(2) | 7.463(2) | 1077.1(4) | 0.9580 | 0.6212 |

* The presence of a tiny compressed air bubble in the sample chamber indicated that the pressure in the diamond cell was significantly less than 1 kbar, though more than 1 bar.

cluded for pressure calibration. Details of diamond-cell design, crystal mounting, pressure measurements, and cell operation are given in Hazen and Finger (1982).

The unit-cell parameters of cubic sodalite and tetragonal scapolite were determined from reflections measured on an automated four-circle diffractometer with Zr-filtered Mo radiation. Each reflection was centered in eight equivalent positions after the method of King and Finger (1979). Sodalite was measured at five pressures between 1 bar and 26 kbar; eight reflections with $32° < 2\theta < 35°$ were used in the cell determination. The sodalite crystal deteriorated irreversibly when pressure was increased to above 30 kbar. This effect might have resulted from crushing between the diamond anvils, but the gasket was significantly thicker than the crystal at the time of the change. We suspect that the sodalite experienced a reconstructive transition to an unknown high-pressure form. Scapolite was measured at twelve pressures between 1 bar and 41 kbar; as many as 16 reflections with $28° < 2\theta < 33°$ were used for cell-parameter determination.

Unit-cell dimensions for both phases were refined initially without constraint (i.e., as triclinic). No significant deviations from ideal cubic and tetragonal dimensionality for sodalite and scapolite, respectively, were observed at any pressure. Final reported cell constants (Tables 1 and 2) were refined with appropriate symmetry constraints. Pressure-volume data were fit by least-squares procedures to a first-order Birch-Murnaghan equation of state based on an assumed value of 4 for the pressure derivative of the bulk modulus, $K'$ (see, e.g., Hazen and Finger, 1982).

## RESULTS AND DISCUSSION

**Sodalite compressibility.** Cubic sodalite experienced a 4.5% volume decrease between 1 bar and 26 kbar, corresponding to a bulk modulus of 0.52 ± 0.08 Mbar. Linear compressibility is 6.4 ± 0.3 × 10⁻⁴ kbar⁻¹. No discontinuities in the pressure-volume relation were observed, and the material retained cubic dimensionality with no peak broadening or deterioration of diffraction intensity to 26 kbar. It appears, therefore, that below 26 kbar, Mont St. Hilaire sodalite does not undergo a reversible "polyhedral tilt" phase transition that is typical of several other high-symmetry, Na-bearing framework silicates, including alkali feldspar (Hazen, 1976), carnegieite (Cohen and Klement, 1976), analcime (Hazen and Finger, 1979), and zeolite 4A (Hazen and Finger, 1984).

**Scapolite compressibility.** Ca-rich Monte Somma scapolite undergoes a 4.2% volume decrease between 1 bar and 41 kbar. Scapolite bulk modulus is 0.90 ± 0.12 Mbar, and the pressure response is essentially isotropic with compressibilities of 3.5 ± 0.1 × 10⁻⁴ parallel and 3.7 ± 0.1 × 10⁻⁴ kbar⁻¹ perpendicular to the tetragonal c axis.

There were no detectable discontinuities in the pressure-volume data, and scapolite remains tetragonal throughout the range from 1 bar to 41 kbar. The c/a axial ratio remains constant at approximately 0.6215, reflecting the isotropic compressibility of the phase.

**Compression mechanisms.** Hazen and Finger (1982, 1985) demonstrated that the principal compression mechanism in most framework silicates is T–O–T bond bending (i.e., framework distortion) coupled with compression of alkali–oxygen and alkaline earth–oxygen bonds. Cation–oxygen bond compression was shown to be primarily a Coulombic effect: bond compression is inversely proportional to cation charge. Thus, while individual framework-forming tetrahedra are relatively rigid, the large monovalent and divalent cation sites typical of feldspars, feldspathoids, zeolites, and other framework aluminosilicates display significant compression.

Sodalite and scapolite conform to this model. The ratio of average large-cation charges is 1.00:1.88—almost identical to the ratio of bulk moduli, 0.50:0.92. Furthermore, the 0.5-Mbar compressibility of sodalite is similar to that of other Na-bearing framework silicates such as nepheline (0.50 Mbar; Yoder and Weir, 1951), analcime (0.45 Mbar; Hazen and Finger, 1979), and albite (0.70 Mbar; Angel et al., 1988), whereas the 0.92 bulk moduli of calcic scapolite is close to that of anorthite (0.94 Mbar; Angel et al., 1988).

## CONCLUSIONS

The high-pressure behaviors of sodalite and scapolite are similar to those of many other framework silicates. Pressure-volume data from this study suggest that individual Si and Al tetrahedra undergo little compression or other deformation, while T–O–T angles change in response to compression of Na–O or Ca–O bonds. It has been shown from previous studies that Na–O bonds are almost twice as compressible as Ca–O bonds—principally a Coulombic effect. It is important to remember, therefore, that the equation-of-state parameters reported here apply only to the alkali and alkaline-earth cation compositions of these specific samples. Changes in the ratio

of monovalent to divalent cations will have a dramatic effect on the compressibilities of these phases. End members of solid-solution series related by the coupled substitution $NaSi \rightleftharpoons CaAl$, including the scapolites marialite-meionite, the plagioclases albite-anorthite, and a number of feldspathoid and zeolite structure types, are expected to display bulk moduli that differ by almost a factor of two across the complete compositional series.

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