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The crystal structure of the meteoritic mineral krinovite, $NaMg_2CrSi_3O_{10}$

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Abstract. Krinovite, a meteoritic silicate mineral with ideal crystal chemical formula $Na_2Mg_4Cr_2[Si_6O_{18}]O_2$, is triclinic, space group $P\bar{1}$, with a = 10.238(4), b = 10.642(4), c = 8.780(3) Å, α = 105.15(3)°, β = 96.50(4)°, γ = 125.15(3)°. The crystal structure of krinovite has been refined to $R = 0.065$, $R_w = 0.067$ for 1661 independent reflections. Krinovite is a member of the aenigmatite group, and is characterized by octahedral walls connected through tetrahedral chains with appendices and additional insular octahedra.

Introduction

Krinovite is an uncommon meteoritic silicate mineral. Occurrences of krinovite in meteorites from Canyon Diablo and Wichita County, USA, and from Youndegin, Australia, were reported by Olsen and Fuchs (1968). According to them, krinovite is produced by the reaction:

$$\begin{array}{lcl} NaCrSi_2O_6 & + Mg_2SiO_4 = & NaMg_2CrSi_3O_{10} \\ \text{kosmochlor}^{1} & + \text{ forsterite } = & \text{krinovite}\,. \end{array}$$

It has been actually found associated with either of these minerals in Canyon Diablo and Wichita County, respectively.

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[1] The IMA Commission on New Minerals and Mineral Names (Nickel, Mandarino, 1987) adopted for the clinopyroxene of composition $NaCrSi_2O_6$ the name kosmochlor; Olsen and Fuchs (1968) refer to kosmochlor using the name ureyite, now discredited.

Later Merlino (1972) stressed the chemical relationships between krinovite and aenigmatite, which is triclinic with marked pseudomonoclinic symmetry (Merlino, 1970; Cannillo, Mazzi, Fang, Robinson, Ohya, 1971), established a triclinic unit cell for krinovite analogous in orientation to that of aenigmatite, and hypothesized close structural relationships between these two minerals.

The only available chemical analysis for krinovite is for a sample from Canyon Diablo (Olsen, Fuchs, 1968), and indicates the chemical formula $NaMg_2CrSi_3O_{10}$, with minor substitution of iron for magnesium.

Experimental

Among various crystals tested by Weissenberg and rotation photographs, a very small crystal (dimensions *ca.* 0.1 × 0.1 × 0.1 mm) of krinovite from Wichita County was found which appeared unaffected by twinning. The intensity data were collected with an *Ital Structures* four-circle automatic diffractometer, using graphite monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å). The following unit cell parameters were obtained through least-squares fit of 2ϑ values of 26 reflections ($25^\circ < 2\vartheta < 30^\circ$): $a = 10.238(4)$, $b = 10.642(4)$, $c = 8.780(3)$ Å, $\alpha = 105.15(3)^\circ$, $\beta = 96.50(4)^\circ$, $\gamma = 125.15(3)^\circ$. 1661 unique reflections out of those measured ($2\vartheta_{max} = 55^\circ$) were considered observed having $I > 3\sigma(I)$, and were used in the least-squares calculations after reduction for Lorentz and polarization factors. The structure refinement started using the fractional coordinates of aenigmatite given by Cannillo et al. (1971); the SHELX76 least-squares program (Sheldrick, 1976) was employed. Isotropic refinement converged to R = 0.095. An empirical correction for the absorption effects was then carried out, using the DIFABS program by Walker and Stuart (1983). After the absorption correction (correction factors on F in the range 0.83 – 1.19), the reliability indices dropped to $R = 0.065$, $R_w = 0.067$ ($w = 1/[\sigma^2(F_o) + 0.0025(F_o)^2]$) for all the observed reflections, using isotropic thermal parameters. A further refinement with anisotropic thermal parameters for the cations only has been tried: the improvement was not significant according to the Hamilton test computed on RG values (Hamilton, 1965). A list of observed and calculated structure factors has been deposited[2].

Description of the structure

The final positional and thermal parameters are listed in Table 1, whereas bond distances are reported in Table 2. The refinement confirmed that

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[2] Additional material to this paper can be ordered from the Fachinformationszentrum Energie-Physik-Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 53800, the names of the authors and the title of the paper.

Table 1. Refined cation occupancies, fractional coordinates and isotropic U thermal parameters $(\text{Å})^2$ for krinovite. The temperature factor expression used was $\exp(-8\pi^2 U \sin^2\vartheta/\lambda^2)$.

Site	Cation occupancy	*x*	*y*	*z*	*U*
M1	Cr	0.0	0.0	0.5	0.0063(6)
M2	Cr	0.0	0.5	0.0	0.0071(6)
M3	92% Mg – 8% Fe	0.3132(5)	0.8508(5)	0.1787(5)	0.0049(13)
M4	94% Mg – 6% Fe	0.7716(5)	0.8201(5)	0.1500(5)	0.0067(14)
M5	96% Mg – 4% Fe	0.0933(5)	0.9381(5)	0.0600(5)	0.0049(14)
M6	98% Mg – 2% Fe	0.5957(5)	0.9410(5)	0.0615(5)	0.0039(14)
M7	Cr	0.9943(3)	0.7380(3)	0.2629(3)	0.0052(4)
M8	Na	0.2093(7)	0.6300(6)	0.3901(6)	0.0126(11)
M9	Na	0.6605(6)	0.6116(6)	0.3737(6)	0.0118(11)
T1	Si	0.4759(4)	0.2339(4)	0.3334(4)	0.0030(7)
T2	Si	0.9820(4)	0.2297(4)	0.3399(4)	0.0021(6)
T3	Si	0.7877(4)	0.3370(4)	0.2369(4)	0.0028(6)
T4	Si	0.2770(4)	0.3393(4)	0.2236(4)	0.0047(7)
T5	Si	0.6475(4)	0.9479(4)	0.4408(4)	0.0040(7)
T6	Si	0.3555(4)	0.5609(4)	0.0453(4)	0.0038(7)
O1		0.3542(11)	0.0661(10)	0.1665(11)	0.0062(17)
O2		0.8541(10)	0.0633(10)	0.1693(10)	0.0023(16)
O3		0.5555(11)	0.9570(10)	0.2892(10)	0.0050(17)
O4		0.0180(10)	0.9331(10)	0.2751(10)	0.0042(17)
O5		0.2411(11)	0.8752(10)	0.3942(11)	0.0051(17)
O6		0.7576(11)	0.8868(10)	0.3875(10)	0.0033(17)
O7		0.4957(11)	0.1983(10)	0.4997(10)	0.0054(17)
O8		0.9582(11)	0.7855(10)	0.4917(10)	0.0036(17)
O9		0.8928(10)	0.3179(10)	0.3729(10)	0.0055(17)
O10		0.4042(11)	0.3385(11)	0.3553(11)	0.0080(18)
O11		0.6572(11)	0.1691(10)	0.0665(10)	0.0059(18)
O12		0.1544(10)	0.1664(10)	0.0614(10)	0.0044(17)
O13		0.5297(11)	0.7132(10)	0.0338(10)	0.0036(17)
O14		0.0590(10)	0.7238(10)	0.0671(10)	0.0032(16)
O15		0.2436(11)	0.6122(11)	0.1103(11)	0.0050(18)
O16		0.7501(11)	0.6058(11)	0.1319(11)	0.0050(17)
O17		0.4012(11)	0.5035(10)	0.1899(10)	0.0054(17)
O18		0.9364(11)	0.5062(10)	0.2147(11)	0.0056(17)
O19		0.1623(10)	0.3663(10)	0.3180(10)	0.0059(17)
O20		0.6708(10)	0.3640(10)	0.3339(10)	0.0061(17)

krinovite is isostructural with aenigmatite, as already shown for serendibite (Buerger, Venkatakrishnan, 1974) and for sapphirine-1A[3] (Merlino, 1980). The structure of krinovite is characterized by walls formed by $[MgO_6]$ and $[CrO_6]$ octahedra, and by a distorted $[NaO_8]$ square antiprism. Such walls are connected through open branched vierer single chains, according to the

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[3] The use of the suffix A (for anorthic) to indicate triclinic polytypes has been recommended (Nickel, Mandarino, 1987). Merlino (1980) used the suffix Tc.

Table 2. Bond distances (Å) for krinovite.

M1–O4	1.984(9)	M2–O14	1.978(11)	M3–O1	2.114(13)
M1–O6	1.992(10)	M2–O15	2.001(10)	M3–O3	2.007(11)
M1–O8	2.045(12)	M2–O18	2.060(10)	M3–O5	2.115(12)
Average	2.007	Average	2.013	M3–O11	2.181(10)
				M3–O14	2.059(10)
				M3–O15	2.083(13)
				Average	2.093
M4–O2	2.159(12)	M5–O1	2.108(11)	M6–O1	2.115(11)
M4–O4	2.051(10)	M5–O2	2.141(10)	M6–O2	2.101(10)
M4–O6	2.070(10)	M5–O4	2.121(11)	M6–O3	2.070(10)
M4–O12	2.091(11)	M5–O12	2.080(11)	M6–O11	2.114(13)
M4–O13	2.011(11)	M5–O12	2.128(13)	M6–O11	2.121(11)
M4–O16	2.121(15)	M5–O14	2.118(13)	M6–O13	2.040(13)
Average	2.084	Average	2.116	Average	2.093
M7–O4	1.918(12)	M8–O5	2.426(14)	M9–O6	2.453(13)
M7–O5	2.014(10)	M8–O7	2.336(11)	M9–O8	2.361(10)
M7–O8	2.069(10)	M8–O9	2.507(12)	M9–O10	2.497(10)
M7–O14	1.912(10)	M8–O9	2.965(9)	M9–O10	2.546(12)
M7–O16	2.002(10)	M8–O15	2.495(12)	M9–O16	2.406(12)
M7–O18	2.081(12)	M8–O18	2.375(12)	M9–O17	2.349(12)
Average	1.999	M8–O19	2.440(14)	M9–O19	2.956(12)
		M8–O20	2.557(12)	M9–O20	2.631(14)
		Average	2.513	Average	2.525
T1–O1	1.596(7)	T2–O2	1.611(7)	T3–O9	1.647(12)
T1–O7	1.621(11)	T2–O8	1.619(11)	T3–O11	1.618(7)
T1–O10	1.636(15)	T2–O9	1.644(14)	T3–O18	1.641(9)
T1–O20	1.647(9)	T2–O19	1.651(9)	T3–O20	1.655(12)
Average	1.625	Average	1.629	Average	1.640
T4–O10	1.646(13)	T5–O3	1.599(12)	T6–O13	1.617(9)
T4–O12	1.599(7)	T5–O5	1.635(8)	T6–O15	1.625(14)
T4–O17	1.598(10)	T5–O6	1.648(14)	T6–O16	1.645(8)
T4–O19	1.623(12)	T5–O7	1.678(10)	T6–O17	1.675(12)
Average	1.616	Average	1.640	Average	1.640

definition of Liebau (1985), first found by Moore (1969) in the crystal structure of sapphirine-2M. Additional chromium cations fill octahedral cavities between the walls.

The average M–O distances confirm that chromium is located in M1, M2 and M7 sites; M1 and M2 are the "interlayer" octahedra between adjacent octahedral walls, where the term "octahedral wall" is retained for the sake of simplicity, although the sodium cations within the walls (M8 and M9 sites) reach eightfold coordination. As the chemical data for krinovite from Canyon Diablo indicate a minor substitution of iron for magnesium, the occupancies in the M3, M4, M5 and M6 sites were refined. The results are reported in Table 1 and correspond to an average occupancy of 95% Mg and 5% Fe.

The mean cation–oxygen distances in polyhedra (Cr–O 2.006 Å, Mg–O 2.097 Å, Na–O 2.519 Å) compare well with the values calculated on the basis of the effective ionic radii given by Shannon and Prewitt (1969) and revised by Shannon (1976), which are 1.995, 2.10 and 2.50 Å respectively.

As regards the mean Si–O distances within the tetrahedra, the range between them (1.616 – 1.640 Å) could seem anomalously wide. However, if we couple the tetrahedra according to their connectedness, we have the following average values: T1 1.625 and T4 1.616 Å (connectedness 3), T2 1.629 and T3 1.640 Å (connectedness 2), T5 1.640 and T6 1.640 Å (connectedness 1). Within each of these groups the differences are lower; moreover, the shortest average T–O distances correspond to the tetrahedra with greatest connectedness, and *vice versa*, as to be expected.

Among the structures of the various natural phases in the aenigmatite group of minerals, those of rhönite (Walenta, 1969) and welshite (Moore, 1978) have not been refined to date; in order to get a deeper knowledge of the behaviour of the aenigmatite framework with different chemical compositions, a complete structural study of rhönite and welshite deserves consideration.

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References

Buerger, M., Venkatakrishnan, V.: Serendibite, a complicated, new, inorganic crystal structure. Proc. Nat. Acad. Sci. USA **71** (1974) 4348–4351.

Cannillo, E., Mazzi, F., Fang, J. H., Robinson, P. D., Ohya, Y.: The crystal structure of aenigmatite. Am. Mineral. **56** (1971) 427–446.

Hamilton, W. C.: Significance tests on the crystallographic R factors. Acta Crystallogr. **18** (1965) 502–510.

Liebau, F.: *Structural Chemistry of Silicates*, p. 347. Berlin: Springer-Verlag 1985.

Merlino, S.: Crystal structure of aenigmatite. Chem. Commun. **20** (1970) 1288–1289.

Merlino, S.: X-ray crystallography of krinovite. Z. Kristallogr. **136** (1972) 81–88.

Merlino, S.: Crystal structure of sapphirine-1Tc. Z. Kristallogr. **151** (1980) 91–100.

Moore, P. B.: The crystal structure of sapphirine. Am. Mineral. **54** (1969) 31–49.

Moore, P. B.: Welshite, $Ca_2Mg_4Fe^{3+}Sb^{5+}O_2Si_4Be_2O_{18}$, a new member of the aenigmatite group. Mineral. Mag. **42** (1978) 129–132.

Nickel, E. H., Mandarino, J. A.: Procedures involving the IMA Commission on New Minerals and Mineral Names and guidelines on mineral nomenclature. Am. Mineral. **72** (1987) 1031–1042.

Olsen, E., Fuchs, L.: Krinovite, $NaMg_2CrSi_3O_{10}$: a new meteorite mineral. Science **161** (1968) 786–787.

Shannon, R. D.: Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. **A32** (1976) 751–767.

Shannon, R. D., Prewitt, C. T.: Effective ionic radii in oxides and fluorides. Acta Crystallogr. **B25** (1969) 925–946.

Sheldrick, G. M.: SHELX. *Program for Crystal Structure Determination*. Univ. of Cambridge, England 1976.

Walenta, K.: Zur Kristallographie des Rhönits. Z. Kristallogr. **130** (1969) 214–230.

Walker, N., Stuart, D.: An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. **A39** (1983) 158–166.