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Cation partitioning in an unusual strontian potassicrichterite from Siberia: Rietveld structure refinement and Mössbauer spectroscopy

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ABSTRACT

The crystal structure of strontian potassicrichterite ($\text{Mg}_{4.871}\text{Fe}_{0.126}^{3+}\text{Mn}_{0.052}\text{Si}_{8.048}\text{O}_{22}(\text{OH})_{2.15}(\text{Na}_{1.425}\text{Ca}_{0.348}\text{Sr}_{0.297})_{\Sigma 2.07}\text{K}_{0.873}$) – an unusual amphibole containing up to 3.7 wt.% SrO from the Murun alkaline massif, Eastern Siberia has been refined from X-ray powder diffraction data in monoclinic space group $C2/m$, with $a = 10.0325(1) \text{ \AA}$, $b = 17.977(1) \text{ \AA}$, $c = 5.2698(1) \text{ \AA}$, and $\beta = 104.70(1)^\circ$. According to Mössbauer spectroscopy, nearly all iron occurs as Fe^{3+} in octahedral coordination. Rietveld refinement shows the Fe^{3+} to be ordered onto the $M(2)$ site. Sr is completely ordered onto $M(4)$.

KEYWORDS: richterite, amphibole, crystal structure, Rietveld refinement, Mössbauer spectroscopy, Murun alkaline massif, Siberia.

Introduction

AN unusual amphibole containing up to 3.7 wt.% SrO was found in the Murun alkaline massif, Eastern Siberia. Usually, the maximum content of SrO in natural amphiboles does not exceed 0.15 wt.%. Oberti *et al.* (1992) studied the behaviour of Ti in amphiboles and presented structural data for six richterites, none of which contained Sr. On the other hand, Robert *et al.* (1993) investigated synthetic Sr-rich K-rich richterites and established that, for these, Sr orders onto the $M(4)$ site.

Sample description

The sample studied here occurs in a blue jade, containing up to 1% feldspar, which was formed

metasomatically at the magmatic stage of grorudite (alkaline granite) development (Konev, 1996). Strontium-rich amphibole occurs as entangled, fibrous, jade-like masses of bright to pale-blue coloured crystals (Fig. 1), sometimes of gemstone quality (the mineral is available through dealers under the unofficial name dianaite). The chemical composition of the mineral varies significantly. We studied a bright-blue variety of Sr-rich amphibole with a composition determined from electron microprobe (wt.%), of SiO_2 57.48, Fe_2O_3 1.19, MnO 0.44, MgO 23.34, CaO 2.32, SrO 3.66, Na_2O 5.25, K_2O 4.89, H_2O 2.30; total 100.87. Assuming 23 oxygens, this corresponds to a chemical formula of $(\text{Mg}_{4.871}\text{Fe}_{0.126}^{3+}\text{Mn}_{0.052})_{\Sigma 5.049}(\text{Na}_{1.425}\text{Ca}_{0.348}\text{Sr}_{0.297})_{\Sigma 2.07}\text{K}_{0.873}\text{Si}_{8.048}\text{O}_{22}(\text{OH})_{2.15}$ (Konev *et al.*, 1988). We analysed for Al_2O_3 and TiO_2 but they were not detected. FeO was absent.

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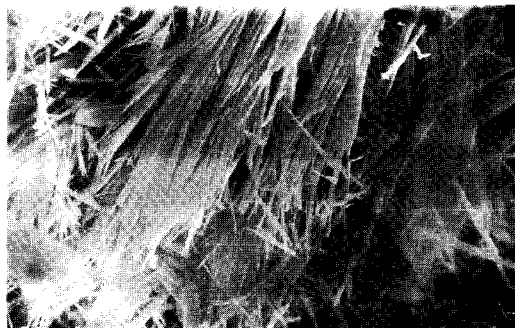


FIG. 1. SEM image of blue jade or strontian potassicrichterite fibrous crystals (magnification $\times 790$).

Experimental details

Powder diffraction

Powder diffraction data were collected according to the procedure described by Wölfel (1981) on a focusing STOE-STADIP diffractometer, equipped with a curved Ge (111) primary monochromator

TABLE 1. Crystallographic data for strontian potassicrichterite

Cell parameters:	
a (Å)	10.0325(1)
b (Å)	17.976(1)
c (Å)	5.2698(1)
β (°)	104.70(1)
V (Å ³)	919.3(4)
Z	2
Space group	$C2/m$
$D_{\text{calc.}}$ (g/cm ³)	3.04
2θ (°)-range	3–42.9
Asymmetry, 2θ (°)	<40
Bragg reflections	594
Refined parameters	66
R_p	3.35
R_{wp}	4.41
R_{exp}	3.21
R_B	5.01
R_F	4.19
s^*	1.35
DWD^{**}	0.69
σ_x^{***}	1.35

* $s = R_{\text{wp}}/R_{\text{exp}}$, R_{exp} : expected value of R_{wp} ,

** DWD : Durbin-Watson d statistics (Hill and Flack, 1987)

*** σ_x : a multiplier for the ESDs (Bérar and Lelann, 1991)

producing monochromatic Mo- $K\alpha_1$ radiation ($\lambda = 0.70926$ Å) with a minimum full width at half maximum (FWHM) of 0.08° . The sample was placed in a quartz capillary, which was rotated to minimize preferred orientation. The diffraction pattern was collected in a stepwise overlapping mode with a linear position sensitive detector, which had about 5° acceptance angle and 0.02° wide channels (Wölfel, 1983) giving 2000 data points in the range $3^\circ < 2\theta < 42.9^\circ$.

Rietveld structure refinement

Rietveld refinement was performed using the program Wyriet, version 3.3 (Schneider, 1989). Ionic scattering factors and a Pearson VII profile function were used. The atomic coordinates of Sr-free potassicrichterite from Robert *et al.* (1993) were used as the starting model. The site occupancies of the A - and M -sites were assigned in accordance with the microprobe data. We did not take into account the minor Mn^{2+} content. Cell parameters, pattern parameters and agreement indices from the Rietveld analysis are given in Table 1. Atomic coordinates and isotropic displacement factors are given in Table 2 and selected inter-atomic distances are listed in Table 3.

Mössbauer spectroscopy

The sample of strontian potassicrichterite was gently ground in an agate mortar with acetone. A quantity of 137 mg of powder was mounted in a 12 mm diameter plexiglass sample-holder, giving an effective sample thicknesses of 1 mg Fe/cm^2 , close to the ideal sample thickness for this composition (Long *et al.*, 1983). Samples were run at room temperature (293 K) on a conventional transmission Mössbauer spectrometer.

Data were fitted to one Lorentzian doublet (components constrained to equal widths and areas) which was sufficient to account for all absorption (Fig. 2). The isomer shift was $0.38(1) \text{ mm/s}$ (relative to $\alpha\text{-Fe}$), the quadrupole splitting was $0.67(1) \text{ mm/s}$ and the FWHM was $0.78(2) \text{ mm/s}$.

Optical spectroscopy

We also collected an optical spectrum of strontian potassicrichterite using an SF-16 spectrometer. The fibrous nature of the crystals (Fig. 1), however, made it difficult to prepare a good

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TABLE 2. Atomic coordinates and isotropic displacement factors for strontian potassicrichterite

Site	Occupancy*	x	y	z	$B_{\text{iso.}} (\text{\AA}^2)$
T(1)	1.0(1)Si	0.274(2)	0.088(6)	0.3001(2)	1.3(3)
T(2)	1.0(1)Si	0.285(2)	0.1712(6)	0.8028(2)	1.2(3)
M(1)	1.0(1)Mg	0	0.090(1)	0.5	1.3(5)
M(2)	0.92(1)Mg+0.08(1)Fe ³⁺	0	0.1802(9)	0	1.0(5)
M(3)	1.0(1)Mg	0	0	0	0.8(7)
M(4)	0.68(2)Na+0.18(1)Ca+0.14(1)Sr	0	0.2795(7)	0.5	1.6(4)
A	0.92(1)K+0.08(1) Na	0	0.5	0	1.7(6)
O(1)		0.1107(2)	0.088(1)	0.2153(4)	0.9(7)
O(2)		0.1154(2)	0.172(1)	0.7143(4)	1.4(7)
O(3)		0.1066(4)	0	0.7190(5)	0.6(9)
O(4)		0.3594(4)	0.2486(1)	0.7954(5)	1.0(7)
O(5)		0.3324(4)	0.128(1)	0.0934(5)	1.1(5)
O(6)		0.3364(4)	0.117(1)	0.6053(5)	1.7(5)
O(7)		0.3292(4)	0	0.3085(5)	1.3(9)

* this column is blank if site is fully occupied by atom specified in the label

sample, and the optical spectrum that we obtained was not well resolved. It showed only one broad band near 585 nm.

Results and discussion

The Rietveld refinement and Mössbauer spectroscopy results give the following crystal chemical formula:

$(\text{K}_{0.92}\text{Na}_{0.08})_{\Sigma 1.00}(\text{Na}_{1.36}\text{Ca}_{0.36}\text{Sr}_{0.28})_{\Sigma 2.00}\text{Mg}_3(\text{Mg}_{1.84}\text{Fe}_{0.16})_{\Sigma 2.00}\text{Si}_8\text{O}_{22}(\text{OH},\text{F})_2$, $Z = 2$, space group $C2/m$, $D_{\text{calc.}} = 3.04 \text{ g/cm}^3$, $D_{\text{meas.}} = 3.00(1) \text{ g/cm}^3$.

In accordance with Leake *et al.* (1997), this mineral is termed potassicrichterite. Strontium is completely ordered onto the M(4) site which comprises $\text{Na}_{0.68}\text{Ca}_{0.18}\text{Sr}_{0.14}$ (Table 2). The A site is occupied by K and Na, and Mg resides predominantly on the M(1–3) sites of the octahedral chain. The average interatomic distances for TO_4 , MO_6 , and AO_8 polyhedra are in good agreement with the corresponding average interatomic distances for Robert's sample 'KSr_o' (Robert *et al.*, 1993).

We compared the interatomic distances in this strontian potassicrichterite structure with those of

TABLE 3. Selected interatomic distances (Å) in strontian potassicrichterite

T(1)–O(1)	1.584(1)	M(2)–O(1)x2	2.149(2)
T(1)–O(5)	1.562(2)	M(2)–O(2)x2	2.125(1)
T(1)–O(6)	1.667(1)	M(2)–O(4)x2	2.005(2)
T(1)–O(7)	1.638(3)	<M(2)–O>	2.093
<T(1)–O>	1.613	M(3)–O(1)x4	2.096(2)
T(2)–O(2)	1.647(1)	M(3)–O(3)x2	2.035(1)
T(2)–O(4)	1.584(2)	<M(3)–O>	2.076
T(2)–O(5)	1.672(1)	M(4)–O(2)x2	2.390(2)
T(2)–O(6)	1.606(2)	M(4)–O(4)x2	2.405(1)
<T(2)–O>	1.627	M(4)–O(5)x2	2.887(2)
M(1)–O(1)x2	2.081(1)	M(4)–O(6)x2	2.636(2)
M(1)–O(2)x2	2.030(2)	<M(4)–O>	2.580
M(1)–O(3)x2	2.109(2)		
<M(1)–O>	2.073		

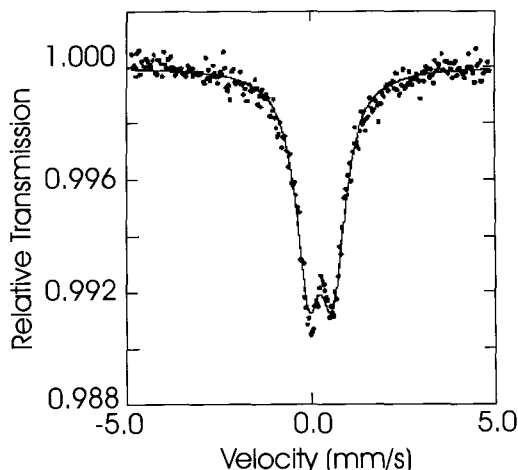


FIG. 2. Room-temperature Mössbauer spectrum of strontian potassicrichterite.

a K-richterite from W. Kimberley, Australia (Oberti *et al.*, 1992). Richterite from W. Kimberley is characterized by a chemical formula of $(\text{Ti}_{0.03}\text{Mg}_{4.981})_{\Sigma 5.011}(\text{Ca}_{1.053}\text{Na}_{0.919})_{\Sigma 1.972}\text{K}_{0.969}(\text{Si}_{7.565}\text{Al}_{0.077}\text{Ti}_{0.358})_{\Sigma 8.00}\text{O}_{22}(\text{OH})_2$. The cell parameters ($a = 10.028 \text{ \AA}$, $b = 18.039 \text{ \AA}$, $c = 5.289 \text{ \AA}$, $\beta = 105.0^\circ$) are nearly identical to those of our sample. The presence of Al^{3+} in the T sites in potassicrichterite results in $\langle\text{Si}-\text{O}\rangle$ bond lengths of 1.624 \AA for Si(1) and 1.648 \AA for Si(2), which are longer than the corresponding values for strontian potassicrichterite (1.613 \AA and 1.627 \AA respectively). The $\langle M-\text{O}\rangle$ bond lengths are comparable within experimental error for strontian potassicrichterite and the K-richterite from W. Kimberly. The presence of about 8% of Fe^{3+} on the $M(2)$ site does not influence the length of $\langle M(2)-\text{O}\rangle$: 2.093 \AA (our sample) and 2.094 \AA (Oberti *et al.*, 1992). Based on values of effective ionic radii (Shannon, 1976), the radius of a 'mixed' cation ($0.92\text{Mg} + 0.08\text{Fe}^{3+}$) on the $M(2)$ site of strontian potassicrichterite is 0.713 \AA . For fluor-richterites, Hawthorne (1983) reported that the reason for the smaller $\langle M(3)-\text{O}\rangle$ bond lengths associated with the larger constituent-cation radius was unclear. In the crystal structure of strontian K-richterite the constituent-cation radius is smaller than the ionic radius of 6-coordinated Mg^{2+} (0.720 \AA), but the $\langle M(2)-\text{O}\rangle$ distances are the same for two minerals. The reason for this difference is also unclear. The mean $\langle A-\text{O}\rangle$ distance in natural

strontian potassicrichterite is 2.580 \AA , while the value for K-richterite is 2.565 \AA (Oberti *et al.*, 1992). This increase in bond length results not from the presence of 14% of Sr^{2+} (8-coordinated, $r = 1.26 \text{ \AA}$), but mainly from the large amount of Na^+ (8-coordination, $r = 1.18 \text{ \AA}$) compared to Ca^{2+} ($r = 1.12 \text{ \AA}$).

The Mössbauer spectrum of strontian potassicrichterite consists almost entirely of a single doublet, which from the centre shift value is assigned to Fe^{3+} in octahedral co-ordination. Comparison of hyperfine parameters with those for other sodic amphiboles (e.g. Ernst and Wai, 1970) suggests that Fe^{3+} resides primarily on the $M(2)$ site. Trial fits with doublets having larger quadrupole splitting (corresponding to Fe^{3+} in $M(1)$ and $M(3)$ sites) were unsuccessful, suggesting that the large line-widths of the Fe^{3+} doublet are due to variations in next-nearest neighbour environment of the $M(2)$ site. In the structure, the $M(2)$ octahedron shares edges with two $M(4)$ octahedra, which can be filled with either Na^+ , Ca^{2+} or Sr^{2+} . The differences in charge and cation size are probably sufficient to produce a distribution in hyperfine parameters, and hence cause the observed line broadening.

We consider the bright-blue colour of strontian potassicrichterite to result from charge transfer between Fe^{3+} and Fe^{2+} . As charge transfer bands are generally intense, only small numbers of Fe^{2+} - Fe^{3+} pairs are required to produce an observable colour. These amounts are below the detection limit of Mössbauer spectroscopy (estimated to be 2–3% for the spectrum of strontian potassicrichterite). The broad band near 585 nm, registered in the optical spectrum, is consistent with the presence of Fe^{2+} - Fe^{3+} charge transfer, falling as it does within the range observed for Fe^{2+} - Fe^{3+} charge transfer in other minerals (Burns, 1993).

Conclusions

In conclusion, refinement of the crystal structure of strontian potassicrichterite from X-ray powder diffraction data has revealed that ordering of Sr atoms occurs onto the $M(4)$ site of this structure. Furthermore, nearly all iron occurs as Fe^{3+} in octahedral coordination, whereas Fe^{3+} appears primarily to occupy the $M(2)$ site.

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