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Crystal structure of rasvumite, KFe_2S_3

JOAN R. CLARK

U.S. Geological Survey
345 Middlefield Road
Menlo Park, California 94025

AND GORDON E. BROWN, JR.

Department of Geology, Stanford University
Stanford, California 94305

Abstract

Rasvumite, KFe_2S_3, isostructural with $BaFe_2S_3$ described by Hong and Steinfink (1972), is orthorhombic, *Cmcm*, $a = 9.049(6)$, $b = 11.019(7)$, $c = 5.431(4)$Å, $V = 541.5$Å^3, Z = 4, density (calc) = 3.029 g cm^{-3}. Least-squares refinement of 332 single-crystal *hkl* reduced the conventional residual to 0.081. The structure contains double edge-sharing chains of Fe–S tetrahedra parallel to *c* and face-sharing pairs of K–S polyhedra that also form double chains parallel to *c*. The average bond distances are: Fe–S = 2.264, Fe–Fe = 2.710, K–S = 3.515Å. By analogy to $BaFe_2S_3$, rasvumite has high-spin iron with delocalized electrons such that the average oxidation state is close to the 2.5+ indicated by the formula.

Introduction

Rasvumite was discovered at the Khibina massif, Kola Peninsula, USSR, and described by Sokolova *et al.* (1970). The chemical formula originally proposed, $K_3Fe_{19}S_{14}$, with Z = 1 in the orthorhombic cell, was not compatible with the symmetry. The correct formula, KFe_2S_3, was assigned by Czamanske *et al.* (1979) after discovery and study of rasvumite at Coyote Peak, Humboldt County, California.

The Coyote Peak rasvumite has not been found in crystals as excellent as those found in the Khibina massif. Through the courtesy of M. N. Sokolova, Academy of Sciences, Moscow, some of the original crystals were made available to us for study, and one of these was selected for structural analysis.

Comparison of the crystallographic data for rasvumite with those reported for synthetic $BaFe_2S_3$ by Hong and Steinfink (1972) left little doubt that the two are isostructural despite the differences in chemistry and formal valence. The isostructural relationship is confirmed by the results of our refinement for the rasvumite structure. A brief preliminary description was given by Clark *et al.* (1979).

Experimental data

Crystallography, collection of data

The crystallographic data for rasvumite given by Czamanske *et al.* (1979) were confirmed upon examination of the Khibina crystal selected for the structural study. That crystal was a prismatic fragment 0.5 mm long and 0.2 × 0.05 mm in cross-section. It was impossible to obtain a more nearly equant crystal because of its tendency, noted by Sokolova *et al.* (1970), to split into fine needles when pressed. A least-squares fit of the angular coordinates of 29 automatically centered reflections in the 2θ range 30° to 46° gave the values in Table 1. For comparison, the values reported by Sokolova *et al.* and by Czamanske *et al.* (1979) are also listed in Table 1, together with those for the isostructural synthetics, $BaFe_2S_3$ (Hong and Steinfink, 1972) and $CsCu_2Cl_3$ (Brink *et al.*, 1954).

A total of 458 reflections in the angular 2θ range of 5° to 60° was measured using an ω–2θ scan mode, a scan range of 2°, graphite-monochromatized Mo$K\alpha$ radiation, and a solid-state detector system. Two

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Table 1. Crystallographic data compared for rasvumite and $BaFe_2S_3$.[1] Orthorhombic, *Cmcm* (no. 63), Z = 4

Parameter	Rasvumite, KFe_2S_3			$BaFe_2S_3$
	U.S.S.R. Kola Peninsula		U.S.A. California	Synthetic
	This study[2]	Sokolova *et al.* (1970)[3]	Czamanske *et al.* (1979)[3]	Hong and Steinfink (1972)[3]
a(A)	9.049(6)	9.12	9.035(1)	8.7835(9)
b(A)	11.019(7)	11.08	11.022(1)	11.219(1)
c(A)	5.431(4)	5.47	5.426(1)	5.2860(5)
V(A^3)	541.5	[552.7]	540.4	[520.9]
Density, (g/cm^3)				
calc.	3.029	3.19	3.035	4.40
obs.	---	3.1	∼3.1	4.00

[1] $CsCu_2Cl_3$ is also isostructural: a = 9.49(2), b = 11.88(2), c = 5.61(4)A (Brink *et al.*,1954).

[2] One estimated standard deviation for the last decimal place given is shown in parentheses; for 9.049(6), read 9.049 ± 0.006A, *etc.*

[3] Values calculated by us are enclosed in brackets.

standard reflections, one at $\chi = 0°$ and one at $\chi = 90°$, were monitored after each group of 30 reflections had been measured. There was no significant variation in integrated intensity during the 24 hours required for the data collection. Of the 458 reflections, 118 had intensities less than $3\sigma(I)$, where $\sigma(I)$ is one standard deviation of the intensity I as calculated from the formula by Corfield *et al.* (1967) using an instrumental instability constant of 0.04. Random failures during processing of the paper-tape output eliminated 8 reflections, so the final data set contained 332 observations with $I > 3\sigma(I)$. These data were corrected for Lorentz and polarization factors. Unfortunately, the crystal was moved before its correct orientation had been recorded, and an attempt to apply an absorption correction ($\mu = 71$ cm^{-1}, Mo$K\alpha$) based on a "best guess" was unsuccessful. Commitments for diffractometer time prevented repetition of the data collection.

Refinement of the data

Computer programs of Stewart (1976), particularly DATRDN, ABSORB, NORMSF, LOADAT, CRYLSQ, FOURR, BONDLA, and LISTFC, were used for the data processing and refinement. Neutral atomic scattering factors derived from the coefficients for the analytical expression (Doyle and Turner, 1968) and anomalous dispersion values (Cromer and Liberman, 1970), both taken from Ibers and Hamilton (1974, p. 99, 148–149), were applied to the data. Normalized structure factors were calculated so the statistical distribution could be examined; the presence of a center of symmetry was confirmed. Least-squares refinement was initiated using the atomic parameters for $BaFe_2S_3$ (Hong and Steinfink, 1972). The conventional unweighted residual $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ began at 0.664 for the 332 observed data. After only 3 cycles of refinement for scale and positional parameters (unit weights used throughout), R had dropped to 0.147. After 6 more cycles, 3 to refine isotropic temperature parameters and 3 to refine anisotropic thermal parameters, the final R was 0.081 and the average shift/error was 0.01. A final three-dimensional difference Fourier was featureless.

The atomic parameters are given in Table 2 together with those for the isostructural $BaFe_2S_3$. Because the data are uncorrected for absorption, anisotropic thermal parameters and ellipsoids are not given, although all these were reasonable, without abnormalities. The observed and calculated factors for rasvumite are compared in Table 3.[1]

Discussion of the structure

The principal feature of the structure is the presence of double chains formed by pairs of Fe–S tetrahedra sharing edges with other pairs so that the chains are oriented parallel to *c*. The chains pack two per cell at $x = 0$ and $x = 1/2$. Within the spaces remaining, pairs of face-sharing, K-coordination polyhedra form another set of double chains parallel to *c*. These are crosslinked by edge-sharing to complete

Table 2. Atomic and thermal parameters for rasvumite and $BaFe_2S_3$[1]

Atom	Position, *Cmcm*	Parameter *x*	*y*	*z*	Equiv. isotropic B(A^2)
Fe	8e	0.3502(3) *.3464(4)*	0.5000	0.	1.18 *0.63*
S(1)	4c	0.5000	0.6191(5) *.6147(9)*	0.2500	1.16 *0.79*
S(2)	8g	0.2174(5) *.2074(9)*	0.3859(5) *.3768(7)*	0.2500	1.74 *1.41*
K/Ba	4c	0.5000	0.1699(7) *.1859(3)*	0.2500	2.33 *1.72*

[1] Values in italics are for $BaFe_2S_3$ from Hong and Steinfink (1972); equivalent isotropic B values calculated from their data. Numbers in parentheses are one estimated standard deviation; for 0.3502(3) read 0.3502±0.0003, *etc.*

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[1] To obtain a copy of this table, order Document AM-80-135 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue, N.W., Washington, D.C. 20009. Please remit $1.00 in advance for the microfiche.

the space-filling array. The tetrahedral double chains and a face-sharing pair of K atoms are illustrated in Figure 1 as viewed along *b*. In Figure 2 both are seen on end, viewed along *c*; the edge-sharing of K coordination polyhedra is visible. The chain structure parallel to *c* undoubtedly accounts for the fibrous character and elongation of the crystals in that direction. Sokolova *et al.* (1970) reported perfect cleavage parallel to (110); this cleavage cuts across the double chains between the K-coordination polyhedra (Fig. 2).

The Fe–S tetrahedra and chains

There is only one crystallographically distinct tetrahedron in the structure. To form the pairs, it shares a S(1)–S(1)e edge[2] with its equivalent related by the twofold axis parallel to *a*. These pairs share S(1)–S(2) edges with equivalents related by the mirror planes normal to *c* at 1/4, 3/4, thus forming the double chain. Bond distances and angles are given in Table 4, where they are compared with those reported for the synthetic Ba analogue. The tetrahedron appears to be less regular in rasvumite, although the average Fe–S distances are nearly the same in both, and the Fe–Fe(e) approach corresponding to the chain formation is about 0.07Å longer in rasvumite. Substitution of Cu, Ni, *etc.*, for Fe might be anticipated in the natural material; however, in the microprobe analyses reported by Czamanske *et al.* (1979) Cu or Ni were not detected above the 0.01 wt.% level. Perhaps the electronic orbitals of iron (discussed in another section) are essential to the double chain, thus making substitution of another element unlikely. The three S–Fe–S angles of the tetrahedron are close to the average tetrahedral angle in value (109.5°), but the S(2)–Fe–S(2)e angle opens out to 114°–115° in rasvumite and $BaFe_2S_3$, probably increased because this angle is toward the open side of the chain.

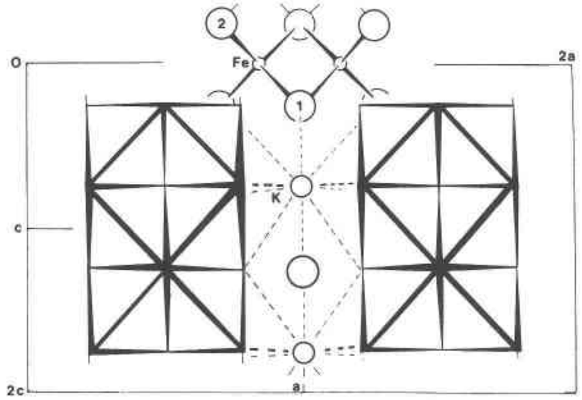

Fig. 1. A view on (010) of selected atoms in the rasvumite structure, showing the edge-sharing double tetrahedral chains and a face-sharing pair of K-coordination polyhedra. Large circles represent sulfur atoms.

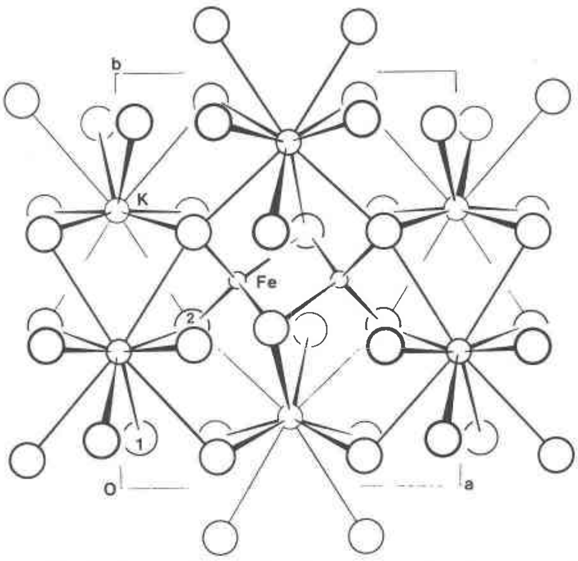

Fig. 2. A view on (001) of selected atoms in the rasvumite structure, showing the linkage of K-coordination polyhedra and two tetrahedra of one double chain. Large circles represent sulfur atoms.

Aside from these isostructural compounds, no other structures containing similar double Fe–S tetrahedral chains have been reported. Single chains of edge-sharing Fe–S tetrahedra occur in the structures of $KFeS_2$ (Boon and MacGillavry, 1942; Stevens, 1979), $RbFeS_2$ and $CsFeS_2$ (Bronger, 1968), erdite, $NaFeS_2 \cdot 2H_2O$ (Konnert and Evans, 1980), and $Ba_9Fe_{16}S_{32}$ (Hoggins and Steinfink, 1977). The average Fe–S distances range from 2.21Å to 2.38Å in the single chains; the average double-chain Fe–S distance is 2.27Å. The average Fe–Fe approaches are closer in the double chains, 2.69Å, compared to the range of 2.71–2.87Å for the single chains.

The large cation-coordination polyhedra

The K–S distances and K–K approaches are listed in Table 5, where they are compared with values for Ba–S and Ba–Ba in $BaFe_2S_3$ (Hong and Steinfink, 1972), and the Cs–Cl distances in the isostructural $CsCu_2Cl_3$ (Brink *et al.*, 1954). For the latter, the authors described the Cs coordination polyhedron as a trigonal prism with two additional Cl atoms on two lateral faces and two at somewhat longer distances on the third lateral face. The K-coordination polyhedron in rasvumite can also be described this way

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[2] See Table 4 for definition of the atom labelling.

Table 4. The Fe–S tetrahedra compared for rasvumite and $BaFe_2S_3$[1]

Atoms[2]	Distance (A)		Atoms	Angles (°)	
	Rasvumite This study	$BaFe_2S_3$ Hong & Steinfink (1972)	S atoms in S-Fe-S	Rasvumite This study	$BaFe_2S_3$ Hong & Steinfink (1972)
Fe-S(1), S(1)e	2.322(4)	2.28(1)	1, 1e	108.7(1)	107.6(4)
-S(2), S(2)e	2.205(4)	2.27(1)	1, 2; 1e, 2e	106.3(1)	108.9(4)
average	2.264	2.275	1, 2e; 1e, 2	110.7(2)	108.1(4)
			2, 2e	114.1(2)	114.9(4)
Fe-Fe(f) [pairs]	2.706	2.699(5)			
-Fe(e) [chains]	2.713	2.643(5)	Fe-S(1)-Fe(f)	71.3	72.4
average	2.710	2.671	Fe-S(2)-Fe(e)	75.9	71.2
S(1)-S(1)e	3.776(6)	3.689			
S(1)-S(2), S(1)e-S(2)e	3.625(7)	3.705			
S(1)-S(2)e, S(1)e-S(2)	3.730(7)	3.688			
S(2)-S(2)e	3.701(5)	3.825			
average	3.698	3.717			

[1] Numbers in parentheses under distance and angles are one estimated standard deviation; for 2.322(4), read 2.322±0.004A, etc.

[2] Atoms designated e and f are related to the basic set (Table 2) as follows: e = *x*, 1-*y*, ½+*z*; f = 1-*x*, *y*, *z*.

(Fig. 2). However, the K–S distances associated with the corners of the trigonal prism differ more than do the Cs–Cl distances: K–S 3.406Å(×4), 3.574Å(×2); Cs–Cl 3.62Å(×4), 3.66Å(×2). Hong and Steinfink considered the Ba atom to be 8-coordinated, the two longest distances referred to above being 3.92Å, about 0.5Å greater than the other eight. The divalent Ba cation, having a stronger attraction for anions than univalent K, shortens some distances and so is satisfied with fewer neighbors. Iglesias and Steinfink (1975) discussed the packing of the Ba–S trigonal prisms in $BaFe_2S_3$ (and $BaFe_2Se_3$), comparing it with the hexagonal close-packed layers in $SnNi_3$ and showing the distortions required to go from the latter to the Ba compounds. The average K–S distance in rasvumite, 3.515Å for 10-coordination, is longer than the average K–S distance of 3.39Å for 8-coordinated K in $KFeS_2$ (Boon and MacGillavry, 1942).

Table 5. Comparison of the large cation-coordination polyhedra in rasvumite, $BaFe_2S_3$, and $CsCu_2Cl_3$

Atoms, M-S [Cs-Cl]	Bond multiplicity	Distance (A)[1]		
		Rasvumite	Synthetics	
		KFe_2S_3	$BaFe_2S_3$	$CsCu_2Cl_3$
		This study	Hong & Steinfink (1972)	Brink *et al.* (1954)
S(2), Cl(I)[2]	4X	3.406(9)	3.29(1)	3.62
S(2), Cl(I)	2X	3.491(9)	3.35(1)	3.70
S(1), Cl(II)[2]	2X	3.574(9)	3.46(1)	3.66
S(2), Cl(I)	2X	3.696(9)	3.92(1)	3.97
average of 8		3.469	3.35	3.65
average of 10		3.515	3.46	3.71
M-M(e)[3]		4.625	4.94	5.17
Angle, M-S(2)-M(e)[Cs-Cl(I)-Cs(e)]		81.1°	86.1°	85.9°

[1] Number in parentheses is one estimated standard deviation; for 3.406(5), read 3.406±0.005 A, *etc.*

[2] These atoms are corners of the trigonal prisms. The others occupy positions near lateral faces of the prisms.

[3] M(e) is at *x*, 1-*y*, ½+*z* (see Table 2 for *x*, *y*, *z*).

The chains of K (and Ba) coordination polyhedra are formed by sharing end faces of the trigonal prisms. However, the edges shared in rasvumite to produce double chains of polyhedra involve those sulfur atoms that are not included in the Ba-coordination polyhedron. Thus the chain structure is more pronounced in rasvumite.

Synthesis

After we began our study of rasvumite, Deane K. Smith, The Pennsylvania State University, University Park, informed us that material synthesized by Howd and Barnes (1975) was identified as rasvumite. He kindly provided some of those synthetic crystals together with their X-ray data, and we have verified the identity, although the synthetic crystals are extremely poor by comparison with the mineral. Hydrothermal synthesis of the rasvumite took place between 425° and 452°C at a pressure of 5900±200psi over a period of 62 hours (Howd and Barnes, 1975, p. 973, Table 1).

Oxidation state of iron

With respect to formal valence, iron in $BaFe_2S_3$ would be in the ferrous state, whereas in KFe_2S_3 its oxidation state would be exactly intermediate between ferrous and ferric at 2.5+. Reiff *et al.* (1975) studied the oxidation state of iron in several barium iron sulfides, including $BaFe_2S_3$, using Mössbauer spectra, electrical resistivity, and magnetic susceptibility measurements. They found that $BaFe_2S_3$ has a rather low resistivity, 0.5 ohm cm at room temperature, and a magnetic moment consistent with Fe^{2+}. The compound is paramagnetic, hence iron is in the high-spin state. However, the Mössbauer spectrum shows only a single quadrupole with an intermediate value of the isomer shift between those expected for divalent and trivalent iron, respectively. Reiff *et al.* interpreted this to mean that electron delocalization occurs to the extent of nearly one-half electron per iron atom. The existence of KFe_2S_3 with the 2.5+ valence for iron appears to confirm this interpretation.

Hoggins and Steinfink (1976) proposed an empirical relationship modeled after one derived by Brown and Shannon (1973) to determine the valence state of iron in tetrahedral coordination with sulfur from observed bond distances. Using their proposed relationship with the Fe–S distances found in rasvumite, the calculated valence is 2.74 for rasvumite, compared with 2.64 for $BaFe_2S_3$. Applying the 2.74 value in the equation proposed by Hoggins and Steinfink for the predicted isomer shift, δ, rasvumite would be expected to have $\delta = 0.30$ mm/sec. For $BaFe_2S_3$, the calculated δ was 0.34 mm/sec and the observed value was 0.41 mm/sec. When sufficient material is available, a Mössbauer study of rasvumite will be made by H. Steinfink, University of Texas, Austin, so that the results for the isostructural compounds can be checked and compared.

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