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Subsilicic ferrian aluminian diopside from the Chelyabinsk coal basin (Southern Urals) – an unusual clinopyroxene

Yurii K. KABALOV*, Oliver OECKLER**, Elena V. SOKOLOVA*,
Aleksei B. MIRONOV***, Boris V. CHESNOKOV***

*Department of Crystallography, Faculty of Geology, Moscow State University,
Vorob'evy Gory, 119899 Moscow, Russia
** Max-Planck-Straße 1, D-81627 München, Germany
*** Institute of Mineralogy, Russian Academy of Sciences, Ural Division, 456301 Miass, Russia

Abstract: The crystal structure of a technogeneous Fe^{3+}-rich diopside from the Chelyabinsk coal basin, Southern Urals, has been refined from X-ray powder diffraction data (CoK_α radiation) using the Rietveld method ($R_{wp} = 0.049$). The refined monoclinic cell dimensions ($Z = 4$, space group $C2/c$) are $a = 9.786(2)$ Å, $b = 8.860(1)$ Å, $c = 5.338(1)$ Å and $\beta = 105.87(1)°$. This technogeneous mineral has previously been described as esseneite according to the empirical formula $Ca_{1.00} Fe^{3+}_{0.51} Ti_{0.02} Al_{0.60} Si_{1.43} O_6$, but in contrast to ideal esseneite (end member: $CaFe^{3+}AlSiO_6$), Fe^{3+} ions are not restricted to the octahedral M(1) site, but are partitioned between the M(1) and the tetrahedral T site. Moessbauer spectroscopy indicates a Fe^{3+} distribution over the M(1) and T sites with a 2:1 ratio. Site occupancy refinement confirms that the M(1) site is occupied by 0.44(3) Mg, 0.35(3) Fe^{3+} and 0.20(3) Al, and the T site by 0.70(2) Si, 0.20(2) Al and 0.08(2) Fe^{3+}.

Key-words: Chelyabinsk coal basin, esseneite, technogeneous clinopyroxene, Rietveld refinement, tetrahedral Fe^{3+}.

Introduction

Esseneite (end member: $CaFe^{3+}AlSiO_6$) is an uncommon $C2/c$ pyroxene that was found as a product of pyrometamorphism in paralava associated with naturally combusted coal seams (Cosca & Peacor, 1987). The crystal chemical formula given for natural esseneite $(Ca_{1.01}Na_{0.01})(Fe^{3+}_{0.72}Mg_{0.16}Al_{0.04}Ti_{0.03}Fe^{2+}_{0.02}Mn_{0.00})(Si_{1.19}Al_{0.81})O_6$ indicates a high proportion of Al in the tetrahedral T site and Fe^{3+} in the octahedral M(1) site.

According to the standard nomenclature of pyroxenes (Morimoto *et al.*, 1988), in esseneite Fe^{3+} formally substitutes for the divalent cation in the M(1) site and Al and Si simultaneously occupy the T site. Nevertheless, Ghose *et al.* (1986) investigated the crystal structure of synthetic $CaFe^{3+}AlSiO_6$ and reported partitioning of Fe^{3+}

between octahedral M(1) and tetrahedral T sites, the T site occupancies being 0.50 Si, 0.41 Al and 0.09 Fe^{3+}. Hafner & Huckenholz (1971) found evidence for Fe^{3+} in the T site of synthetic ferrian diopsides using Moessbauer spectroscopy. Although X-ray structural studies of natural clinopyroxenes rich in Fe^{3+} and Al have not yet revealed the presence of Fe^{3+} in the T site, based on electron microprobe data, Foit *et al.* (1987) estimated a maximum tetrahedral Fe^{3+} content of 0.17 atoms per formula unit (8.5% tetrahedral occupancy) for Fe^{3+}-rich clinopyroxenes in coal-fire buchites (partially fused rocks characterized by a large number of Fe^{3+}-rich minerals) found near Buffalo, Wyoming, USA.

In recent years, several technogeneous minerals with a high Fe^{3+} content from the Chelyabinsk coal basin, Southern Urals, namely, armol-

colite, periclase and magnesioferrite, have been studied using X-ray single-crystal techniques (Sokolova *et al.*, 1991, 1992, 1993). A Ca, Fe^{3+}, Al-rich pyroxene from the same locality was also reported by Chesnokov & Shcherbakova (1991) and referred to as "esseneite". Accurate site occupancy data for this pyroxene are still lacking. Knowing its Fe^{3+} distribution would be of general interest in order to compare this technogeneous mineral with natural esseneite and its synthetic analogues. Single crystals of this Chelyabinsk pyroxene suitable for X-ray structure refinement are not available. Therefore, the present study was carried out by means of Moessbauer spectroscopy and X-ray powder diffraction analysis[1].

Occurrence

Technogeneous Fe^{3+}, Al-rich Ca-pyroxenes form within the burning heaps of waste rocks in the Chelyabinsk coal basin, Southern Urals (Chesnokov & Shcherbakova, 1991), favoured by the very oxidizing conditions. They occur in skarn-like silicate shells covering fragments of mineralized wood. At high temperatures, these fragments, originally composed mainly of dolomite and ankerite, transform to periclase, srebrodolskite and calcium oxide. The skarn-like shells are the products of high-temperature chemical reactions with surrounding Si- and Al-rich rocks, which are mainly pyrometamorphic argillites. Aggregates of Fe^{3+}, Al-rich pyroxene crystals are found on the inner surface of those shells. We may estimate Chelyabinsk pyroxene to have formed at a temperature not lower than 1000°C and cooled to 300–500°C within a time ranging from some days to some weeks. Associated minerals are anorthite, hematite, melilite, fluoromagnesiohastingsite, and anhydrite.

Usually, the pyroxene crystals have prismatic habit and sometimes reach 1 mm in length. They have inclusions of hematite and are often covered with black crusts. The colour varies from yellow to orange and sometimes to reddish-brown, depending on iron content. The sample chosen for this study was a powder obtained from yellow crystals.

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[1]Details concerning data collection and structure refinement are available from the authors.

Chemical composition

The chemical composition of Chelyabinsk pyroxenes was determined by electron microprobe by Chesnokov & Shcherbakova (1991). The results for the sample used for the present study are given in Table 1. Analyses of other samples did not indicate significantly different compositions except some small variations in Fe^{3+} content. Our sample contains about 30% less iron than natural esseneite from combusted coal seams (Cosca & Peacor, 1987).

Table 1. Electron microprobe analysis of "esseneite" from the Chelyabinsk coal basin, Southern Urals (after Chesnokov, 1991).

Oxide	weight percent
SiO_2	36.99
TiO_2	0.59
CaO	24.19
Na_2O	0.03
Al_2O_3	13.04
Fe_2O_3	17.42
MgO	7.70
Cr_2O_3	0.02
MnO	–
total	99.89

calculated formula:
$Ca_{1.00}Fe^{3+}_{0.51}Mg_{0.45}Ti_{0.02}Al_{0.60}Si_{1.43}O_6$
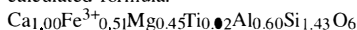
Moessbauer spectroscopy

The Moessbauer spectrum of "esseneite" was recorded with a YAGRS-YM spectrometer operating in constant acceleration mode (room temperature, 256 channels, source: ^{57}Co in Rh). The weight of the sample was about 100 mg. The spectrum was analyzed with the SPECTR least-squares fitting program (Fig. 1). Following Kurepin *et al.* (1981), the spectrum was interpreted as formed by two absorption doublets. As the sample had almost no texture, symmetric doublets of equal width were used for curve fitting.

The first doublet with an isomer shift $\delta = 0.65(2)$ mm/s relative to sodium nitroprusside and a quadrupole splitting $\Delta = 0.99(2)$ mm/s can be assigned to $^{VI}Fe^{3+}$ in the M(1) site, the second doublet ($\delta = 0.41(2)$ mm/s, $\Delta = 1.46(2)$ mm/s) to $^{IV}Fe^{3+}$ in the T site. The δ and Δ values of Chelyabinsk pyroxene are similar to those of a synthetic ferrian diopside $Ca(Mg_{0.74}Fe^{3+}_{0.26})(Si_{1.74}Fe^{3+}_{0.26})O_6$ (Hafner & Huckenholz, 1971). The Moessbauer spectrum shows considerable broadening of the

absorption peaks (0.50 mm/s) due to quadrupole broadening and/or imperfectness of the sample. According to the total integrated intensities the ratio $^{VI}Fe^{3+}/^{IV}Fe^{3+}$ is 1.95 ± 0.15. A small amount of hematite ($\approx2\%$) did not affect the accuracy of the results, as the most intensive peaks of hematite are beyond the range of velocities examined here.

Rietveld refinement

In order to confirm the results of Moessbauer spectroscopy and to determine the crystal structure of Chelyabinsk pyroxene, a Rietveld profile refinement was carried out using X-ray powder diffraction data. The powder diffraction pattern was recorded on an ADP-2 diffractometer in Bragg-Brentano geometry using CoK_α radiation ($\lambda_{\alpha1} = 1.78897$ Å, $\lambda_{\alpha2} = 1.79285$ Å) and Fe filter. The data were collected at room temperature over the $20.8°-130°$ 2θ range with a step interval of $0.02°$ and a step counting time of 15 s. The WY-RIET Rietveld program (Schneider, 1989) was used for profile refinement (ionized scattering factors). The slightly modulated background was treated by automatic linear non-recursive filtering.

Detailed examination of the diffraction pattern showed that in addition to the pyroxene the sample contained small amounts of hematite, the most frequently observed impurity, and quartz. As both hematite and quartz show several non-overlapping peaks, their contributions can be determined quite exactly and should not seriously affect the refinement of the pyroxene structure.
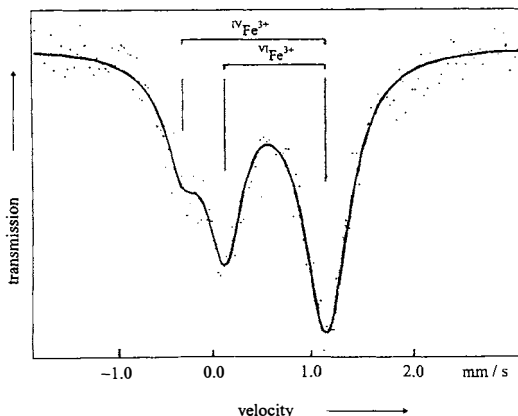

Fig. 1. ^{57}Fe Moessbauer spectrum of technogeneous Fe^{3+}-rich diopside with assignment of the Fe^{3+} absorption doublets (solid line: least-squares fit).

Initial structural parameters were taken from the single-crystal refinement results of natural esseneite from Wyoming (Cosca & Peacor, 1987). The pseudo-Voigt peakshape function was used and a total of 45 independent parameters were allowed to vary during the refinement, including 28 structural parameters for the pyroxene. The structural parameters for quartz and hematite were not varied, but different profile parameters were used for the three phases (avoiding overparametrization for minor phases). Comparison of calculated and observed patterns revealed consider-

Table 2. Atomic coordinates, isotropic Debye-Waller factors and site occupancies from the Rietveld refinement of Fe^{3+}-rich diopside from the Chelyabinsk coal basin, space group $C2/c$.

atom	x	y	z	B (Å^2)	occupancy*	
M(1)	0	0.096(1)	3/4	1.0(3)	Fe^{3+}	0.35(3)
					Al	0.20(3)
					Mg	0.44(3)
M(2)	0	0.697(1)	3/4	0.8(2)	Ca	0.96(3)
T	0.211(1)	0.408(1)	0.774(2)	1.0(3)	Fe^{3+}	0.08(2)
					Si	0.70(2)
					Al	0.20(2)
O(1)	0.396(2)	0.412(2)	0.865(4)	1.2(7)		1.01(5)
O(2)	0.144(2)	0.242(2)	0.648(4)	0.9(7)		0.99(5)
O(3)	0.148(2)	0.481(2)	0.020(4)	0.4(5)		1.06(5)

unit-cell parameters:

$a = 9.786(2)$ Å, $b = 8.860(1)$ Å, $c = 5.338(1)$ Å, $\beta = 105.87(1)°$

*ΣFe^{3+} and ΣAl^{3+} constrained to 0.51 and 0.60 apfu, respectively, according to chemical analysis.
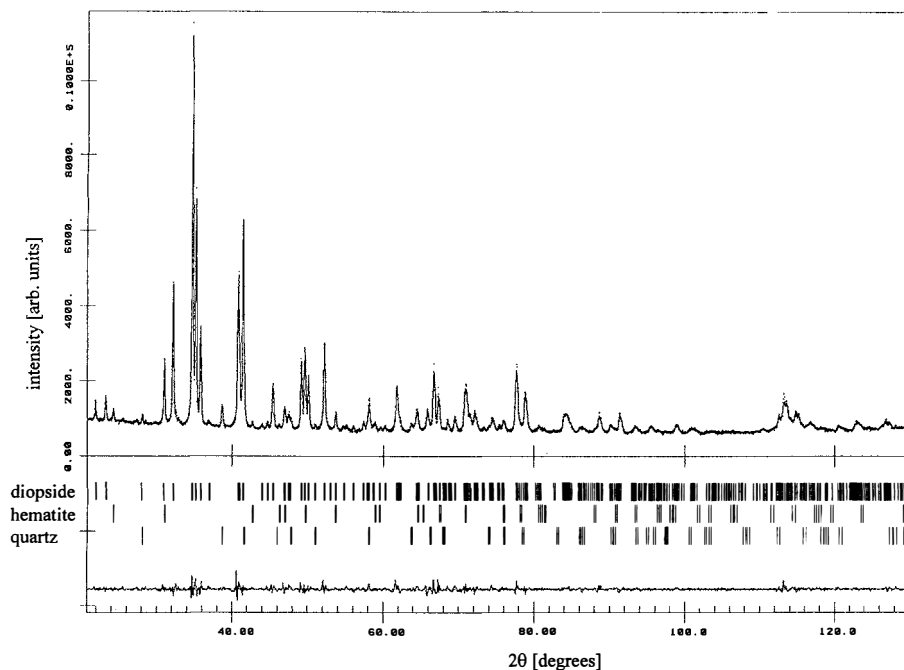
Fig. 2. Observed (dots), calculated (solid line) and difference (below) intensity profiles for the Rietveld refinement of the structure of technogeneous Fe^{3+}-rich diopside from the Chelyabinsk coal basin, including reflection markers for diopside, hematite and quartz.

Table 3. Selected interatomic distances (Å) from refined structural parameters of technogeneous Fe^{3+}-rich diopside from the Chelyabinsk coal basin.

tetrahedron T		octahedron M(1)		polyhedron M(2)	
T – O(1)	1.74(2)	M(1) – 2 O(1)	2.10(2)	M(2) – 2 O(1)	2.31(2)
– O(2)	1.67(2)	– 2 O(1)′	2.03(2)	– 2 O(2)	2.27(2)
– O(3)	1.72(2)	– 2 O(2)	2.09(2)	– 2 O(3)	2.59(2)
– O(3)′	1.65(2)			– 2 O(3)	2.65(2)
mean	1.70	mean	2.07		

able texture effects, which were corrected with the March-Dollase model (preferred orientation vector [110]).

During the first refinement cycles the site occupancies were fixed at the values indicated by chemical analysis and Moessbauer spectroscopy, then the Fe^{3+} site occupancies were varied with the constraint that the sum is constant and later Si, Mg and Ca occupancies were also varied. In the final least-squares cycles all occupancies were varied without constraints. Due to correlation with one another and with Debye-Waller factors, not all occupancies of light atoms could be refined simul-

taneously, so different groups of these parameters were varied alternately. No significant changes were observed, so that correlations appear to be of little importance. In addition, site occupancies, especially Fe^{3+} distribution, were manually altered at several stages of the refinement with the result of higher R-values.

Refinement results are shown in Table 2. Final agreement indices were $R_{wp} = 4.89\%$, $R_p = 3.77\%$, goodness of fit S = 1.48, derived Bragg R-factors $R_B = 3.01\%$ and $R_F = 2.93\%$. Observed, calculated and difference intensity profiles are shown in Fig. 2.

Conclusion

The refined atomic positional parameters for Chelyabinsk pyroxene are close to those of both natural and synthetic $CaFe^{3+}AlSiO_6$ (Cosca & Peacor, 1987; Ghose *et al.*, 1986). Interatomic distances have reasonable values (Table 3). Although oxygen positions cannot be refined with enough accuracy by means of powder diffraction to permit distinction between bonds to bridging and to non-bridging oxygen atoms, the average distance in the T tetrahedron (1.70 Å) is the same as that determined for synthetic $CaFe^{3+}AlSiO_6$. Even if the refinement of oxygen positions and Debye-Waller factors may not be very reliable, the impact of Fe^{3+} distribution on the calculated intensities is much greater, so that site occupancies could be refined with satisfactory accuracy.

We propose the crystal chemical formula $Ca_{1.00}$ $(Mg_{0.45}Fe^{3+}_{0.35}Ti_{0.02}Al_{0.18})$ $(Si_{0.71}Al_{0.21}Fe^{3+}_{0.08})_2O_6$ for the investigated Fe^{3+}-rich Ca-clinopyroxene. This formula takes into account the chemical analysis as well as the results of Moessbauer spectroscopy and Rietveld refinement, which are in very good agreement. Due to the unusual Fe^{3+} distribution, Mg is prevalent in the M(1) site. Thus this pyroxene should be called subsilicic ferrian aluminian diopside (Morimoto *et al.*, 1988).

The high proportion of Fe^{3+} in the tetrahedral T site is most probably due to the unique conditions in Chelyabinsk burning heaps. High temperatures and very oxidizing conditions promoted the formation of Fe^{3+}-rich pyroxenes, whereas diopside typically contains some Fe^{2+} in the M(1) site (solid solution series diopside – hedenbergite). High cooling rates might have contributed to "freeze" disorder and the unusual ion distribution. The high degree of disorder in the "quenched" pyroxene might also account for the low distortion of the M(2) polyhedron and of the T tetrahedron.

Chelyabinsk technogeneous diopside is unusual from two points of view: the total high Fe^{3+} content and its presence in the tetrahedral T site. There is a close relationship between technogeneous Fe^{3+}-rich diopside and both synthetic and natural esseneite.

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