IRON ATOM STATE AND THE SCHEMES
OF ISOMORPHIC SUBSTITUTIONS IN HIGH VESUVIANITES

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The research of a high vesuvianite collection by Mössbauer spectroscopy method are carried out for the first time in this work to define valence and structure state of Fe – ions and schemes of isomorphic substitutions. Vesuvianite, one of the most widespread and poorly investigated rock-forming minerals, is the complex structure of ortho-disilicate with the general schematic formula $X_{19}Y_{13}Z_{18}T_5O_{68}W_{10}$, where X - Ca and other large cations in 8-coordinated positions; Y - Al, Mg, Fe, Ti in octahedra and 5-coordinated positions; Z - Si in tetrahedra; T – B, □; W – OH, O or F. The space group of high vesuvianite is P4/nnc [1].

The experiment was carried out at MS1101E Mössbauer spectrometer using constant accelerations with saw-shaped time dependence of Doppler velocity at room temperature. The source of ^{57}Co isotopes in an Rh-matrix was used in. The special program SPECTR, a part of MSTools software [2] was applied to model fitting the obtained spectra.

As a result of processing and the analysis of high vesuvianite experimental Mössbauer spectra it has been established, that they consist generally of five quadrupole doublets with various relative intensity. Mössbauer spectra obtained for investigated samples with essential variations of relative contents of Fe^{3+} ions are given at fig.1.
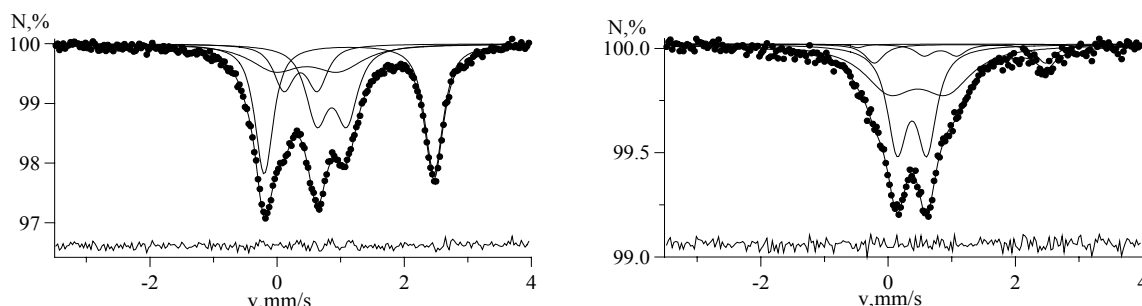

Fig.1.

The typical values of parameters of each of five quadrupole doublets obtained at model spectrum fitting of all investigated samples are given in the table.

Table.

Typical parameters of Mössbauer subspectra of ^{57}Fe nuclei for various crystallographic positions of high vesuvianite structure.

N	δ^*,mm/s	ε^*,mm/s	Γ^*,mm/s	Fe^{2+}/Fe^{3+}	Coordination position
1	1.23÷1.29	1.71÷1.76	0.23÷0.29	Fe^{2+}	$Y_{10A}(1A)$, O_5
2	1.12÷1.15	1.32÷1.37	0.34÷0.39	Fe^{2+}	$Y_{10A}(1B)+Y_{10B}(1A)$, O_5
3	0.81÷0.88	0.22÷0.26	0.33÷0.49	Fe^{2+}	$Y(3)$, O_6
4	0.43÷0.48	0.46÷0.53	0.92÷1.01	Fe^{3+}	$Y_{10A}(1B)+Y_{10B}(1A)+Y_{10B}(1B)$, O_5
5	0.35÷0.41	0.23÷0.31	0.26÷0.45	Fe^{3+}	$Y(3)$, O_6

*δ, ε и Γ - isomer shift, quadrupole shift and width of components of subspectra.

The intervals of typical values of shifts δ of subspectra and average distances R_{Fe-O} for various positions of Fe atoms in high vesuvianite structure are given in a fig.2. The dashed lines in this figure illustrate data from [3] for crystallographically non-equivalent positions of Fe^{2+} and Fe^{3+} in various mineral systems obtained using the least-squares method. The comparative analysis of the data, submitted in a fig.2, has allowed us to offer internally not inconsistent, physically proved model of distribution of Fe ions for crystallographically non-equivalent positions of high vesuvianites structure (see table).

Two of three quadrupole doublets corresponding Fe^{2+} ions have hyperfine parameters, typical for five coordinated position. According to X-ray structure research [4] four crystallographically non equivalent five-coordinated positions with the following average distances: 2.02Å, 2.06Å, 2.08Å and 2.12Å may be distinguished in high vesuvianite structure. The Mössbauer research has allowed to quantitatively determine the distribution of Fe ions in these split positions that could not be done by X-ray methods. The third doublet corresponds to subspectrum of Fe^{2+} ions located in octahedral position. Two last quadrupole doublets are identified as subspectra of trivalent Fe ions located in five and six-coordinated positions.
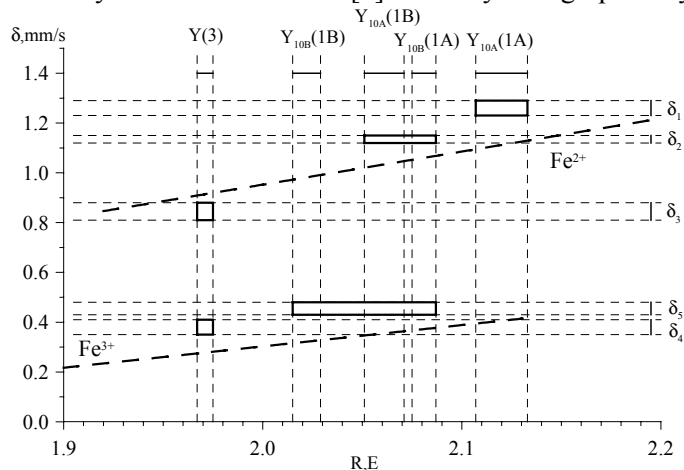

Fig.2.

Linear correlations between the sums of corresponding cations have been found out (fig.3) as a result of the definition of the relative contents of Fe^{2+} and Fe^{3+} ions and the analysis of the chemical composition of the samples.
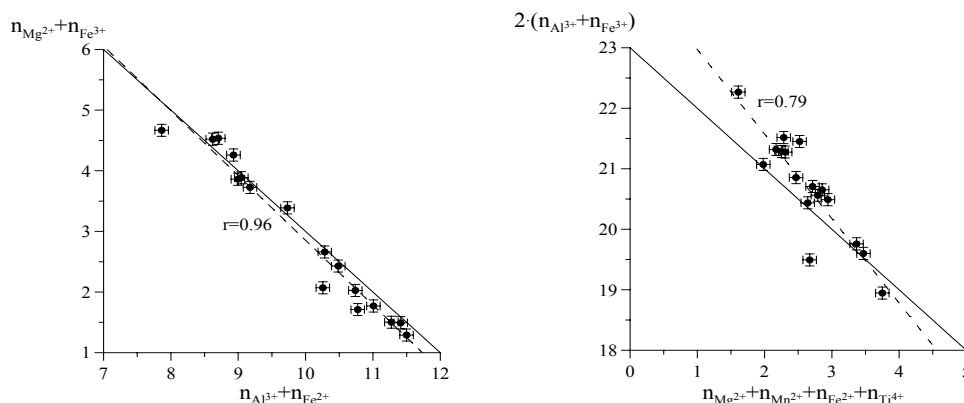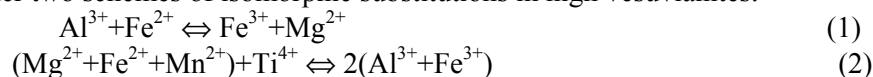

Fig.3.

This allowed us to consider two schemes of isomorphic substitutions in high vesuvianites:

$$Al^{3+}+Fe^{2+} \Leftrightarrow Fe^{3+}+Mg^{2+} \qquad (1)$$
$$(Mg^{2+}+Fe^{2+}+Mn^{2+})+Ti^{4+} \Leftrightarrow 2(Al^{3+}+Fe^{3+}) \qquad (2)$$

In these schemes a complete balance of the valence is not achieved, as there is no precise linear correlation between contents of corresponding isovalent atoms. Thus, it is possible to conclude, that these schemes are realized simultaneously and supply each other. The linear correlation coefficients show, that the basic isomorphic substitution scheme for the studied samples of high vesuvianites is the scheme (1), and the scheme (2) has subordinated role.

References:

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