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GEOCHEMISTRY

Crystal Structure and Refined Formula of Garyansellite $Mg_2Fe^{3+}(PO_4)_2(OH) \cdot 2H_2O$

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Abstract—Single-crystal study of the structure ($R = 0.0268$) was performed for garyansellite from Rapid Creek, Yukon, Canada. The mineral is orthorhombic, *Pbna*, $a = 9.44738(18)$, $b = 9.85976(19)$, $c = 8.14154(18)$ Å, $V = 758.38(3)$ Å^3, $Z = 4$. An idealized formula of garyansellite is $Mg_2Fe^{3+}(PO_4)_2(OH) \cdot 2H_2O$. Structurally the mineral is close to other members of the phosphoferrite–reddingite group. The structure contains layers of chains of $M(2)O_4(OH)(H_2O)$ octahedra which share edges to form dimers and connected by common edges with isolated from each other $M(1)O_4(H_2O)_2$ octahedra. The neighboring chains are connected to the layer through the common vertices of $M(2)$ octahedra and octaahedral layers are linked through PO_4 tetrahedra.

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Garyansellite is a rare phosphate belonging to the phosphoferrite–reddingite group and the only member with the species-defining Mg. It was described as a new mineral from the Rapid Creek region (Yukon, Canada) [1], but its structure has still not been studied.

The comparative crystal chemistry of minerals related to the phosphoferrite structure type was originally developed in [2]. The phosphoferrite–reddingite group contains orthorhombic phosphates with the general formula $M(1)M(2)_2(PO_4)_2(H_2O,OH)_3$, where octahedral M sites may contain Mn^{2+}, Fe^{2+}, Fe^{3+}, or Mg as the major components [3]. Mn^{2+}, the largest of these cations, usually occupies the largest $M(2)$ octahedron, whereas the Mn-rich members of this group contain Mn^{2+} in $M(1)$ as well. For example, Mn predominates in both M sites of reddingite $Mn_3^{2+}(PO_4)_2 \cdot 3H_2O$; in recently discovered correianevesite $Fe^{2+}Mn_2^{2+}(PO_4)_2 \cdot 3H_2O$ (formulas of end-members are given), Mn predominates in the $M(2)$ site and additionally enters $M(1)$ as an impurity to Fe^{2+} [4].

The chemical composition of the primary (holotype) sample of garyansellite corresponds to the following empirical formula:

$$(Mg_{1.45}Fe^{3+}_{1.39}Mn_{0.14}Al_{0.01}Fe^{2+}_{0.01})_{\Sigma 3}(PO_4)_{1.99}(OH)_{1.43} \cdot 1.5H_2O$$

(calculated for three metals; OH/H_2O is calculated by the charge balance). Without structural data, the researchers [1] suggested the following simplified formula for the mineral:

$$(Mg,Fe^{3+})_3(PO_4)_2(OH)_{1.5} \cdot 1.5H_2O.$$

This formula possibly with small variations

$$[(Mg,Fe^{3+})_3(PO_4)_2(OH,H_2O)_3 \text{ or } (Mg,Fe^{3+})_3(PO_4)_2(OH,O) \cdot 1.5H_2O]$$

is given in modern reference books and databases.

We studied garyansellite from the original occurrence (Rapid Creek). This mineral in the studied sample associates with kryzhanovskite, metavivianite, and siderite. Garyansellite forms perfect dipyramidal chocolate-brown crystals with glassy luster, size up to 1 × 2 mm, {111} and {011} faces, and elongation by [100]. According to the electron microprobe data (the total of all components analyzed by this method is 5), the atomic proportions of the components in the empirical formula of garyansellite are $Fe_{1.51}Mg_{1.22}Mn_{0.20}P_{2.07}$. It is not possible to correctly estimate the anionic composition by these data alone, because the valent state of Fe and Mn is not known. The formula calculated with account for the structural data is given below.

The crystal structure of garyansellite was refined for the single crystal with a size of 0.06 × 0.20 × 0.27 mm. The three-dimensional set of diffraction data was obtained at room temperature using an Xcalibur S CCD single-crystal diffractometer and MoK_α radiation ($\lambda = 0.71073$ Å) for the whole sphere of reciprocal space within the θ range of 3.90°–30.50°. The experimental data was processed using the CrysAlis v. 1.171.35.21 software. The total number of reflections is 15418 including 1164 independent ones ($R_{int} = 0.0394$). The parameters of the orthorhombic cell

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Coordinates (x, y, z), parameters of thermal displacement parameters (U_{eq}, Å^2) of atoms and site occupancy factors (s.o.f.) in the garyansellite structure

Site	x	y	z	U_{eq}	s.o.f.
$M(1)$	0.0	0.0	0.0	0.01129(17)	$Fe_{0.708(3)}Mg_{0.29}$
$M(2)$	0.04975(5)	0.11075(5)	0.63425(5)	0.01345(13)	$Mg_{0.49}Fe_{0.41}Mn_{0.10}$
P	0.20853(5)	0.10528(5)	0.28807(6)	0.00740(12)	1
O(1)	0.21259(15)	0.25745(14)	0.33043(18)	0.0115(3)	1
O(2)	0.11104(15)	0.03149(14)	0.41207(18)	0.0111(3)	1
O(3)	0.35919(15)	0.04543(15)	0.29912(19)	0.0128(3)	1
O(4)	0.15460(17)	0.08959(17)	0.11350(19)	0.0172(3)	1
Oh	−0.0608(3)	0.25	0.5	0.0179(4)	1
H	−0.1504(11)	0.25	0.5	0.057(18)*	1
Ow	−0.03101(16)	0.33865(16)	0.14427(19)	0.0136(3)	1
H(1)	0.019(2)	0.280(2)	0.097(3)	0.016*,**	1
H(2)	−0.1148(13)	0.306(2)	0.148(3)	0.016*,**	1

* U_{iso}; ** $U_{iso}(H) = 1.2U_{eq}(Ow)$.

refined using 8352 reflections are the following: $a = 9.44738(18)$ Å, $b = 9.85976(19)$ Å, $c = 8.14154(18)$ Å, $V = 758.38(3)$ Å^3, $Z = 4$. The structure was determined on the basis of direct methods within the *Pbna* space group and refined in anisotropic approximation of atomic thermal displacements (except for H) using the SHELX-97 software [5]. The final R factor is 0.0268 for 1141 independent reflections with $I > 2\sigma(I)$. The coordinates of atoms and their displacement parameters are given in table.

The structure of garyansellite (Fig. 1a) is topologically similar to those of other minerals of the phosphoferrite–reddingite group. All these structures contain octahedral layers perpendicular to the a axis (Fig. 1b) and composed of chaains of edge-sharing dimerss of $M(2)O_4(OH)(H_2O)$ octahedra connected via common edges with isolated from each other $M(1)O_4(H_2O)_2$ octahedra. The neighboring chains are connected to the layer through the common vertices of $M(2)$ octahedra and octahedral layers are linked by PO_4 tetrahedra (Fig. 1a).

The $M(1)$ site in the garyansellite structure is Fe^{3+}-dominant with an admixture of Mg. Based on the data of structural refinement, its occupancy is $Fe_{0.708(3)}Mg_{0.29}$. The $M(1)$–O distances are in the range from 1.9410(15) to 2.1552(15) Å with an average of 2.032 Å, which indicates the predomination of Fe^{3+} in the $M(1)$ octahedron and the incorporation of Mn^{2+} admixture is unlikely. Mg predominates in the $M(2)$ site, but the content of Fe is quite significant as well. $M(2)$ cations center octahedra with $M(2)$–O distances from 2.0206(16) to 2.2166(15) Å with an average of 2.078 Å, which indicates the predominantly divalent state of Fe and incorporation of Mn^{2+} in this site. The composition of the $M(2)$ site refined from the structural data with account for the electron microprobe analysis is $Mg_{0.49}Fe_{0.41}Mn_{0.10}$. The PO_4 tetrahedra are characterized by P–O distances from 1.5177(16) to 1.5481(15) Å. H atoms were localized from the difference synthesis and refined with O–H distances restrained to 0.85(1) Å and for water molecule, with additonal restraint of the H(1)–H(2) distance to 1.37(2) Å (to hold an optimal geometry). It is necessary to mention that the H atom belonging to the OH group was initially localized in an intermediate position between those corresponding to the positions of hydrogen in the OH group and the water molecule. Further refinement showed that the position of the hydrogen atom in the OH group was preferable; however, the position Oh (table) should be considered as the position of the oxygen atom of the OH group statistically replaced by the water molecule. This is indirectly confirmed by the results of the study of occupation of the M sites. Thus, the structural formula of the studied sample is

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$${}^{M(1)}(Fe^{3+}_{0.71}Mg_{0.29})^{M(2)}(Mg_{0.98}Fe^{2+}_{0.82}Mn_{0.20})_{\Sigma 2}(PO_4)_2[(OH)_{0.71}(H_2O)_{0.29}] \cdot 2H_2O,$$

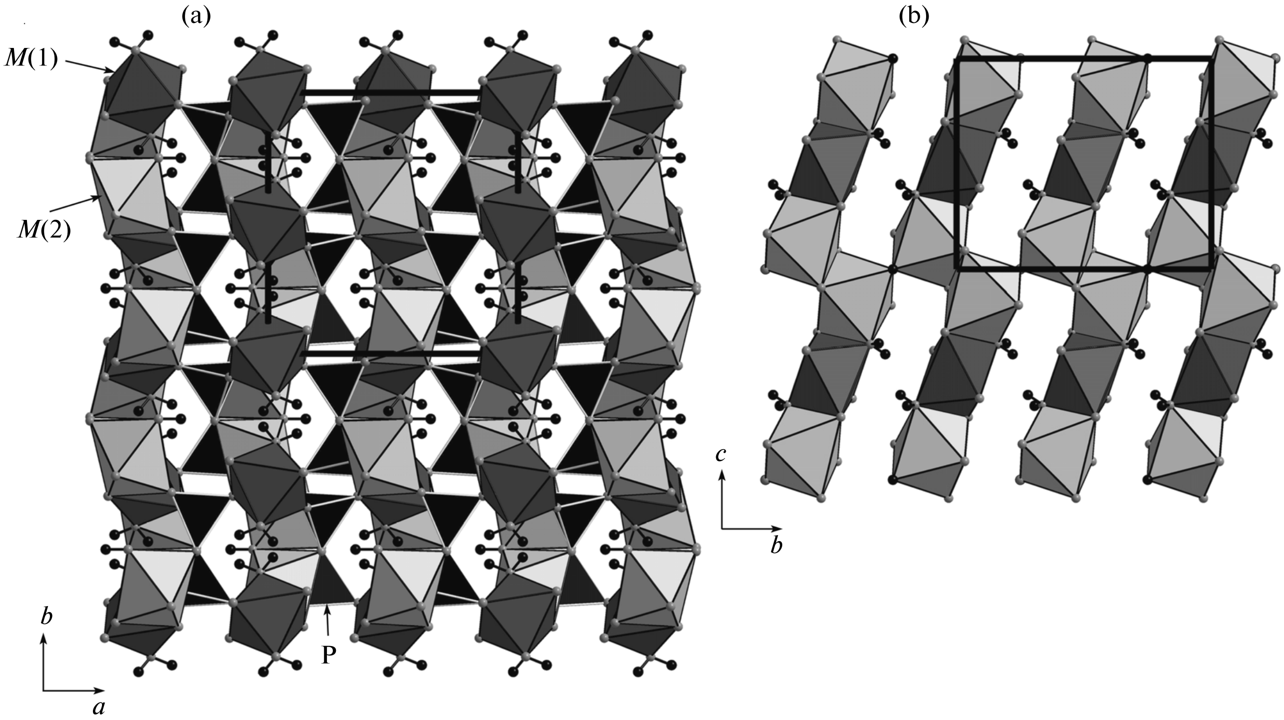

Fig. 1. Crystal structure of garyansellite (a) and the layer of $M(1)$ and $M(2)$ centered octahedra (b). Oxygen atoms are shown by gray circles; hydrogen atoms are shown by black circles. Unit cell is shown.

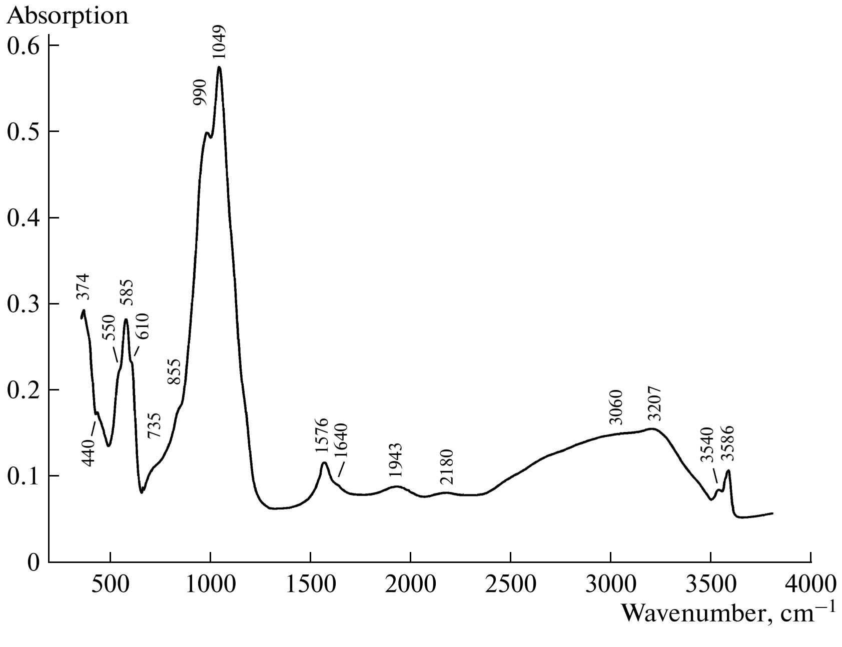

Fig. 2. IR spectrum of garyansellite.

where OH/H_2O is calculated by the charge balance with account for the data on the position of the hydrogen atom in the OH group.

This formula is in good agreement with the data of IR spectroscopy as well. The IR absorption spectrum of the studied garyansellite (Fig. 2) contains peaks of O–H stretching vibrations of the OH groups surrounded by different cation combinations and forming weak hydrogen bonds (at 3586 and 3540 cm^{-1}), as well as peaks corresponding to tight hydrogen bonds presumably formed by H_2O molecules (at 3207 and 3060 cm^{-1}). The presence of a shoulder at 1640 cm^{-1}

on a nondegenerate peak of the H–O–H bend vibrations (with a maximum at 1576 cm^{-1}) provides evidence for the presence of two types of H_2O molecules with one of them predominating. The weak peaks at 2180 and 1943 cm^{-1} are related to an admixture of HPO_4^{2-} groups formed as a result of protonation of phosphate groups, according to the dynamic equilibrium of $PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH^-$ strongly shifted to the left. Similar peaks are observed in the IR spectrum of correianevesite [4], for which the presence of acid phosphate groups was also supported by the data of IR spectroscopy [6]. The low content of HPO_4^{2-} groups does not allow us to identify them by X-ray structural analysis.

This formula is consistent with the assumption that all the iron in the *M*(2) site is divalent; however, the structural and IR spectroscopic data do not contradict the idea that some iron may occur as Fe^{3+}. This will result in an increase of OH/H_2O in the mineral according to the scheme $Fe^{2+} + H_2O^0 \leftrightarrow Fe^{3+} + OH^-$.

Thus, the simplified formula of garyansellite obtained from combination of the chemical and structural data is

$$(Mg,Fe)_2(Fe^{3+},Mg)\ (PO_4)_2(OH,H_2O) \cdot 2H_2O,$$

and the idealized formula of its end-member is $Mg_2Fe^{3+}(PO_4)_2(OH) \cdot 2H_2O$. We should note that the first analysis of the mineral reported in [1] is consistent with this formula.

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