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Crystal structure refinement of magnesian alleghanyite

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Abstract

Alleghanyite from the Sterling Mine, Ogdensburg, New Jersey [$(Mn_{0.568}Mg_{0.390}Zn_{0.037}Fe_{0.004}Ca_{0.001})_5(SiO_4)_2(OH_{1.06}F_{0.94})$, $P\,2_1/b$, $a = 4.815(2)$, $b = 10.574(3)$, $c = 8.083(3)$Å, $\alpha = 108.74(2)°$] was refined to $R = 0.048$ ($R_w = 0.053$) using 1873 structure factors. The mean Si–O distance is 1.629Å. Site refinement with Zn assigned to M(3) yielded Mg/(Mg+Mn) ratios of 0.14 in the $M(1)O_6$ octahedron ($\langle M–O\rangle = 2.191$Å) and 0.10 in the $M(2)O_5(F,OH)$ octahedron ($\langle M–O\rangle = 2.212$Å). The $M(3)O_4(OH,F)_2$ site ($\langle M–O\rangle = 2.118$Å) is occupied by 0.81 Mg, 0.10 Mn and 0.09 Zn atoms. Cations in this and all previously studied humite group minerals are ordered on the octahedral sites according to size criteria, although ligancy (O,OH,F) may be the controlling factor where charge balance and crystal-field effects are involved.

Introduction

The humite group, strictly, is the group of four homologues characterized by the general formula $nMg_2SiO_4 \cdot Mg(OH,F)_2$ where n = 1 for norbergite, n = 2 for chondrodite, n = 3 for humite and n = 4 for clinohumite. Alleghanyite, the manganese analogue of the n = 2 homologue, was first described from Bald Knob, Alleghany County, North Carolina by Ross and Kerr (1932). Its isotypism with chondrodite was proposed by Rogers (1935) and subsequently established by Rentzeperis (1970). Alleghanyite was recognized in specimens from the mines at Franklin and Ogdensburg, Sussex County, New Jersey by Cook (1969) where it occurs in at least two parageneses—as isolated anhedral crystals in the Franklin marble and as euhedral crystals in veinlets cutting the ore. An example of the latter from the Sterling Mine (Harvard University #109468) exhibits crystals of magnesian alleghanyite among a druse of brilliant black cube-octahedrons of franklinite on a slickensided surface of red willemite–franklinite–calcite ore. The crystal structure of an untwinned crystal from this specimen approximately 0.3 × 0.2 × 0.1 mm in size was refined as part of an investigation of Mg/Mn ordering in the olivines and humites (Francis, 1980; Francis and Ribbe, 1978, 1980).

Experimental procedures

Chemical composition was determined on an automated ARL-EMX electron microprobe operating at 15 kv accelerating potential and 0.02 μA sample current on brass. Intensity data were reduced on line using the technique of Bence and Albee (1968) and the correction factors of Albee and Ray (1970). Simple oxides and silicates, including synthetic tephroite (Takei, 1976), were used as standards. The formula, $Mn_{2.840}Mg_{1.948}Zn_{0.184}Fe_{0.023}Ca_{0.005}(SiO_4)_2(OH_{1.06}F_{0.94})$ represents the average of fifteen analyses on two crystals. The rather large amount of zinc and very minor amounts of iron and calcium are typical of Mn-rich olivines (Francis, 1980) and humites (Ribbe, 1982) from the Franklin marble.

The crystal was mounted on a Picker FACS-1 four-circle diffractometer with its diad nearly parallel to the phi axis and was oriented in terms of the nonstandard space group $P2_1/b$ to conform with previous studies (Taylor and West, 1928; Gibbs et al., 1970; Yamamoto, 1977) and the recommendations of Jones (1969). The unit cell dimensions: $a = 4.815(2)$, $b = 10.574(3)$, $c = 8.083(3)$Å, and $\alpha = 108.74(2)°$ were refined from twelve, individually-centered, high-angle reflections ($2\theta \geq 40°$). Intensity data were collected in one quadrant ($2\theta \leq 72°$) at 18°C using Nb-filtered Mo$K\alpha_1$ radiation ($\lambda = 0.70926$Å) and a 2θ scan rate of 1° per minute. Twenty second background measurements were made on either side of dispersion-corrected scan ranges (1.2° 2θ base width).

Two reflections monitored after every fifty data were used to calibrate the data set by linear interpolation. The data were corrected for background, Lorentz and polarization effects. The shape of the crystal was approximated by a polyhedral envelope in the absorption correction ($\mu = 55.6$ cm^{-1}). Structure factors for which $F_{obs} < 2\sigma$ were considered unobserved, leaving a data set of 1873 observations.

Refinement

Full matrix, least-squares refinement was carried out using the program RFINE (Finger and Prince, 1975). Scattering curves for neutral atoms were taken from Doyle and Turner (1968). Corrections for anomalous dispersion were taken from the *International Tables for Crystallography* (1974, p. 99, 149). Refinement was initiated using the positional parameters of Gibbs et al. (1970) with the octahedral sites fully occupied by Mn and with isotropic temperature factors of 0.5, 0.3, and 0.5Å^2 for Mn, Si, and O respectively. After the positional parameters converged, Mg was assigned to the octahedral sites according to

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mean M–O distances (Francis and Ribbe, 1978). Refinement of site occupancies, and isotropic temperature factors converged with a conventional R-factor of 0.057 without constraining the total chemistry. Zinc was then assigned to M(3), the smallest site, (cf. Ghose and Weidner, 1974), and the total chemistry was constrained to agree with the chemical analysis. The refinement, including anisotropic temperature factors, rapidly converged to produce a model with $R = 0.048$ ($R_w = 0.053$). Positional parameters, temperature factors, and interatomic distances and angles are listed in Tables 1 and 2.[1]

Stereochemistry

The steric details of the chondrodite–alleghanyite structure, like those of the olivine and other humite structures, result from distortions of the close-packed anion array by cation–cation repulsions across shared polyhedral edges. These have been thoroughly discussed for chondrodite by Gibbs et al. (1970) and Yamamoto (1977) and for alleghanyite by Rentzeperis (1970). For structure diagrams, site nomenclature and a review of the crystal chemistry of the entire humite group see Ribbe (1982). This structure differs from those of others in the series in that the M(3) octahedron is significantly smaller than the other two octahedra resulting in a greater range in ⟨M–O⟩ distances (0.094Å) than in chondrodite (0.038Å) and in alleghanyite (0.022Å). Polyhedral distortions, as measured quantitatively by the bond angle variance parameter (σ^2) of Robinson et al. (1971) are compared in Table 3. The distortion parameters for the silicate tetrahedron, the M(2), and M(3) sites are intermediate between the respective values for chondrodite and alleghanyite, which is consistent with the observation (Robinson et al., 1971) that for the olivines, distortion of the tetrahedron decreases with increasing mean M–O while distortion of the octahedra increases with increasing mean M–O. The M(1) octahedron in magnesian alleghanyite, however, is somewhat more distorted than in alleghanyite. Distortion of the octahedra decreases with increasing number of monovalent ligands.

Cation ordering

The octahedral cations in magnesian alleghanyite are ordered (see Table 4 for details). Although Mn–Mg distribution cannot be uniquely determined because of significant zinc content, the refined occupancies are consistent with the previous results for olivines (Francis and Ribbe, 1980) and manganhumite (Francis and Ribbe, 1978). The smallest octahedron, M(3) with ⟨M–(O,F,OH)⟩ = 2.118Å, is principally occupied by the smallest cation, Mg (r = 0.720Å), while M(1) with ⟨M–O⟩ = 2.191Å and M(2_5) with

[1] To receive a copy of the structure factor and anisotropic temperature factor tables, order document AM-85-259 from the Business Office, Mineralogical Society of America, 2000 Florida Avenue NW. Washington, D.C. 20009. Please remit $5.00 in advance for microfiche.

Table 1. Atomic coordinates and equivalent isotropic temperature factors (Beq) of magnesian alleghanyite

Atom	x	y	z	Beq. (Å)^2
M(1)	½	0	½	0.39
M(2)(5)	0.0107(2)	0.1718(1)	0.3073(1)	0.33
M(3)	0.4897(3)	0.8841(1)	0.0760(1)	0.34
Si	0.0757(2)	0.1445(1)	0.7090(2)	0.27
O(1)	0.7822(7)	0.9946(3)	0.2906(4)	0.50
O(2)	0.7186(7)	0.2446(3)	0.1245(4)	0.55
O(3)	0.2135(7)	0.1698(3)	0.5374(4)	0.57
O(4)	0.2632(6)	0.8550(3)	0.2890(4)	0.55
(OH,F)	0.2614(7)	0.0527(3)	0.0919(4)	0.61

Table 2. Interatomic distances and angles of magnesian alleghanyite

$[SiO_4]$ tetrahedron

Si ... distances (Å)		O ... O distances (Å)		Angles at Si (°)
Si-O(4)	1.623(3)	O(1)-O(3)	2.551(4)^t	103.06(2)
O(4)	1.627(3)	O(1)-O(2)	2.552(4)^t	103.47(2)
O(3)	1.635(3)	O(2)-O(3)	2.588(4)^t	105.03(2)
O(1)	1.632(3)	O(1)-O(4)	2.744(4)	114.92(2)
Mean	1.629	O(2)-O(4)	2.741(4)	114.54(2)
		O(3)-O(4)	2.747(4)	114.44(2)
		Mean	2.654	109.24

$M(1)O_6$ octahedron

M ... O distances (Å)		O ... O distances (Å)		Angles at M(1) (°)
M(1)-O(1)	[2] 2.157(3)	O(1)-O(3)	[2] 2.551(3)^t	71.54(1)
-O(3)	[2] 2.207(3)	O(1)-O(4)	[2] 2.900(3)^e	83.24(1)
-O(4)	[2] 2.209(3)	O(3)-O(4)	[2] 2.937(3)^e	83.37(1)
Mean	2.191	O(3)-O(4)'	[2] 3.298(3)	96.63(1)
		O(1)-O(4)'	[2] 3.264(3)	96.76(1)
Range	0.052	O(L)-O(3)'	[2] 3.541(3)	108.46(1)
		Mean	3.082	90.00

$M(2)O_5(OH,F)$ octahedron

M ... O distances (Å)		O ... O distances (Å)		Angles at M(2) (°)
M(2)5-O(3)	2.107(3)	O(2)-O(3)'	2.588(4)^t	68.53(1)
O(1)	2.139(3)	O(2)-O(4)	2.891(4)^e	77.65(1)
O(4)	2.268(3)	O(3)'-O(4)	2.937(4)^e	81.01(1)
O(3)'	2.253(3)	O(1)-(3)	3.058(4)	92.12(1)
O(2)	2.342(3)	O(3)-O(3)'	3.114(4)	91.09(1)
(OH,F)	2.160(3)	O(3)-O(4)	3.226(5)	94.96(1)
Mean	2.212	O(1)-O(2)	3.341(4)	96.32(1)
		O(1)-O(3)'	3.541(4)	100.82(1)
Range	0.235	(OH,F)-O(1)	2.986(4)	87.97(1)
		(OH,F)-O(4)	3.082(5)	88.16(1)
		(OH,F)-O(2)	3.267(5)	92.97(1)
		(OH,F)-O(3)	3.419(4)	106.50(1)
		Mean	3.121	89.84

$M(3)O_4(OH,F)_2$ octahedron

M ... O distances (Å)		O ... O distances (Å)		Angles at M(3) (°)
M(3)-O(2)	2.017(3)	O(1)-O(2)'	2.552(4)^t	70.66(1)
O(4)	2.141(3)	O(2)'-O(4)	2.891(4)^e	84.41(1)
O(2)	2.162(3)	O(1)-O(4)	2.900(5)^e	82.66(1)
O(1)	2.248(3)	(OH,F)-(OH,F)	2.769(6)	83.98(1)
(OH,F)	2.063(3)	(OH,F)'-O(2)	3.268(5)	92.16(1)
(OH,F)	2.075(3)	(OH,F)-O(4)	3.007(4)	91.32(1)
Mean	2.118	(OH,F)-O(1)	2.916(4)	86.91(1)
		(OH,F)-O(2)	3.069(5)	97.56(1)
Range	0.231	(OH,F)-O(1)	3.143(5)	97.19(1)
		(OH,F)'-O(2)'	3.179(4)	99.12(1)
		O(2)'-O(4)	3.166(4)	98.35(1)
		O(2)'-O(2)	3.163(4)	
		Mean	3.007	89.82

^{t}Edge shared between tetrahedron and octahedron.
^{e}Edge shared between two octahedra.
*Multiplicity indicated in square brackets.

Table 3. Polyhedral distortion parameters (σ^2) for chondrodite, magnesian alleghanyite and alleghanyite

Polyhedron	Chondrodite Gibbs et al. (1970)	Magnesian Alleghanyite	Alleghanyite Rentzeperis (1970)
SiO_4 †	44.6	35.4	29.4
$M(1)O_6$*	101.2	156.5	150.9
$M(2)O_5(F,OH)$*	82.5	106.4	112.8
$M(3)O_4(F,OH)_2$*	59.2	71.4	91.1

†$\sigma^2(tet) = \sum_{i=1}^{6} (\Theta_i - 109.47^\circ)^2/5$

*$\sigma^2(oct) = \sum_{i=1}^{12} (\Theta_i - 90.0^\circ)^2/11$

$\langle M\text{–}(O,F,OH)\rangle$ = 2.212Å are principally occupied by Mn (r = 0.830Å). Site occupancies and consequently the effective ionic radii, $\langle r_m\rangle$ (Shannon, 1976), calculated from the occupancies are both highly correlated with mean octahedral bond length:

$$\langle M\text{–}(O,F,OH)\rangle = 2.216 - 0.1217\ Mg/(Mg+Mn+Zn) \qquad r = -0.986$$

$$\langle M\text{–}(O,F,OH)\rangle = 1.384 + 1.001\ \langle r_m\rangle \qquad r = 0.985$$

Octahedral size in the humite series decreases in the order $M(2_6) > M(2_5) > M(1) > M(3)$ due to increasing numbers of shared edges and the substitution of three-coordinated monovalent anions (OH and F) for four-coordinated oxygens. The difference in size between $M(2_6)$ and M(3) in humite (Ribbe and Gibbs, 1971) and clinohumite, (Robinson et al., 1973) averages 0.053Å which is equivalent to the difference in ionic radii between Mg and Fe^{2+}. Thus, octahedral size must be considered a significant factor affecting cation ordering in humite group minerals.

The relationship between octahedral size and the radius calculated from site occupancy for the M(1), M(2), and M(3) octahedra in four Mg–Mn olivines and eleven humites (data in Francis 1980) are described by the following regression equations.

$$\langle M(1)\text{–}O\rangle = 1.445 + 0.9172\ \langle r_{M(1)}\rangle \quad (r = 0.995)$$

$$\langle M(2_6)\text{–}O\rangle = 1.521 + 0.8459\ \langle r_M(2_6)\rangle \quad (r = 0.997)$$

$$\langle M(2_5)\text{–}(O,OH,F)\rangle = 1.497 + 0.8713\ \langle r_M(2_5)\rangle \quad (r = 0.983)$$

$$\langle M(3)\text{–}(O,OH,F)\rangle = 1.414 + 0.9442\ \langle r_{M(3)}\rangle \quad (r = 0.939)$$

For the M(1) and $M(2_6)$ octahedra, which are exclusively coordinated by oxygen atoms, the correlations are strongly linear. However, the replacement of $OH^{III}(1.36 < r < 1.45Å)$ (Ribbe, 1979) by $F^{III}(r = 1.30Å)$ reduces mean cation–anion distances. For example, the difference between $\langle M(2_5)\text{–}(O,OH)\rangle$ in synthetic hydroxyl chondrodite (Yamamoto, 1977) and $\langle M(2_5)\text{–}(O,F,OH)\rangle$ in a natural fluorine-rich chondrodite (Gibbs et al., 1970) is 0.017Å, which is about 30% of the size difference between $M(2_6)$ and M(3). Accordingly, a term f, defined as one-half the number of fluorine atoms per formula unit times the number of monovalent ligands associated with the octahedron, was included in the regression analyses.

$$\langle M(2)\text{–}(O,OH,F)\rangle = 1.541 + 0.8185\ \langle r_{M(2)}\rangle - 0.01649\ f \quad (r = 0.994)$$

$$\langle M(3)\text{–}(O,OH,F)\rangle = 1.502 + 0.8386\ \langle r_{M(3)}\rangle - 0.02122\ f \quad (r = 0.996)$$

This permitted data for $M(2_4)$, $M(2_5)$, and $M(2_6)$ to be incorporated into a single equation and resulted in significant improvement in the correlation coefficients.

Summary of cation ordering in the humites

Humites may contain Mg, Ca, Ti, Mn, Fe and Zn although only Mg, Mn and Ca form end members. These cations are ordered into the octahedral sites which vary in distortion, ligancy, size, and symmetry. This and the previous refinements of intermediate Mg–Mn humites clearly demonstrate that manganese is concentrated in the larger sites, which decrease in size in the order $M(2_6) > M(2_5) > M(1) > M(3)$. Kato (pers. comm.) has refined the structure of a sonolite (Mn-rich, n = 4 homologue) which is the most calcium-rich natural humite yet reported. Its $\langle M(2_6)\text{–}O\rangle$ and $\langle M(2_5)\text{–}(O,OH)\rangle$ distances are larger than $\langle M\text{–}O\rangle$ distances of olivine and humite octahedra exclusively occupied by Mn, implying that Ca is concentrated in the largest octahedra. Ti^{4+} is believed to be preferentially concentrated in M(3) which is the smallest octahedral site (Ribbe, 1979). While this is consistent with size criteria, the coupled substitution

$$Ti^{4+} + 2O^{2-} = M^{2+} + 2(OH,F)^-$$

is probably the decisive factor. Fe^{2+} was observed by Ribbe and Gibbs (1973) to be concentrated in $M(2_6)$ and M(1), thus avoiding octahedra coordinated by (OH,F). Thus, octahedral cations in the humites are ordered according to size criteria, although ligancy (O,OH,F) may be the controlling factor where charge balance (e.g., Ti^{4+}) and crystal-field effects (e.g., Fe^{2+}) are involved.

Table 4. Octahedral site occupancies, ligancies and mean M–O distances of magnesian alleghanyite

Site	Ligancy	Occupancy Mg	Mn	Zn	No. of edges shared with Tetrahedra	Octahedra	Mean M-(O,F,OH)
M(1)	O_6	0.135(7)	0.865		2	4	2.191
$M(2)_5$	$O_5(F,OH)$	0.098(4)	0.902		1	2	2.212
M(3)	$O_4(F,OH)_2$	0.808	0.100	0.092	1	3	2.118

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