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GROATITE, Na Ca Mn^{2+}_2 (PO_4) [$PO_3(OH)$]$_2$, A NEW MINERAL SPECIES OF THE ALLUAUDITE GROUP FROM THE TANCO PEGMATITE, BERNIC LAKE, MANITOBA, CANADA: DESCRIPTION AND CRYSTAL STRUCTURE

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Abstract

Groatite, ideally Na Ca Mn^{2+}_2 (PO_4) [$PO_3(OH)$]$_2$, is a new mineral species from the Tanco pegmatite at Bernic Lake, Manitoba, Canada. It was found in a phosphate–carbonate mass in a spodumene-rich boulder. Groatite occurs sparingly as slightly divergent sprays of acicular crystals, embedded stellate sprays and as a tabular mass of densely intergrown acicular crystals. Groatite is closely associated with whitlockite, crandallite, an unidentified Na–Al phosphate and quartz; fairfieldite and manganese-rich overite are among the less closely associated phosphates; this assemblage may be secondary, following apparent dissolution of lithiophosphate and possibly of primary lithiophilite. Groatite is translucent, colorless to pale yellow and pale orange with a white streak and vitreous luster; it does not fluoresce under ultraviolet light. The Mohs hardness is 3. Groatite is brittle with an uneven fracture, and has a calculated density of 3.213 g/cm^3. It is biaxial positive with α 1.622, β 1.634, γ 1.663 (all ±0.001), and is nonpleochroic; $2V$(obs.) = 67(1), $2V$(calc.) = 66.5°. It is monoclinic, space group $C2/c$, a 12.5435(9), b 12.4324(9), c 6.7121(4) Å, β 115.332(2)°, V 946.07(19) Å^3, $Z = 4$. The six strongest lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are as follows: 3.187(100)($\bar{1}12$), 2.726(90)($\bar{4}02$, 240), 6.204(80)(020), 2.788(80)(330), 5.653(70)(200), and 2.580(70)($\bar{1}32$, 420). Chemical analysis by electron microprobe gave P_2O_5 46.66, FeO 0.49, MnO 29.31, CaO 12.51, Na_2O 6.87, H_2O (calc.) 3.93, sum 99.77 wt.%, where the H_2O content was determined by crystal-structure refinement as OH = 2.0 *apfu*. The resulting empirical formula, on the basis of 10 O atoms and 2 (OH) groups *pfu*, is $Na_{1.02}\ Ca_{1.02}\ (Mn_{1.90}Fe^{2+}_{0.03})_{\Sigma 1.93}\ P_{3.02}\ O_{10}\ (OH)_2$. The crystal structure of groatite was refined to an R index of 2.7% based on 831 unique reflections collected on a four-circle diffractometer with Mo$K\alpha$ X-radiation and a 4K CCD detector. There are two tetrahedrally coordinated T-sites occupied by P. There are two octahedra, $M(1)$ and $M(2)$, and an eight-coordinated $A(2)$ site which are occupied by Ca, Mn and Na, respectively. The observed site-scattering, mean bond-lengths and bond-valence sums at these sites are in agreement with complete chemical order of Ca at $M(1)$, Mn^{2+} at $M(2)$ and Na at $A(2)$. A (PO_4) group is centered at the $T(1)$ site and a $PO_3(OH)$ group at $T(2)$. The H atom is located near the O(4) anion and provides a strong hydrogen bond to the O(2) anion. Groatite is isostructural with the acid arsenate mineral o'danielite and is a member of the alluaudite group; it is the first alluaudite-group mineral with an acid phosphate group. The new mineral is named in honor of Lee A. Groat, Professor of Mineralogy at the University of British Columbia in Vancouver. The species and the name *groatite* were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2008–054).

Keywords: groatite, new mineral species, alluaudite group, Tanco pegmatite, Bernic Lake, Manitoba, Canada, crystal structure, electron-microprobe analysis.

Sommaire

La groatite, de composition idéale Na Ca Mn^{2+}_2 (PO_4) [$PO_3(OH)$]$_2$, est une nouvelle espèce minérale découverte dans la pegmatite Tanco, au lac Bernic, Manitoba, Canada, dans une masse de phosphates et de carbonates dans un bloc riche en spodumène. La groatite forme des gerbes légèrement divergentes de cristaux aciculaires, des groupes de cristaux en forme d'étoiles, et aussi une masse tabulaire dense de cristaux enchevrêtrés. Elle est étroitement associée à la whitlockite, la crandallite, un

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phosphate Na–Al non identifié et le quartz; la fairfieldite et l'overite riche en Mn sont aussi présentes. Cet assemblage pourrait bien être secondaire, conséquent à la dissolution apparente de lithiophosphate et possiblement de lithiophilite primaire. La groatite est translucide, incolore à jaune pâle ou orangé, avec une rayure blanche et un éclat vitreux. Elle ne montre aucune fluorescence en lumière ultraviolette. Sa dureté de Mohs est 3. La groatite est cassante avec une fracture inégale, et sa densité calculée est égale à 3.213 g/cm^3. C'est un minéral biaxe positif, avec α 1.622, β 1.634, γ 1.663 (tous ±0.001), et non pléochroïque; $2V$(obs.) = 67(1), $2V$(calc.) = 66.5°. La groatite est monoclinique, groupe spatial $C2/c$, a 12.5435(9), b 12.4324(9), c 6.7121(4) Å, β 115.332(2)°, V 946.07(19) Å^3, $Z = 4$. Les six raies les plus intenses du spectre de diffraction X (méthode des poudres) [d in Å(I) (hkl)] sont: 3.187(100)($\bar{1}12$), 2.726(90)($\bar{4}02$, 240), 6.204(80)(020), 2.788(80)(330), 5.653(70)(200), et 2.580(70)($\bar{1}32$, 420). Une analyse chimique effectuée avec une microsonde électronique a donné P_2O_5 46.66, FeO 0.49, MnO 29.31, CaO 12.51, Na_2O 6.87, H_2O (calc.) 3.93, pour un total de 99.77% (poids). La teneur en H_2O a été déterminée par affinenement de la structure cristalline selon OH = 2.0 *apfu*. La formule empirique qui en résulte, fondée sur une base de 10 atomes d'oxygène et deux groupes OH par formule unitaire, est $Na_{1.02}\,Ca_{1.02}\,(Mn_{1.90}Fe^{2+}_{0.03})_{\Sigma 1.93}\,P_{3.02}\,O_{10}\,(OH)_2$. La structure cristalline de la groatite a été affinée jusqu'à un résidu R de 2.7% en utilisant 831 réflexions uniques prélevées avec un diffractomètre à quatre cercles, un rayonnement Mo$K\alpha$ et un détecteur CCD 4K. La structure contient deux sites tétraédriquement coordonnés où loge le phosphore. Il y a deux octaèdres, M(1) et M(2), et un site A(2) à coordinence [8] où logent Ca, Mn et Na, respectivement. La dispersion observée à ces sites, les longueurs de liaison et les sommes des valences de liaison concordent avec l'hypothèse qu'il y a mise en ordre complète de Ca sur M(1), Mn^{2+} sur M(2) et Na sur A(2). Un groupe (PO_4) est centré sur le site T(1), et un groupe PO_3(OH), sur le site T(2). L'atome H est situé près de l'anion O(4) et assure une forte liaison hydrogène à l'anion O(2). La groatite possède la même structure que l'arsenate acide o'danielite, et fait partie du groupe de l'alluaudite, en fait le premier membre à avoir un groupe phosphate acide. Le minéral est nommé en l'honneur de Lee A. Groat, Professeur de minéralogie à l'Université de la Colombie-Britannique à Vancouver, L'espèce nouvelle et son nom ont reçu l'approbation de la Commission des Nouveaux Minéraux, de Nomenclature et de Classification de l'Association Minéralogique Internationale (IMA 2008–054).

(Traduit par la Rédaction)

Mots-clés: groatite, nouvelle espèce minérale, groupe de l'alluaudite, pegmatite de Tanco, lac Bernic, Manitoba, Canada, structure cristalline, données de microsonde électronique.

INTRODUCTION

Groatite was collected on the dumps at the Tanco mine by one of the authors (RAR) in 1980. Systematic identification of the minerals in phosphate–carbonate parageneses revealed a possibly new phase, and this was subsequently shown to be the case. Using crystal-structure refinement and electron-microprobe analysis, we characterized the phase as a new alluaudite-group mineral, and present the results here. The new mineral is named in honor of Lee A. Groat (b. 1959), Professor of Mineralogy at the Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada, for his extensive contributions to Mineralogy in general, and to pegmatite mineralogy in particular. The species and the name *groatite* were approved by the Commission on New Minerals, Nomenclature and Classification, International Mineralogical Association (IMA 2008–054). Type groatite is deposited in the mineral collection of the Department of Natural History, Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario L8S 4M1, Canada, catalogue number M40501.

OCCURRENCE

The type locality of groatite, the Tanco granitic pegmatite, is located on the northwestern shore of Bernic Lake, Manitoba, close to the border of Manitoba and Ontario, about 180 km east–northeast of Winnipeg, Manitoba. The geology of the Tanco pegmatite was described most recently by Stilling *et al.* (2006). It is a zoned petalite-subgroup pegmatite (Černý 1991) hosted by the Bird River Greenstone Belt of the Superior Province. Groatite was found in a vug in a single 5–10 cm mass of phosphate–carbonate mineralization in a spodumene-rich boulder found on the dumps of the Tanco mine. The assemblage is primarily rhodochrosite, quartz, whitlockite, apatite, fairfieldite, an unidentified Na–Al phosphate, calcite and crandallite, with minor overite, groatite and metaswitzerite; a small mass of sphalerite with inclusions of galena and bismuthinite also is present. Surficially altered crystals of spodumene penetrate this assemblage. Groatite itself is most closely associated with whitlockite, crandallite, the unidentified Na–Al phosphate and quartz.

Groatite occurs sparingly as slightly divergent sprays of colorless to pale yellow acicular crystals on whitlockite (Fig. 1). Some crystals approach 1 mm in length, but the typical length is less than 0.5 mm. It also occurs as stellate sprays embedded in whitlockite and the unidentified Na–Al phosphate and as a tabular mass of densely intergrown acicular crystals. Groatite is part of a late-stage assemblage that may be secondary, derived from dissolution of lithiophosphate and primary lithiophilite by hydrothermal solutions.

The groatite-bearing assemblage from the Tanco pegmatite has never been described, so we take this opportunity to do so here. Whitlockite, ideally $Ca_9Mg(PO_3OH)(PO_4)_6$, is the main component of open boxwork structures; similar boxworks of apatite resulting from the dissolution of lithiophosphate

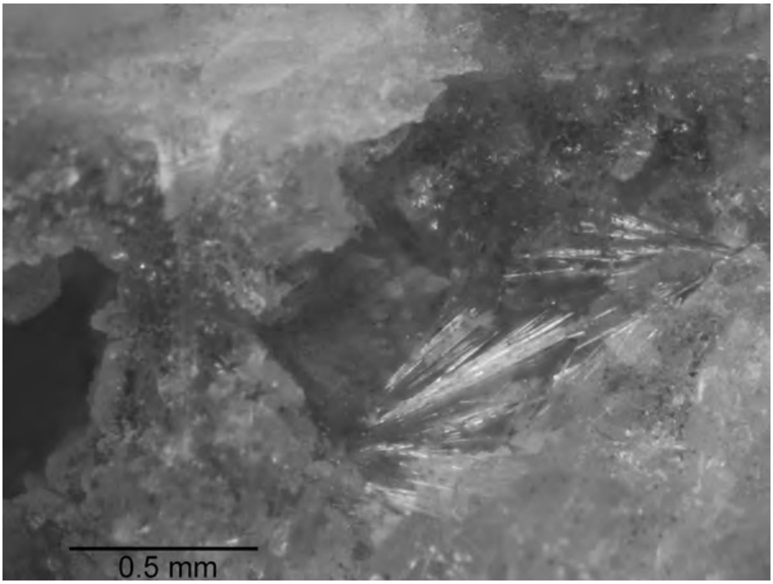

FIG. 1. Divergent sprays of colorless acicular crystals of groatite on whitlockite.

crystals are known elsewhere in the pegmatite. The boxwork surfaces are coated with euhedral crystals of whitlockite and other phosphates, including groatite. Pale yellowish brown hemispheres of crandallite, ideally $CaAl_3(PO_4)_2(OH)_5(H_2O)$, commonly coat the whitlockite, as do white flaky to powdery aggregates composed mainly of crandallite. Strontium-rich crandallite is closely associated with groatite; Ba-bearing crandallite was found elsewhere. Two distinct generations of fairfieldite, ideally $Ca_2Mn(PO_4)_2(H_2O)_2$, were noted: subparallel, platy white crystals, and a later generation of delicate sprays of white bladed crystals. A near end-member composition is indicated by semiquantitative energy-dispersive spectrometry.

The unidentified Na–Al phosphate mentioned earlier is white, shows at least one prominent cleavage, and provides a powder-diffraction pattern close to that of fairfieldite. Freely grown crystals have not been found. Manganese-bearing overite, $(Ca,Mn)MgAl(PO_4)_2(OH)(H_2O)_4$, forms tabular, colorless, transparent to translucent crystals grown on whitlockite. In some instances, overite crystals have been partly overgrown by sprays of a second generation of fairfieldite. An electron-microprobe analysis of a crystal indicated chemical homogeneity; the analysis gave CaO 12.3, Na_2O 0.3, MnO 2.6, FeO 0.5, MgO 10.3, Al_2O_3 14.0, P_2O_5 37.8, total 77.8 weight percent, with H_2O 22.8 wt% by difference (pers. commun., Pete Dunn, 1980). Manganese and Na likely substitute for Ca, and Fe for Mg. Overite is also known from an epithermal occurrence near the village of Zlatousha in western Bulgaria, and from the sediment-hosted type occurrence at Clay Canyon, near Fairfield, Utah. The Tanco mine is the sole occurrence in a pegmatite on record; the "overite" of the Mangualde pegmatite in Portugal was found to correspond to a "jahnsite-like" phase, and subsequently, other overite-like crystals have been characterized as rittmannite (pers. commun., Paolo Orlandi, 2007).Note that the Tanco pegmatite is also the type locality for two other phosphate minerals, tancoite (Ramik *et al.* 1980, Hawthorne 1983) and ercitite (Fransolet *et al.* 2000, Cooper *et al.* 2009).

PHYSICAL PROPERTIES

Groatite is translucent, colorless to pale yellow, and pale orange where massive, with a white streak and vitreous luster. Crystals do not fluoresce under ultraviolet light and are too small in cross-section to observe cleavage. The Mohs hardness is 3; the crystals are brittle with an uneven fracture; no parting or twinning was observed. The calculated density is 3.213 g/cm^3. Optical properties in transmitted light were measured on a Bloss spindle stage in monochromated Na light (λ = 590 nm) on the single crystal used for the crystal-structure study, and the program EXCALIBR II (Bartelmehs *et al.* 1992) was used to determine optic orientation (Gunter & Twamley 2001). Groatite is biaxial positive with α 1.622, β 1.634, γ 1.663 (all ±0.001), and is nonpleochroic; $2V$(obs.) = 67(1), $2V$(calc.) = 66.5°, $X \wedge a = 35.4$ (in β obtuse), $Y \wedge c = 10.1°$ (in β acute), $Z \parallel b$.

CHEMICAL COMPOSITION

A crystal was analyzed with a Cameca SX–100 electron microprobe operating in the wavelength-dispersion mode with an accelerating voltage of 15 kV, a specimen current of 10 nA, and a beam diameter of 3 μm. The following standards were used: apatite (P, Ca), fayalite (Fe), spessartine (Mn), and albite (Na). In addition, Sr, Ba, Pb, Mg, Al, K, Zn and As were sought but not detected; groatite is extremely homogeneous. The data were reduced and corrected by the PAP method of Pouchou & Pichoir (1985). Table 1 gives the chemical composition (mean of four determinations) and the formula unit based on 12 anions with 2 (OH) groups *pfu* (per formula unit) as determined by bond-valence requirements. Zinc was detected in one sample by micro X-ray-fluorescence spectrometric analysis. The empirical formula for groatite is $Na_{1.02}Ca_{1.02}Mn^{2+}_{1.90}Fe_{0.03}P_{3.02}O_{12}H_2$, and the end-member formula is $Na\,Ca\,Mn^{2+}_2\,(PO_4)\,[PO_3(OH)]_2$.

TABLE 1. CHEMICAL COMPOSITION AND CHEMICAL FORMULA OF GROATITE

P_2O_5 wt.%	46.66	P *apfu*	3.02
FeO	0.49	Fe	0.03
MnO	29.31	Mn	1.90
CaO	12.51	Ca	1.02
Na_2O	6.87	Na	1.02
H_2O*	3.93	OH	2
Total	99.77		

* calculated as two (OH) groups per formula unit.

X-RAY POWDER DIFFRACTION

A small aggregate of crystals was crushed and mounted on a Debye–Scherrer powder camera, and the powder-diffraction pattern was recorded with Ni-filtered Cu*K*α X-radiation (λ = 1.54178 Å). Table 2 shows the X-ray powder-diffraction data for groatite. The unit-cell dimensions were refined from 32 reflections (marked with asterisks in Table 2) representing values between 3.879 and 1.485 Å which could be indexed unambiguously on the basis of intensities from the single-crystal diffraction work. These values (Table 2) are close to the values determined by single-crystal diffraction (Table 3). The strongest six lines in the X-ray powder-diffraction pattern [d in Å(I)(hkl)] are as follows: 3.187(100)($\bar{1}12$), 2.726(90)($\bar{4}02$, 240), 6.204(80)(020), 2.788(80)(330), 5.653(70)(200), and 2.580(70)(32, 420).

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR GROATITE

$I_{est.}$	d_{meas} Å	d_{calc} Å	*h*	*k*	*l*
10	8.346	8.359	1	1	0
80	6.204	6.201	0	2	0
5	5.867	5.863	$\bar{1}$	1	1
70	5.653	5.658	2	0	0
5	4.201	4.180	2	2	0
*10	3.879	3.883	1	3	0
*30	3.608	3.609	3	1	0
3	3.513	3.511	$\bar{1}$	3	1
*100	3.187	3.188	$\bar{1}$	1	2
10	3.118	3.101	0	4	0
10	3.087	3.070	1	3	1
*20	3.005	3.002	$\bar{3}$	1	2
*5	2.833	2.829	4	0	0
*80	2.788	2.786	3	3	0
90	2.726	2.730	$\bar{4}$	0	2
		2.719	2	4	0
*5	2.661	2.658	3	1	1
70	2.580	2.578	$\bar{1}$	3	2
		2.574	4	2	0
*10	2.491	2.499	$\bar{4}$	2	2
*5	2.312	2.309	2	4	1
3	2.266	2.268	$\bar{2}$	4	2
*20	2.227	2.226	5	1	0
*30	2.185	2.183	$\bar{3}$	1	3
*5	2.150	2.150	2	2	2
10	2.118	2.121	$\bar{1}$	1	3
		2.119	$\bar{3}$	5	1
*20	2.071	2.072	3	5	0
*10	2.049	2.050	$\bar{5}$	3	2
*10	1.987	1.985	5	3	0
*10	1.962	1.963	$\bar{6}$	2	1
20	1.942	1.942	2	6	0
		1.935	$\bar{3}$	5	2
*5	1.886	1.886	6	0	0
*15	1.852	1.852	5	1	1
*10	1.833	1.833	3	5	1
*10	1.810	1.809	$\bar{2}$	4	3
*30	1.787	1.788	3	3	2
*10	1.746	1.747	$\bar{6}$	2	3
*5	1.725	1.721	$\bar{6}$	4	1
*5	1.701	1.704	$\bar{6}$	4	2
10	1.691	1.692	1	3	3
		1.692	0	4	3
*5	1.672	1.672	5	5	0
*30	1.649	1.649	$\bar{2}$	0	4
*15	1.627	1.626	$\bar{1}$	5	3
*5	1.609	1.611	6	4	0
*20	1.565	1.563	$\bar{8}$	0	2
*5	1.538	1.538	$\bar{3}$	7	2
*30	1.506	1.506	7	3	0
*30	1.485	1.485	3	7	1

* reflections used to calculate the unit-cell dimensions: *a* 12.519(7), *b* 12.402(6), *c* 6.700(5) Å, β 115.33(5)°.

CRYSTAL-STRUCTURE REFINEMENT

A single crystal of groatite was attached to a glass fiber and mounted on a Bruker *P*4 diffractometer equipped with a 4K CCD detector and a Mo*K*α X-ray tube. A total of 5,800 reflections was measured (2,873 in the Ewald sphere) out to 50°2θ with a frame time of 120 s and a frame width of 0.2°. The data were corrected for absorption, Lorentz, polarization and background effects, averaged and reduced to structure factors. After data collection, the crystal used for X-ray diffraction was used for measurement of optical properties as described above.

All calculations were done with the SHELXTL C (Plus) system of programs; *R* indices are expressed as percentages. Systematic absences in the single-crystal X-ray-diffraction data are consistent with the space groups *C*2/*c* and *Cc*. The structure was solved by direct methods in the space group *C*2/*c*. The resulting arrangement of atoms is isostructural with that of o'danielite (Keller & Hess 1988), and the structure was refined using the site nomenclature of Hatert *et al.* (2000). Full-matrix least-squares refinement of all variables converged rapidly to an *R* index of 2.7% based on 831 unique reflections. At the final stages of refinement,

TABLE 3. MISCELLANEOUS INFORMATION ABOUT GROATITE

a (Å)	12.5435(9)	crystal size (μm)	7 × 12 × 260
b	12.4324(9)	radiation/monochromater	Mo*K*α / Graphite
c	6.7121(4)	No. of reflections	5800
β (°)	115.332(2)	No. in Ewald sphere	2873
V (Å³)	946.07(19)	No. unique reflections	831
Space group	*C*2/*c*	No. $\vert F_o\vert > 4\sigma(\vert F\vert)$	743
Z	4	R_{merge} %	2.5
D_{calc} (g/cm³)	3.213	R_1 %	2.7
		wR_2 %	6.4

$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$

$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{½}$, $w = 1/[\sigma^2F_o^2 + (aP)^2 + bP]$ and a = 0.0299, b = 5.29 and $P = [\max(F_o^2,0) + 2F_c^2]/3$

TABLE 4. COORDINATES AND DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN GROATITE

		x	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
A(2)'	Na	0	–0.0439(2)	0.25	0.0284(6)	0.0196(13)	0.0455(16)	0.0152(11)	0	0.0029(10)	0
M(1)	Ca	0	0.28883(8)	0.25	0.0119(3)	0.0116(6)	0.0098(5)	0.0155(5)	0	0.0070(5)	0
M(2)	Mn	0.28243(5)	0.66313(4)	0.36073(9)	0.01008(18)	0.0111(3)	0.0080(3)	0.0112(3)	0.0002(2)	0.0049(2)	0.0001(2)
T(1)	P	0	0.68999(10)	0.25	0.0085(3)	0.0090(7)	0.0078(6)	0.0081(6)	0	0.0031(5)	0
T(2)	P	0.21416(8)	0.89604(7)	0.11515(14)	0.0089(2)	0.0104(5)	0.0070(4)	0.0091(4)	0.0000(3)	0.0041(4)	0.0000(4)
O(1)		0.4548(2)	0.7384(2)	0.5439(4)	0.0119(6)	0.0117(14)	0.0132(13)	0.0094(12)	–0.0019(10)	0.0032(11)	0.0002(11)
O(2)		0.0980(2)	0.6176(2)	0.2399(4)	0.0136(6)	0.0111(14)	0.0094(12)	0.0198(13)	–0.0009(11)	0.0062(11)	0.0006(11)
O(3)		0.3403(2)	0.6683(2)	0.0986(4)	0.0129(6)	0.0161(14)	0.0117(12)	0.0114(13)	–0.0003(10)	0.0064(11)	–0.0018(11)
O(4)	(OH)	0.1528(2)	0.4220(2)	0.3401(4)	0.0144(6)	0.0121(14)	0.0085(13)	0.0226(14)	0.0011(11)	0.0074(12)	0.0023(11)
O(5)		0.2178(2)	0.8289(2)	0.3081(4)	0.0115(6)	0.0105(14)	0.0115(12)	0.0110(13)	0.0005(10)	0.0032(11)	0.0010(10)
O(6)		0.3501(2)	0.5020(2)	0.4042(4)	0.0127(6)	0.0120(14)	0.0093(12)	0.0163(13)	0.0020(10)	0.0057(11)	–0.0006(11)
H(1)		0.128(5)	0.4970(16)	0.305(10)	0.07(2)						

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN GROATITE

T(1)– O(1)c,i	1.535(2)	×2	*M*(2)– O(1)	2.188(3)	
T(1)– O(2),j	1.548(3)	×2	*M*(2)– O(2)	2.174(3)	
<*T*(1)–O>	1.542		*M*(2)– O(3)	2.173(2)	
			M(2)– O(5)	2.187(3)	
T(2)– O(3)g	1.525(3)		*M*(2)– O(5)c	2.227(2)	
T(2)– O(4)k	1.597(3)		*M*(2)– O(6)	2.147(3)	
T(2)– O(5)	1.525(3)		<*M*(2)–O>	2.183	
T(2)– O(6)k	1.521(3)				
<*T*(2)–O>	1.542		*A*(2) – O(1)a,e	2.722(3)	×2
			A(2) – O(3)b,d	3.203(3)	×2
M(1)– O(1)b,d	2.359(2)	×2	*A*(2) – O(5)f,h	3.034(3)	×2
M(1)– O(3)b,d	2.356(3)	×2	*A*(2) – O(6)a,e	2.336(3)	×2
M(1)– O(4),j	2.406(3)	×2	*A*(2) – O(6)b,d	2.568(3)	×2
<*M*(1)–O>	2.374		<*A*(2) –O>	2.665	
O(4)– H(1)	0.9800(11)				
H(1)....O(2)	1.562(7)				
O(4)– O(2)	2.539(4)				
O(4)–H(1)–O(2)	174(6)				

a: $\bar{x} + ½$, $\bar{y} + ½$, $\bar{z} + 1$; b: x – ½, y – ½, z; c: $\bar{x} + ½$, $\bar{y} + {}^3/_2$, $\bar{z} + 1$; d: $\bar{x} + ½$, y – ½, $\bar{z} + ½$; e: x–½, $\bar{y} + ½$, z – ½; f: x, y – 1, z; g: $\bar{x} + ½$, $\bar{y} + {}^3/_2$, $\bar{z}$; h: $\bar{x}$, y – 1, $\bar{z} + ½$; i: x – ½, $\bar{y} + {}^3/_2$, z – ½; j: $\bar{x}$, y, $\bar{z} + ½$; k: $\bar{x} + ½$, y + ½, $\bar{z} + ½$.

a small residual peak was observed in the difference-Fourier map ~1 Å from the O(4) site. A hydrogen atom was inserted into the refinement at this position, H(1), and was refined with the soft constraint that O(4)–H be approximately 0.98 Å. Final refined coordinates and anisotropic-displacement factors are listed in Table 4, and selected interatomic distances and angles are given in Table 5. Observed and calculated structure-factors may be obtained from the Depository of Unpublished Data, MAC website [document Groatite CM47_1225].

CRYSTAL STRUCTURE

Groatite is isostructural with other synthetic compounds with the protonated alluaudite-type structure (*e.g.*, Leroux *et al.* 1995a, b). There are two *T* sites occupied by P. The *T*(1) site is tetrahedrally coordinated by O atoms with a <*T*(1)–O> distance of 1.542 Å, close to the grand <P–O> distance of 1.537 Å given for phosphate minerals by Huminicki & Hawthorne (2002). The *T*(2) site is tetrahedrally coordinated by three O atoms and one (OH) group with a <*T*(2)–O> distance of 1.542 Å. As noted above, O(4) is the O atom of an (OH) group, and location of the H atom allows resolution of the pattern of hydrogen bonding in groatite (Table 5). The H(1) atom hydrogen-bonds to O(2) at a distance of 1.562 Å and an O(4)–H(1)...O(2) angle of 174°. The incident bond-valence sum at O(2) without considering the hydrogen bond is 1.56 *vu* (valence units) (Table 6), indicating a strong hydrogen bond. The incident bond-valence sum at O(4) without considering the hydrogen bond is 2.37 *vu* [0.31 + 1.06 + 1 *vu* from *M*(1) + *T*(2) + H; Table 6]. Assigning a hydrogen bond of strength 0.35 *vu* to O(2) brings the incident bond-valence sums of O(2) and O(4) close to the value of 2 *vu* required by the valence-sum rule (Brown 2002). This is a strong hydrogen bond, in accord with the short H(1)...O(2) distance (Table 5) and the almost straight O(donor)–H...O(acceptor) angle: 174°.

There are two octahedrally coordinated sites, *M*(1) and *M*(2). The observed site-scattering, mean bond-lengths (Table 5) and incident bond-valence sums (Table 6) at these sites are in agreement with complete chemical order of Ca at *M*(1) and Mn^{2+} at *M*(2). There is one *A*(2)' site, occupied by Na and surrounded by ten anions.

RELATION TO ALLUAUDITE-GROUP MINERALS AND COMPOUNDS

The crystal structure of alluaudite was solved by Moore (1971). Since then, there has been a considerable amount of work on alluaudite-group minerals and synthetic compounds, both structural and paragenetic (Fransolet 1977, Hatert *et al.* 2006). Minerals of this structure type occur as both phosphates [*e.g.*, hagendorfite, $(Na,Ca)MnFe_2(PO_4)_3$, Redhammer *et al.* (2005)] and arsenates [o'danielite, $Na(Zn,Mg)_3H_2(AsO_4)_3$, Keller *et al.* (1981a), Keller & Hess (1988); johillerite, $Na(Mg,Zn)_3Cu(AsO_4)_3$, Keller *et al.* (1982), Keller & Hess (1988), Tait & Hawthorne (2004); carynite, $NaCa_2Mn^{2+}{}_2(AsO_4)_3$, Ercit (1993), yazganite, $NaFe^{3+}{}_2(Mg,Mn)\ (AsO_4)_3(H_2O)$, Sarp & Černý (2005)]. The alluaudite structure-type has been investigated extensively with regard to synthesis and characterization of both mineralogically similar compositions [*e.g.*, $Na_2(Fe^{3+}{}_{0.5}Fe^{2+}{}_{0.5})_2Fe^{2+}(PO_4)_3$, Yakubovich *et al.* (1977); $NaMn_3(PO_4)(HPO_4)_2$, Leroux *et al.* (1995b); $Na_{1.50}Mn_{2.48}Al_{0.85}(PO_4)_3$, Hatert (2006); $(Na_{1-x}Li_x)MnFe_2(PO_4)_3$, Hatert *et a*l. (2000, 2004); $Na_2(Mn_{1-x}Fe^{2+}{}_x)_2Fe^{3+}(PO_4)_3$, Hatert *et al.* (2005)] and compositions that are unlikely as minerals but are of crystal-chemical interest [*e.g.*, $Na_3In_2(AsO_4)_3$, Khorari *et al.* (1997), Hatert *et al.* (2003); $Na_{1.5}(Mn_{1-x}M^{2+}{}_x)_{1.5}Fe_{1.5}(PO_4)_3$ (x = 0 to 1, $M^{2+} = Cd^{2+}, Zn^{2+}$), Hatert (2008)].

TABLE 6. BOND-VALENCE* (*vu*) TABLES

	A(2)'	*M*(1)	*M*(2)	*T*(1)	*T*(2)	H(1)	Σ
			Groatite				
O(1)	$0.08^{\times2}\downarrow$	$0.35^{\times2}\downarrow$	0.34	$1.25^{\times2}\downarrow$			2.02
O(2)			0.35	$1.21^{\times2}\downarrow$		0.35	1.91
O(3)	$0.02^{\times2}\downarrow$	$0.35^{\times2}\downarrow$	0.36		1.28		2.01
O(4)		$0.31^{\times2}\downarrow$			1.06	0.65	2.02
O(5)	$0.04^{\times2}\downarrow$		0.34 0.31		1.28		1.97
O(6)	$0.24^{\times2}\downarrow$ $0.13^{\times2}\downarrow$		0.38		1.30		2.05
Σ	1.02	2.02	2.08	4.92	4.92	1.00	
			$NaCo_3(PO_4)[PO_3(OH)]_2$				
O(1)	$0.05^{\times2}\downarrow$	$0.30^{\times2}\downarrow$	0.30	$1.24^{\times2}\downarrow$			1.89
O(2)			0.34	$1.21^{\times2}\downarrow$		**	1.55
O(3)	$0.05^{\times2}\downarrow$	$0.30^{\times2}\downarrow$	0.35		1.24		1.94
O(4)		$0.27^{\times2}\downarrow$			1.09	**	1.36
O(5)	$0.03^{\times2}\downarrow$		0.34 0.33		1.29		1.99
O(6)	$0.27^{\times2}\downarrow$ $0.18^{\times2}\downarrow$		0.36		1.31		2.12
Σ	1.16	1.74	2.02	4.90	4.93		
			$NaFe_3(PO_4)[PO_3(OH)]_2$				
O(1)	$0.04^{\times2}\downarrow$	$0.35^{\times2}\downarrow$	0.27	$1.23^{\times2}\downarrow$			1.89
O(2)			0.36	$1.22^{\times2}\downarrow$		**	1.58
O(3)	$0.04^{\times2}\downarrow$	$0.30^{\times2}\downarrow$	0.39		1.26		1.99
O(4)		$0.27^{\times2}\downarrow$			1.08	**	1.35
O(5)	$0.03^{\times2}\downarrow$		0.33 0.36		1.30		2.02
O(6)	$0.25^{\times2}\downarrow$ $0.18^{\times2}\downarrow$		0.37		1.30		2.10
Σ	1.08	1.84	2.08	4.90	4.94		
			$NaMn_3(PO_4)[PO_3(OH)]_2$				
O(1)	$0.03^{\times2}\downarrow$	$0.31^{\times2}\downarrow$	0.31	$1.25^{\times2}\downarrow$			1.90
O(2)			0.37	$1.18^{\times2}\downarrow$		**	1.55
O(3)	$0.05^{\times2}\downarrow$	$0.31^{\times2}\downarrow$	0.37		1.28		2.01
O(4)		$0.27^{\times2}\downarrow$			1.08	**	1.35
O(5)	$0.03^{\times2}\downarrow$		0.36 0.33		1.30		2.02
O(6)	$0.26^{\times2}\downarrow$ $0.17^{\times2}\downarrow$		0.40		1.28		2.11
Σ	1.08	1.78	2.14	4.86	4.94		

* Bond-valence curves from Brown & Altermatt (1985); ** hydrogen bonding not interpreted.

Groatite, Na Ca $Mn^{2+}{}_2$ (PO_4) $[PO_3(OH)]_2$, is isostructural with o'danielite, ideally Na (Zn,Mg)$_3$ (AsO_4) $[AsO_3(OH)]_2$ (Keller *et al.* 1981a, Keller & Hess 1988). The list of protonated alluaudite-structure compounds of general formula $A\ M(1)\ M(2)_2\ [T(1)O_4]\ [T(2)O_3(OH)]_2\ \{T = P, As\}$ with refined structures is quite extensive, and contains two minerals, groatite and o'danielite (Table 7). Groatite contains the largest *M*(1) cation thus far for the structure type (*i.e.*, Ca), and further extends the chemical diversity already present within this group of structures.

CATION ORDERING IN GROATITE

The chemical and structural results for groatite show that Na is fully ordered at the *A*(2)' site, Ca at *M*(1) and Mn^{2+} at *M*(2). This general distribution of cations is expected within the alluaudite family of structures. However, complete order of these constituents over these structural sites is somewhat unexpected in a mineral. For example, one might anticipate minor Na,Ca disorder over *A*(2)' and *M*(1), or perhaps some degree of Mn-for-Ca solid solution at *M*(1) as being likely in a mineral. However, within the experimental errors of the electron-microprobe data and structure refinement for the sample of groatite studied here, neither of these more complicated patterns of cation distribution occur; groatite is completely ordered.

STRUCTURAL TRENDS IN PROTONATED ALLUAUDITE-SUBGROUP PHASES

There are four known phosphate members of the protonated alluaudite subgroup that contain Na at the *A*(2)' site (the first four compounds in Table 7), and these differ only in terms of the occupants of the octahedrally coordinated *M* sites. The three synthetic compounds each contain only one type of *M* cation (Co^{2+}, Fe^{2+} or Mn^{2+}), whereas groatite contains two types of *M* cation [$M(1) = Ca$, $M(2) = Mn^{2+}$]. There are well-defined linear relations between <*M*–O> distance and constituent-cation radius for the *M*(1) and *M*(2) sites, with slopes of 0.89 and 0.97, respectively (Fig. 2). Figure 3 shows the variation in <*M*(2)–O> distance with the <*M*(1)–O> distance for the four phosphate structures (shaded circles) and the three arsenate structures (crosses) of the protonated alluaudites that contain Na at the *A*(2)' site. All data (except those for groatite) lie along a linear trend that is displaced ~0.05 Å above the 1:1 reference line.

For synthetic compounds with the same cation at *M*(1) and *M*(2), the *M*(1) polyhedron is systematically larger than the *M*(2) polyhedron, which shares two of its edges (Redhammer *et al*. 2005, Hatert 2008). O'danielite plots close to the linear trend defined by the synthetic phases, even though the constituent *M*(1) and *M*(2) cations differ appreciably; this is because the radii (Shannon 1976) for Mg (0.72 Å) and Zn (0.74 Å) are very similar, and the site occupancies, *M*(1) = $Zn_{0.6}Mg_{0.4}$ and *M*(2) = Zn (Keller & Hess 1988), lead to very similar constituent radii at the two sites [$^{M(1)}r$ = 0.732 , $^{M(2)}r$ = 0.740 Å]. Groatite plots far above the linear relation for the other compounds, consistent with the occupancy of *M*(1) by a large cation ($^{[6]}$Ca = 1.00 Å) and *M*(2) by a smaller cation ($^{[6]}Mn^{2+}$ = 0.83 Å). The P and As structures show the same trend in Figure 3, indicating that the two octahedra in this structure type respond in a very similar fashion irrespective of the tetrahedrally coordinated cation.

Distortion indices for *M*-site bond-lengths $BLD = 100 \sum_{i=1}^{6} |(M - O)_i - (\langle M - O \rangle)| / 6 \langle M - O \rangle$ (Renner & Lehmann 1986) and bond angles $OAV = \sum_{i=1}^{12} (\theta_i - 90°)^2 / 11$ (Robinson *et al*. 1971) are shown for the phosphates in Figures 4a and 4b, respectively. For the three synthetic compounds: (1) *BLD* increases in the sequence $Co^{2+} \rightarrow Mn^{2+} \rightarrow Fe^{2+}$ (Fig. 4a); (2) *OAV* is essentially invariant at *M*(1) and increases at *M*(2) in the same $Co^{2+} \rightarrow Mn^{2+} \rightarrow Fe^{2+}$ sequence, with the *M*(1) polyhedron showing greater angular distortion than the *M*(2) polyhedron (Fig. 4b). If groatite is compared to the synthetic phase with *M*(2) = Mn^{2+}, it is apparent that the presence of Ca at *M*(1) in groatite leads to a relative reduction in both *BLD* (Fig. 4a) and *OAV* (Fig. 4b) at the adjacent *M*(2) site, whereas the OAV of the *M*(1) polyhedron in groatite is much larger than in the other synthetic phases (Fig. 4b), in accord with the conclusion of Redhammer *et al*. (2005) that the angular distortion of the *M*(1) octahedron is large where there is a large difference in size between the *M*(1) and *M*(2) cations.

The variation in cell parameters for the phosphate alluaudite structures is shown as a function of <*M*(1)–O> in Figure 5. For the synthetic compounds (*M* = Co^{2+}, Mn^{2+}, Fe^{2+}), the radius of the *M*(1) cation increases from 0.745 to 0.83 Å, and the corresponding increase in <*M*(1)–O> is positively correlated with an increase in all cell parameters. In groatite, the incorporation of a significantly larger cation at *M*(1) ($^{[6]}$Ca = 1.00 Å) results in a large expansion of the unit cell along the *a* axis and only marginal increases along the *b* and *c* axes, relative to the synthetic Mn analogue (Fig. 5a). The β

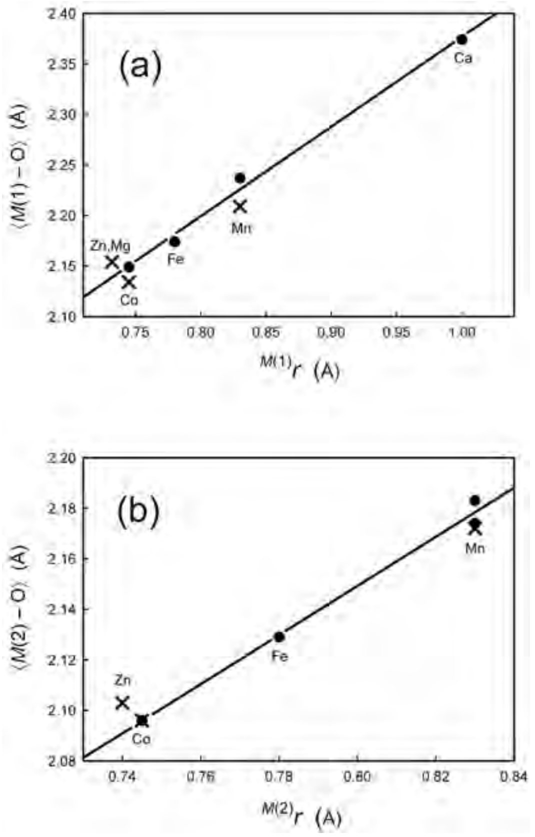

FIG. 2. Variation in <*M*–O> distance as a function of constituent-cation radius, ^{M}r, for the protonated-phosphate-based alluaudite structures: (a) *M*(1), (b) *M*(2); circles: phosphates; crosses: arsenates. Regression lines (for the phosphates only) are shown. <*M*(1)–O> = 1.49(4) + 0.89(5) $^{M(1)}r$ [r^2 = 0.994(14)]; <*M*(2)–O> = 1.37(5) + 0.97(6)$^{M(2)}r$ [r^2 = 0.992(6)].

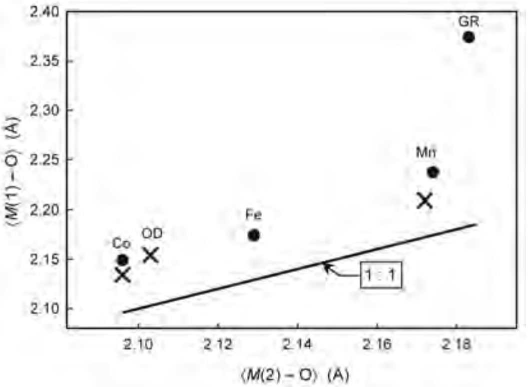

FIG. 3. Variation in <*M*(1)–O> *versus* <*M*(2)–O> distance for the protonated alluaudite structures; legend as in Figure 2, OD: o'danielite, GR: groatite. The 1 : 1 line is included for comparative purposes.

TABLE 7. PROTONATED ALLUAUDITE-LIKE COMPOUNDS: $A\ M(1)\ M(2)_2\ [T(1)O_4)]\ [T(2)O_3(OH)]_2$

Formula unit					*a*	*b*	*c*	β	V	Ref.
Na	Co	Co_2	(PO_4)	$[PO_3(OH)]_2$	11.865(2)	12.137(2)	6.512(1)	114.12(1)	855.9(2)	[1]
Na	Fe	Fe_2	(PO_4)	$[PO_3(OH)]_2$	11.998(1)	12.328(1)	6.500(1)	114.185(6)	877.04	[2],[9]
Na	Mn	Mn_2	(PO_4)	$[PO_3(OH)]_2$	12.179(2)	12.405(1)	6.6602(8)	114.616(7)	914.7(2)	[3]
Na	**Ca**	**Mn_2**	**(PO_4)**	**$[PO_3(OH)]_2$**	**12.5435(9)**	**12.4324(9)**	**6.7121(4)**	**115.332(2)**	**946.08(19)**	**[4]**
Na	Zn,Mg	Zn_2	(AsO_4)	$[AsO_3(OH)]_2$	12.113(3)	12.445(4)	6.793(1)	112.87(2)	943.52	[5]
Na	Co	Co_2	(AsO_4)	$[AsO_3(OH)]_2$	12.054(1)	12.378(1)	6.780(2)	113.01(1)	931.0(3)	[1]
Na	Mn	Mn_2	(AsO_4)	$[AsO_3(OH)]_2$	12.299(3)	12.735(3)	6.893(2)	113.587(4)	989.5(4)	[6]
Ag	Ni	Ni_2	(PO_4)	$[PO_3(OH)]_2$	11.865(4)	12.117(3)	6.467(2)	113.82(3)	850.6(4)	[7]
Ag	Co	Co_2	(PO_4)	$[PO_3(OH)]_2$	12.035(2)	12.235(2)	6.541(2)	114.14(2)	878.9(3)	[8]
Ag	Mn	Mn_2	(PO_4)	$[PO_3(OH)]_2$	12.263(1)	12.446(1)	6.649(1)	114.708(8)	921.9(2)	[9]
Ag	Zn	Zn_2	(AsO_4)	$[AsO_3(OH)]_2$	12.169(2)	12.495(3)	6.755(1)	112.77(1)	947.06	[10]
Ag	Co	Co_2	(AsO_4)	$[AsO_3(OH)]_2$	12.159(6)	12.438(7)	6.782(3)	113.16(3)	943.01	[10]
Ag	Mn	Mn_2	(AsO_4)	$[AsO_3(OH)]_2$	12.397(2)	12.707(2)	6.8904(6)	113.57(1)	994.8(2)	[11]
K	Mn	Mn_2	(AsO_4)	$[AsO_3(OH)]_2$	12.706(3)	12.731(3)	6.937(2)	113.175(5)	1031.6(4)	[6]

[1] Lii & Shih (1994), [2] Corbin *et al.* (1986), [3] Leroux *et al.* (1995b), [4] this work, [5] o'danielite = Keller & Hess (1988), [6] Stock *et al.* (2001), [7] Ben Smail & Jouini (2002), [8] Guesmi & Driss (2002), [9] Leroux *et al.* (1995a), [10] Keller *et al.* (1981b), [11] Stock & Bein (2003).

angle shows a near-linear positive correlation with the size of the $M(1)$ polyhedron (Fig. 5b). The departure of groatite from the linear trend in the cell volume *versus* $<M(1)–O>$ plot (Fig. 5b) results from the mixed $M(1)$ = Ca, $M(2)$ = Mn^{2+} composition in groatite; the cell volume shows a linear relation with $^{M}< r >$ (adjusted for site multiplicity) (Fig. 6).

Bond valences are shown for the three synthetic phosphates in Table 6. The greatest difference between the three synthetic phosphates and groatite occurs for the bond-valence sums at the $M(1)$ and O(1) sites. The mean valence-sums at $M(1)$ and O(1) in the synthetic compounds are 1.79 and 1.89 *vu*, compared to 2.02 and 2.02 *vu*, respectively, in groatite. It is thus apparent that a relatively larger cation at the $M(1)$ site and a smaller cation at $M(2)$ lead to lower structural strain than identically sized cations at both sites. This should affect the partitioning of cations between the $M(1)$ and $M(2)$ sites in the alluaudite-type structures, and inspection of site populations in some of the chemically more simple alluaudite-group minerals (*sensu lato*) shows this to be the case. Thus in carynite (Ercit 1993), $M(1)$ = 0.67 Ca + 0.33 Mn^{2+} and $M(2)$ = 0.72 Mn^{2+} + 0.28 Mg, and in arseniopleite (Tait & Hawthorne 2003), $M(1)$ = 1.00 Mn^{2+} and $M(2)$ = 0.61Mn^{2+} + 0.26 Mg + 0.13 Fe^{3+}; in both cases, the smaller cations show maximum order at $M(2)$, as suggested above.

In groatite, Ca completely orders at $M(1)$ and Mn^{2+} completely orders at $M(2)$, resulting in an increase in the β angle and *a* cell parameter, relative to the synthetic compound with $M(1)$ = $M(2)$ = Mn^{2+}. The $M(1)$ polyhedron in groatite shows greater angular distortion (relative to other protonated alluaudites), although the bond-valence sums at the *M* sites in groatite are at their

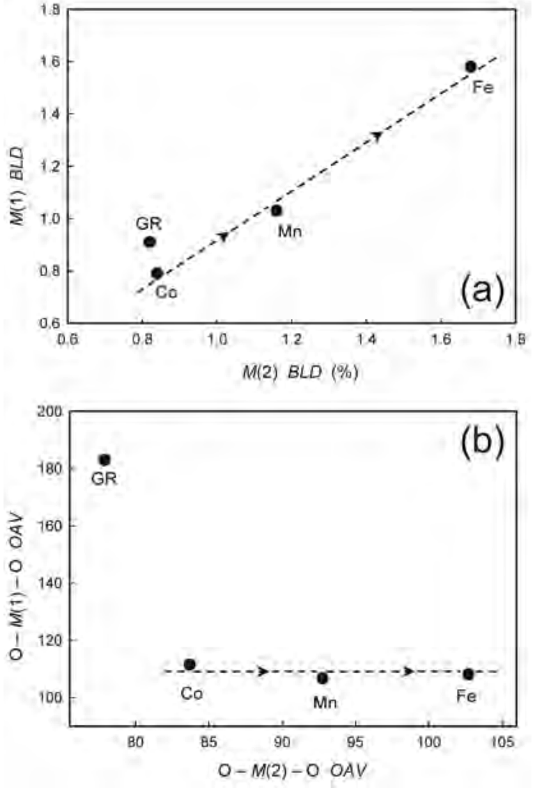

FIG. 4. Variation in (a) bond-length distortion, *BLD;* and (b) bond-angle distortion, *OAV*, for the $M(1)$ *vs* the $M(2)$ octahedra in protonated phosphate–alluaudite structures.

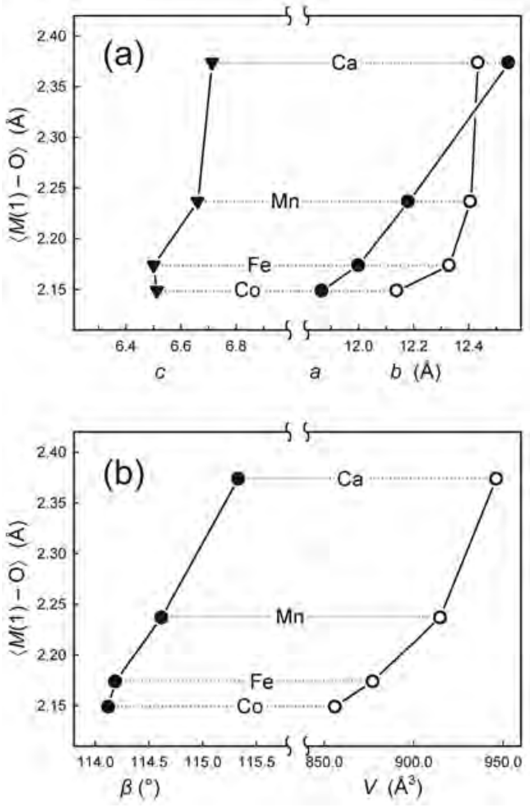

FIG. 5. (a) Variation in <*M*(1)–O> as a function of the *c* (triangles), *a* (black circles) and *b* (white circles) cell dimensions; (b) variation in <*M*(1)–O> as a function of β (black circles) and V (white circles).

ideal values, indicating that the groatite structure has minimum strain with the larger Ca cation at *M*(1) and the smaller Mn^{2+} cation at *M*(2). The *M*(1) polyhedron in groatite has an *OAV* value of 183, which is at the lower end of the range for the unprotonated alluaudite compounds examined by Redhammer *et al*. (2005) (*OAV* ≈ 180–300), and indicates that the angular distortion at the *M*(1) polyhedron in groatite is not anomalously high. The unprotonated alluaudite compounds listed by Redhammer *et al*. (2005) have ${}^{M(2)}r\ /\ {}^{M(1)}r$ values between 0.8 and 0.9. The synthetic protonated alluaudite structures [with the same cation at *M*(1) and *M*(2)] have ${}^{M(2)}r\ /\ {}^{M(1)}r$ values of 1, whereas groatite has an ${}^{M(2)}r\ /\ {}^{M(1)}r$ value of 0.83, comparable with that of the unprotonated alluaudite compounds. Where more than one type of cation (suitable for the *M* sites) is available during crystallization, it seems that the alluaudite structure (protonated and unprotonated) prefers to accommodate larger cations at *M*(1) and smaller cations at *M*(2). For the synthetic protonated alluaudite compounds examined here, only one suitable *M* cation was available during formation, and that cation occupies both *M* sites, apparently leading to structural strain, as indicated by the low bond-valence sums at the *M*(1) site. The structure of o'danielite raises an interesting issue concerning *M*-site cation ordering: two differently sized cations were available during crystallization (Zn: ${}^{[6]}r = 0.74$, Mg: ${}^{[6]}r = 0.72$ Å), and the smaller of the two cations is completely ordered at the larger *M*(1) polyhedron [$M(1) = Zn_{0.6}Mg_{0.4}$; $M(2) = Zn$]. With regard to the relative variation of the *M*(1) and *M*(2) octahedra (Fig. 3), o'danielite falls on the same trend as the other phosphates and arsenates of the protonated alluaudites, and we are left to conclude that Zn prefers the more regular polyhedron [*i.e*., *M*(2)].

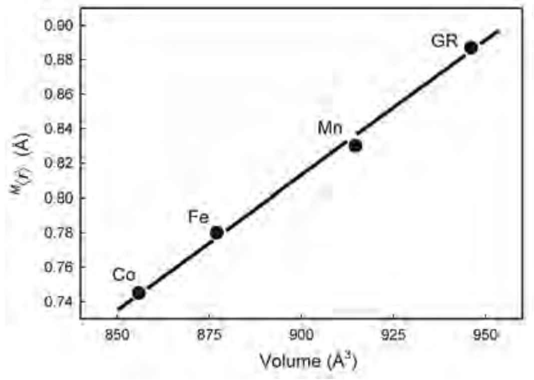

FIG. 6. Variation in mean radius of the *M* cation as a function of cell volume, *V*, in the protonated phosphate–alluaudite structures; legend as in Figures 2 and 3.

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