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Palenzonaite, berzeliite, and manganberzeliite: $(As^{5+},V^{5+},Si^{4+})O_4$ tetrahedra in garnet structures

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ABSTRACT

Schäferite, $NaCa_2Mg_2(V^{5+}O_4)_3$; palenzonaite, $NaCa_2Mn^{2+}_2(V^{5+}O_4)_3$; berzeliite, $NaCa_2Mg_2(As^{5+}O_4)_3$; and manganberzeliite, $NaCa_2Mn^{2+}_2(As^{5+}O_4)_3$, are cubic minerals with garnet structures (space group $Ia\bar{3}d$) in which tetrahedrally coordinated V^{5+} and/or As^{5+} at the *Z* site are charge balanced by disordered Na^+ and Ca^{2+} at the *X* site, and divalent Mg^{2+} and Mn^{2+} cations at the octahedrally coordinated *Y* site. The crystal chemistry of palenzonaite (from the Molinello and Gambatesa mines, Italy, and the Fianel mine, Switzerland), berzeliite (from Långban, Sweden, and Montaldo, Italy), and manganberzeliite (from Varenche, Italy, and the Gozaisho mine, Japan) were studied by electron microprobe analysis and single-crystal X-ray diffraction methods. Structure refinements converged to R_1 values of 1.36–2.42%. The tetrahedral site in these garnet structures is mainly occupied by pentavalent As^{5+} or V^{5+} (only up to about 20% randomly distributed Si^{4+} is present). Charge balance is maintained by variations in the Ca/Na ratio at the *X* site. Heterovalent substitution ($Na^+ \leftrightarrow Ca^{2+}$) at the distorted square antiprism *X* site in vanadate- and arsenate-bearing garnets allows full occupancy of the octahedral Y site by divalent cations (primarily Mg^{2+} and Mn^{2+}). There is a positive correlation between the <*Z*–O> and <*Y*–O> bond lengths and the mean ionic radii of the substituent elements, but there is no correlation between the <*X*–O> bond length and the variable Na/Ca site occupancy. The ionic radii of octahedrally coordinated Mg^{2+} and Mn^{2+} are such that the shared octahedral–dodecahedral edges are similar in length to the unshared octahedral edges, which is a measure of lattice distortion in garnet structures.

KEYWORDS: palenzonaite, berzeliite, manganberzeliite, schäferite, garnet, crystal structure, As, V, pentavalent cations, tetrahedral site.

Introduction

THE general formula for minerals with a garnet structure can be written $X_3Y_2(ZO_4)_3$. In the well known rock-forming silicate garnets, the *X* and *Y* sites are occupied by divalent and trivalent cations, respectively. A few non-silicate minerals including schäferite, ideally $NaCa_2Mg_2(V^{5+}O_4)_3$; palenzonaite, ideally $NaCa_2Mn^{2+}_2(V^{5+}O_4)_3$; berzeliite, ideally $NaCa_2Mg_2(As^{5+}O_4)_3$; and manganberzeliite, ideally $NaCa_2Mn^{2+}_2(As^{5+}O_4)_3$, have garnet structures. These vanadates and arsenates contain variable amounts of V^{5+}, As^{5+}, and Si^{4+} at the tetrahedral *Z* site. Due to their rarity, compositional heterogeneity and small crystal size, the structures of these minerals have not been studied in detail. However, the structure and properties of synthetic vanadate and arsenate garnets have been the subject of significant research (e.g. Bayer, 1965; Ito, 1968; Dukhovskaya and Mill, 1974; Schwarz and Schmidt, 1972, 1975; Nakatsuka *et al*., 2003, 2004*a*,*b*; Iishi and Ikuta, 2006). In the vanadate

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and arsenate garnets studied here, the eight-coordinated *X* site contains Na^{+} and Ca^{2+} and the octahedrally coordinated *Y* site contains either Mn^{2+} or Mg^{2+}.

Palenzonaite was first described as thin veinlets in Mn-bearing calcite with braunite, cutting black manganese ore at the Molinello mine, Val Graveglia, Liguria, Italy (Basso, 1987). It also occurs with rare and unusual Mn arsenates, vanadates and silicates at several metamorphic Mn deposits in northern Italy and Switzerland (Brugger, 1995; Barresi *et al*., 2005, Roth and Meisser, 2011).

The only known locality for schäferite is the Bellberg volcano in the Eifel district, Germany, where it was found in a small cavity in a silicate xenolith in leucite tephrite lava (Krause *et al*., 1999).

Manganberzeliite has recently been reported from Varenche, and berzeliite from the Montaldo mine in same district where palenzonaite occurs (Barresi *et al*., 2005; Piccoli *et al*., 2007). Berzeliite and manganberzeliite are among the most common arsenates in skarn manganese ores at Långban, Sweden (Blix and Wickman, 1959; Holtstam and Langhof, 1999). Manganberzeliite also occurs as granular veinlets cutting the franklinite-willemite ore at Franklin, New Jersey (Frondel and Ito, 1963) and as veinlets with rhodonite, Mn(II)-bearing aegirine and rhodochrosite cutting black manganese ore consisting of braunite and hausmannite at the Gozaisho mine, Fukushima, Japan (Matsubara, 1975). Syntheses at 450−480ºC and 150 MPa, show that berzeliite and manganberzeliite form a continuous solid-solution, and their unit-cell parameters vary linearly with Mg/Mn ratio (Ito, 1968).

In this study, the crystal chemistry of three natural palenzonaite, two berzeliite, and two manganberzeliite specimens are reported. The experimental methods used were electron microprobe analysis (EMPA) and single-crystal X-ray diffraction. Variations of $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$-tetrahedra are discussed for a systematic understanding of structural characteristics.

Experimental

Samples

Palenzonaite

One specimen of palenzonaite from each of the following localities was studied: (1) the Molinello mine (type locality; Basso, 1987); (2) the Gambatesa mine, Val Graveglia, Liguria, Italy; and (3) the manganese ore deposit at Fianel, Val Ferrera, Graubünden, Switzerland (Brugger and Berlepsch, 1996). Palenzonaite occurs as small anhedral transparent brownish red crystals (less than 100 μm in diameter) associated with braunite and calcite at the Molinello and Gambatesa mines. It occurs as subhedral to euhedral dark red crystals with an approximately rhombododecahedral shape associated with quartz and yellow transparent nambulite at the Fianel mine (Nagashima and Armbruster, unpublished data).

Berzeliite

Specimens of berzeliite from (1) the Mn-rich skarn at Långban, Sweden (type locality; Blix and Wickman, 1959; Holtstam and Langhof, 1999); and (2) the Montaldo mine, Borgata Oberti, Piedmont, Italy (Piccoli *et al*., 2007) were studied. The transparent yellow anhedral berzeliite crystals from Långban are <0.4 mm in diameter, and associated with calcite and hausmannite. Transparent yellow anhedral berzeliite crystals from Montaldo vary in size from <10 μm (common) to 300 μm (rare) and are associated with quartz and hematite. Recently a Ca-Na-Mn^{3+}-arsenate with a formula $(Ca_{0.84}Na_{0.16})(Ca_{0.46}Na_{0.54})Mn_2^{3+}O(O,OH)(AsO_4)_2$ was reported from the Montaldo mine (Kolitsch, 2008).

Manganberzeliite

Specimens of manganberzeliite from (1) Varenche, Italy (Barresi *et al*., 2005), and (2) the Gozaisho mine, Fukushima, Japan (Matsubara, 1975) were studied. Manganberzeliite crystals from both localities are anhedral, yellowish orange and are slightly darker than berzeliite. They are <150 μm in size.

Chemical analysis (EMPA)

The compositions of palenzonaite, berzeliite and manganberzeliite were investigated using a JEOL JXA-8230 electron probe microanalyser at Yamaguchi University, Japan. The elements Si, P, V, As, Ti, Al, Cr, Fe, Mn, Mg, Ni, Pb, Ca, Sr, Ba, Na, K and Cu were analysed at an accelerating voltage of 15 kV, a beam current of 20 nA and a beam diameter of 1 μm. The following standards were used: natural wollastonite (Si, Ca), synthetic $KTiPO_4$ (P, K), synthetic $Ca_3(VO_4)_2$ (V), synthetic GaAs (As), synthetic rutile (Ti), synthetic corundum (Al), synthetic eskolaite (Cr), synthetic hematite (Fe), synthetic tephroite (Mn), synthetic

periclase (Mg), synthetic bunsenite (Ni), PbVGe-oxide (Pb), $SrBaNb_4O_{12}$ (Sr, Ba), natural albite (Na), natural orthoclase (K) and metallic copper (Cu). The Cr_2O_3 and CuO contents, which are not listed in Table 1, are negligible. The ZAF method was used for data correction. The severe overlap between the Mg$K\alpha$ (1254 eV) and As$L\alpha$ (1282 eV) peaks using a TAP analyser crystal were corrected with JEOL software.

Single-crystal structure analysis

Single-crystal X-ray diffraction data for palenzonaite, berzeliite and manganberzeliite were collected using Bruker SMART APEX II CCD diffractometers at the University of Bern, Switzerland and the Shimane University, Japan. The crystals were mounted on glass fibres and intensity data were measured at room temperature using graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å). Preliminary lattice parameters and an orientation matrix were obtained from twelve sets of frames and refined during the integration of the intensity data. Diffraction data were collected using ω scans at different φ settings (φ-ω scans) (Bruker, 1999). Data were processed using *SAINT* (Bruker, 1999). An empirical absorption correction using *SADABS* (Sheldrick, 1996) was applied. Structural refinement was performed using *SHELXL-97* (Sheldrick, 2008) and scattering factors for neutral atoms were employed. The Ca and Na present was assigned to the *X* site, Mn and/or Mg to the *Y* site, and Si, V and/or As to *Z* site. The Ca and Na site-occupancy was fixed based on the EMPA data. In some specimens, the Ca content was higher than expected due to Si substitution at the tetrahedral *Z* site: $^{X}Ca + {}^{Z}Si^{4+} \leftrightarrow {}^{X}Na + {}^{Z}M^{5+}$. In the Si-bearing samples, the Si content was fixed on the basis of the EMPA results during the refinements. The high crystal quality of berzeliite and manganberzeliite led to signs of extinction and multiple diffraction and an extinction correction was made. The diffraction data did not indicate any lowering of symmetry from cubic $Ia\bar{3}d$.

Results

Chemical composition

The mean compositions of the studied specimens, normalized to eight cations, are listed in Table 1; total Mn, Fe, V and As are reported as MnO, FeO, V_2O_5 and As_2O_5, respectively. With the exception of palenzonaite from the Molinello mine, the total (Si + As + V + P) content based on the average chemical composition sums to 2.94−3.00 atoms per formula unit (a.p.f.u.). In general, the As, V and P ions are pentavalent and occupy tetrahedral sites, however, the palenzonaite from Molinello may contain a small amount of V^{3+} as the total (Si + As + V + P) content is >3 a.p.f.u. and there is a deficiency in the number of octahedrally coordinated *Y*-site cations. Thus, the amount of tetrahedral V^{5+} in palenzonaite from Molinello is calculated as 3 − (Si + As + P), and excess V is assigned as octahedrally coordinated V^{3+}. The possible presence of trivalent arsenic was not considered: As^{3+} in regular octahedral coordination is not expected as the coordination of As^{3+} is governed by its lone electron pair. Palenzonaite from the three different localities can be divided into two compositional variants: the specimen from Fianel has a high arsenic content (1.21 a.p.f.u.) compared to the others (0.17 a.p.f.u.). The compositions of berzeliite from the two different localities are similar, but the FeO content of Montaldo berzeliite is higher. The V_2O_5 content of manganberzeliite in the specimen from Varenche (4.76 wt.% V_2O_5) is higher than that in the Gozaisho specimen (1.07 wt.% V_2O_5). In summary, Σ(Ca + Na + K) tends to be slightly higher and Σ(Si + As + V + P) lower than the ideal values. The homogeneity of each studied specimen was confirmed by backscattered electron imaging; chemical zonation is not significant.

Crystal-structure solution and refinement

Crystallographic data and refinement parameters are summarized in Table 2. The refined atom positions and anisotropic mean-square displacement parameters are listed in Tables 3 and 4. Interatomic distances and selected angles are listed in Table 5. The occupancies of the cation sites are summarized in Table 6. The crystal structure of palenzonaite is shown in Fig. 1. Structure refinements in this study converged to R_1 values of 1.36−2.42%. The observed mean electron densities are almost consistent with the calculated values based on the expected site occupancies derived from the average chemical compositions (Table 6).

Discussion

Variation of the unit-cell parameters and cation distributions

The unit-cell parameters of all of the palenzonaite specimens are similar to each other even though

TABLE 1*a*. Compositions of palenzonaite, berzeliite and manganberzeliite.

	Palenzonaite						Berzeliite				Manganberzeliite			
	Molinello mine, Italy		Gambatesa mine, Italy		Fianel mine, Switzerland		Långban, Sweden		Montaldo mine, Italy		Varenche, Italy		Gozaisho mine, Japan	
	Mean (n = 24)	SD	Mean (n = 8)	SD	Mean (n = 12)	SD	Mean (n = 27)	SD	Mean (n = 22)	SD	Mean (n = 22)	SD	Mean (n = 22)	SD
Oxide composition (wt.%)														
SiO_2	1.98	0.23	1.87	0.11	0.38	0.09	0.73	0.23	0.17	0.05	0.07	0.04	0.43	0.11
P_2O_5	0.00	0.01	0.03	0.07	0.00	0.01	0.25	0.09	0.05	0.03	0.01	0.02	0.00	0.00
V_2O_5	44.37	1.25	42.71	0.71	26.36	1.99	0.33	0.07	1.32	0.11	4.76	1.26	1.07	0.12
As_2O_5	3.44	0.36	3.49	0.68	23.68	2.01	57.40	0.70	57.73	0.67	49.94	1.75	52.99	0.38
TiO_2	0.04	0.07	0.03	0.05	0.04	0.05	0.03	0.04	0.10	0.10	0.01	0.02	0.05	0.05
Al_2O_3	0.02	0.03	0.04	0.06	0.03	0.04	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.01
FeO	0.04	0.06	0.08	0.13	0.13	0.19	0.06	0.06	1.52	0.28	0.02	0.02	0.06	0.05
MnO	23.20	1.50	25.25	0.85	23.79	1.02	3.51	0.32	1.24	0.16	18.26	1.34	20.86	0.29
MgO	0.02	0.03	0.02	0.03	0.32	0.13	11.69	0.30	12.26	0.29	2.93	1.04	1.12	0.15
NiO	0.08	0.12	0.10	0.10	0.15	0.15	0.03	0.03	0.03	0.04	0.02	0.03	0.01	0.02
PbO	0.20	0.16	0.13	0.15	0.75	0.31	0.05	0.05	0.02	0.02	0.00	0.00	0.00	0.00
CaO	22.38	0.30	22.13	0.55	19.49	0.37	20.63	0.24	19.43	0.28	18.44	0.38	18.21	0.21
SrO	0.01	0.02	0.00	0.00	0.04	0.07	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
BaO	0.08	0.10	0.06	0.15	0.06	0.10	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02
Na_2O	4.30	0.52	4.43	0.35	5.16	0.33	4.82	0.11	5.50	0.15	5.19	0.18	5.05	0.10
K_2O	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01
Total	100.16		100.39		100.37		99.53		99.37		99.69		99.90	
Composition on the basis of eight cations														
Si	0.19	0.02	0.17	0.01	0.04	0.01	0.07	0.02	0.02	0.00	0.01	0.00	0.04	0.01
P^{5+}	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00
V^{5+}	2.75	0.09	2.63	0.05	1.69	0.12	0.02	0.00	0.08	0.01	0.32	0.09	0.07	0.01
As^{5+}	0.17	0.02	0.17	0.03	1.21	0.11	2.89	0.02	2.89	0.03	2.64	0.08	2.86	0.02
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	0.00	0.01	0.01	0.01	0.01	0.02	0.00	0.00	0.12	0.02	0.00	0.00	0.01	0.00
Mn^{2+}	1.84	0.08	1.99	0.05	1.96	0.07	0.29	0.02	0.10	0.01	1.57	0.12	1.82	0.02
Mg	0.00	0.00	0.00	0.00	0.05	0.02	1.68	0.03	1.75	0.04	0.44	0.15	0.17	0.02
Ni	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.00	0.00	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	2.25	0.06	2.21	0.06	2.03	0.03	2.13	0.02	2.00	0.03	2.00	0.04	2.01	0.02

Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na	0.78	0.08	0.80	0.06	0.97	0.06	0.90	0.02	1.02	0.03	1.02	0.04	1.01	0.02
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	8.00		8.00		8.00		8.00		8.00		8.00		8.00	

TABLE 1*b*. Chemical formulae from the compositions listed in Table 1*a*.

Mineral	Locality	Formula
Palenzonaite	Molinello	$(Ca_{2.25}Na_{0.78})_{\Sigma 3.03}(Mn^{2+}_{1.84}Ni_{0.01}V_{0.11})_{\Sigma 1.96}(V^{5+}_{2.64}As^{5+}_{0.17}Si_{0.19})_{\Sigma 3.00}O_{12.06}$
	Gambatesa	$(Ca_{2.21}Na_{0.80})_{\Sigma 3.01}(Mn^{2+}_{1.99}Fe^{2+}_{0.01}Ni_{0.01})_{\Sigma 2.01}(V^{5+}_{2.63}As^{5+}_{0.17}Si_{0.17})_{\Sigma 2.97}O_{11.96}$
	Fianel	$(Ca_{2.03}Na_{0.97})_{\Sigma 3.00}(Mn^{2+}_{1.96}Mg_{0.05}Pb_{0.02}Fe^{2+}_{0.01}Ni_{0.01})_{\Sigma 2.05}(V^{5+}_{1.69}As^{5+}_{1.21}Si_{0.04})_{\Sigma 2.94}O_{11.90}$
Berzeliite	Långban	$(Ca_{2.13}Na_{0.90})_{\Sigma 3.03}(Mg_{1.68}Mn^{2+}_{0.29})_{\Sigma 1.97}(As^{5+}_{2.89}Si_{0.07}V^{5+}_{0.02}P_{0.02})_{\Sigma 3.00}O_{12.02}$
	Montaldo	$(Ca_{2.00}Na_{1.02})_{\Sigma 3.02}(Mg_{1.75}Mn^{2+}_{0.10}Fe^{2+}_{0.12}Ti_{0.01})_{\Sigma 1.98}(As^{5+}_{2.89}Si_{0.02}V^{5+}_{0.08})_{\Sigma 2.99}O_{11.97}$
Manganberzeliite	Varenche	$(Ca_{2.00}Na_{1.02})_{\Sigma 3.02}(Mn^{2+}_{1.57}Mg_{0.44})_{\Sigma 2.01}(As^{5+}_{2.64}V^{5+}_{0.32}Si_{0.01})_{\Sigma 2.97}O_{11.94}$
	Gozaisho	$(Ca_{2.01}Na_{1.01})_{\Sigma 3.02}(Mn^{2+}_{1.82}Mg_{0.17}Fe^{2+}_{0.01})_{\Sigma 2.00}(As^{5+}_{2.86}V^{5+}_{0.07}Si_{0.04})_{\Sigma 2.97}O_{11.92}$

TABLE 2. Experimental details of the single-crystal X-ray diffraction analyses of palenzonaite, berzeliite and manganberzeliite.

	Palenzonaite			Berzeliite		Manganberzeliite	
Locality	Molinello mine	Gambatesa mine	Fianel mine	Långban	Montaldo mine	Varenche	Gozaisho mine
Crystal size (mm)	$0.02 \times 0.025 \times 0.035$	$0.045 \times 0.03 \times 0.01$	$0.035 \times 0.03 \times 0.02$	$0.30 \times 0.25 \times 0.07$	$0.20 \times 0.15 \times 0.07$	$0.08 \times 0.05 \times 0.04$	$0.135 \times 0.10 \times 0.02$
a (Å)	12.543(1)	12.5359(2)	12.5342(2)	12.3450(2)	12.3404(2)	12.4829(1)	12.4929(2)
V (Å^3)	1973.49(3)	1970.00(1)	1969.20(1)	1881.37(1)	1879.26(1)	1945.12(1)	1949.80(1)
D_{calc} (g cm^{-3})	3.77	3.78	3.93	4.06	4.00	4.15	4.22
θ_{min}(°)	4.0	4.0	4.0	4.0	4.0	4.0	4.0
θ_{max}(°)	30.3	36.3	30.0	36.3	36.3	36.0	36.0
μ (mm^{-1})	7.70	7.71	7.71	11.94	11.95	15.14	12.69
Collected refl.	3129	9095	6045	2909	4247	12,372	7808
Unique refl.	245	406	244	383	384	395	388
R_{int} (%)	4.98	4.04	5.53	2.12	1.91	4.19	2.57
R_s (%)	2.33	1.83	2.29	1.47	1.05	1.10	1.10
Index limits	$-13 < h < 10$ $-5 < k < 17$ $-17 < l < 12$	$-12 < h < 20$ $-14 < k < 20$ $-15 < l < 20$	$-17 < h < 16$ $-14 < k < 17$ $-17 < l < 17$	$-11 < h < 20$ $-18 < k < 10$ $-17 < l < 13$	$-18 < h < 15$ $-20 < k < 18$ $-20 < l < 19$	$-19 < h < 20$ $-19 < k < 19$ $-15 < l < 20$	$-20 < h < 20$ $-16 < k < 17$ $-20 < l < 19$
R_1 (%)	2.34	2.42	1.87	1.55	1.37	1.88	1.36
wR_2 (%)	6.17	6.05	4.39	3.90	3.47	4.29	3.28
Parameters	19	19	19	20	20	19	20
Weighting*	$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 2.74P]$	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 0.27P]$	$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2 + 2.79P]$	$w = 1/[\sigma^2(F_o^2) + (0.0179P)^2 + 0.92P]$	$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2 + 0.54P]$	$w = 1/[\sigma^2(F_o^2) + (0.0182P)^2 + 0.92P]$	$w = 1/[\sigma^2(F_o^2) + (0.0120P)^2 + 1.62P]$
$\Delta\rho_{max}$ (e Å^{-3})	0.28	0.34	0.30	0.37	0.31	0.33	0.21
$\Delta\rho_{min}$ (e Å^{-3})	−0.59	−0.81	−0.36	−0.37	−0.52	−0.63	−0.27

* The weighting scheme is $w = 1/(\sigma(F_o^2) + (aP)^2 + bP)$, where $P = (\mathrm{Max}(F_o^2) + 2F_c^2)/3$, and the parameters a and b are chosen to minimize the differences in the variances for reflections in different ranges of intensity and diffraction angle.

TABLE 3. Atom positions and isotropic temperature factors (Å^2) for palenzonaite, berzeliite and manganberzeliite.

		Palenzonaite			Berzeliite		Manganberzeliite	
		Molinello mine, Italy	Gambatesa mine, Italy	Fianel mine, Switzerland	Långban, Sweden	Montaldo mine, Italy	Varenche, Italy	Gozaisho mine, Japan
X	*x*/*a*	⅛	⅛	⅛	⅛	⅛	⅛	⅛
	y/*a*	0	0	0	0	0	0	0
	z/*a*	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.0129(4)	0.0112(2)	0.0135(3)	0.0099(1)	0.0099(1)	0.0110(2)	0.0111(1)
Y	*x*/*a*	0	0	0	0	0	0	0
	y/*a*	0	0	0	0	0	0	0
	z/*a*	0	0	0	0	0	0	0
	U_{eq}	0.0111(3)	0.0095(2)	0.0122(2)	0.0081(3)	0.0084(2)	0.0093(2)	0.0095(1)
Z	*x*/*a*	⅜	⅜	⅜	⅜	⅜	⅜	⅜
	y/*a*	0	0	0	0	0	0	0
	z/*a*	¼	¼	¼	¼	¼	¼	¼
	U_{eq}	0.0074(3)	0.0064(1)	0.0085(2)	0.00506(8)	0.00525(7)	0.00675(9)	0.00637(7)
O	*x*/*a*	0.0329(1)	0.03924(7)	0.0397(1)	0.03903(6)	0.03893(5)	0.03963(8)	0.03973(6)
	y/*a*	0.0542(1)	0.05417(7)	0.0537(1)	0.05125(6)	0.05085(5)	0.05302(8)	0.05317(6)
	z/*a*	0.6584(1)	0.65829(6)	0.6588(1)	0.65664(6)	0.65608(5)	0.65865(8)	0.65912(6)
	U_{eq}	0.0132(5)	0.0118(2)	0.0150(4)	0.0091(2)	0.0088(2)	0.0112(2)	0.0110(2)

TABLE 4. Anisotropic displacement parameters (Å^2) for palenzonaite, berzeliite and manganberzeliite.

		Palenzonaite			Berzeliite		Manganberzeliite	
		Molinello mine, Italy	Gambatesa mine, Italy	Fianel mine, Switzerland	Långban, Sweden	Montaldo mine, Italy	Varenche, Italy	Gozaisho mine, Japan
X	U_{11}	0.0106(6)	0.0087(3)	0.0110(5)	0.0073(2)	0.00736(19)	0.0079(3)	0.0079(3)
	U_{22}	0.0141(4)	0.0124(2)	0.0147(3)	0.01116(16)	0.01113(15)	0.0125(2)	0.0125(2)
	U_{33}	0.0141(4)	0.0124(2)	0.0147(3)	0.01116(16)	0.01113(15)	0.0125(2)	0.0125(2)
	U_{23}	0.0016(4)	0.0016(2)	0.0019(3)	0.00208(16)	0.00158(13)	0.0021(2)	0.0021(2)
	U_{13}	0	0	0	0	0	0	0
	U_{12}	0	0	0	0	0	0	0
Y	U_{11}	0.0111(3)	0.0095(2)	0.0122(2)	0.0081(3)	0.0084(2)	0.0093(2)	0.0093(2)
	U_{22}	0.0111(3)	0.0095(2)	0.0122(2)	0.0081(3)	0.0084(2)	0.0093(2)	0.0093(2)
	U_{33}	0.0111(3)	0.0095(2)	0.0122(2)	0.0081(3)	0.0084(2)	0.0093(2)	0.0093(2)
	U_{23}	−0.0005(2)	−0.00060(9)	−0.0006(2)	−0.00047(14)	−0.00021(12)	−0.00038(10)	−0.00038(10)
	U_{13}	−0.0005(2)	−0.00060(9)	−0.0006(2)	−0.00047(14)	−0.00021(12)	−0.0004(1)	−0.00038(10)
	U_{12}	−0.0005(2)	−0.00060(9)	−0.0006(2)	−0.00047(14)	−0.00021(12)	−0.0004(1)	−0.00038(10)
Z	U_{11}	0.0076(5)	0.0056(2)	0.0079(3)	0.00499(11)	0.00504(9)	0.0065(1)	0.00645(14)
	U_{22}	0.0073(3)	0.0067(2)	0.0088(2)	0.00509(9)	0.00535(8)	0.0069(1)	0.00690(10)
	U_{33}	0.0073(3)	0.0067(2)	0.0088(2)	0.00509(9)	0.00535(8)	0.0069(1)	0.00690(10)
	U_{23}	0	0	0	0	0	0	0
	U_{13}	0	0	0	0	0	0	0
	U_{12}	0	0	0	0	0	0	0
O	U_{11}	0.0131(9)	0.0126(5)	0.0165(7)	0.0091(3)	0.0088(3)	0.0114(5)	0.0114(5)
	U_{22}	0.0143(10)	0.0126(4)	0.0153(7)	0.0104(3)	0.0100(3)	0.0126(4)	0.0126(4)
	U_{33}	0.0122(9)	0.0104(4)	0.0133(7)	0.0078(3)	0.0075(3)	0.0097(4)	0.0097(4)
	U_{23}	0.0008(7)	−0.0006(3)	0.0007(5)	0.0006(2)	0.0004(2)	0.0008(3)	0.0008(3)
	U_{13}	0.0002(8)	−0.0006(3)	−0.0007(5)	−0.0019(3)	−0.0017(2)	−0.0015(3)	−0.0015(3)
	U_{12}	0.0000(7)	−0.0001(3)	0.0005(5)	0.0013(2)	0.0010(2)	0.0012(3)	0.0012(3)

TABLE 5. Selected bond distances and angles for palenzonaite, berzeliite and manganberzeliite.

		Palenzonaite			Berzeliite		Manganberzeliite	
		Molinello mine, Italy	Gambatesa mine, Italy	Fianel mine, Switzerland	Långban, Sweden	Montaldo mine, Italy	Varenche, Italy	Gozaisho mine, Japan
*X*1–O4	(×4)	2.455(2)	2.4540(9)	2.454(1)	2.4143(8)	2.4144(7)	2.442(1)	2.4424(8)
*X*2–O4	(×4)	2.540(2)	2.5381(8)	2.546(1)	2.5308(7)	2.5332(6)	2.543(1)	2.5446(8)
<*X*–*O*>		2.498	2.496	2.500	2.4726	2.4738	2.493	2.4935
<*Y*–O>	(×6)	2.157(2)	2.1542(8)	2.160(1)	2.0908(7)	2.0819(6)	2.1459(9)	2.1538(7)
<*Z*–*O*>	(×4)	1.714(2)	1.7143(8)	1.704(1)	1.6897(7)	1.6927(6)	1.6953(9)	1.6927(7)
O1–*X*2–O2	(×2)	65.87(8)	65.93(4)	65.44(6)	65.99(3)	66.17(3)	65.37(4)	65.17(3)
O1–*X*2–O4	(×4)	74.91(8)	74.84(4)	75.15(6)	73.53(3)	73.17(3)	71.92(3)	71.74(3)
O1–*X*2–O7	(×4)	92.20(5)	92.23(2)	91.95(4)	91.93(2)	91.96(2)	91.85(2)	91.78(2)
O4–*X*2–O6	(×4)	71.61(6)	71.65(3)	71.68(5)	72.99(3)	73.26(2)	74.94(4)	75.22(3)
O4–*X*2–O7	(×2)	69.66(8)	69.64(4)	69.49(6)	69.80(3)	69.82(3)	69.58(4)	69.58(4)
O7–*X*2–O8	(×2)	113.70(8)	113.70(4)	113.94(6)	113.14(3)	113.01(3)	113.79(4)	113.89(3)
O1–*Y*–O4	(×6)	89.54(6)	89.54(3)	89.82(5)	89.83(3)	89.76(2)	90.05(4)	90.05(3)
O1–*Y*–O5	(×6)	90.46(6)	90.46(3)	90.18(5)	90.17(3)	90.24(2)	89.95(4)	89.95(3)
O1–*Z*–O2	(×2)	102.3(1)	102.33(6)	102.27(9)	102.18(5)	102.27(5)	102.10(7)	101.99(5)
O1–*Z*–O3	(×4)	113.19(6)	113.16(3)	113.19(5)	113.24(3)	113.19(3)	113.28(4)	113.33(3)
$\sigma_\theta(\text{oct})^2$*		0.233	0.234	0.034	0.032	0.063	0.002	0.003

* Angular distortion parameters are as defined by Robinson *et al*. (1971); $\sigma_\theta(\text{oct})^2 = \Sigma(\theta_i - 90^\circ)/11$ where θ_i = O–M–O angle.

the specimen from Fianel is rich in arsenic compared to the others (Table 2). This is due to the similar mean ionic radii at the tetrahedral sites, which based on site occupancies are 0.353 Å for the crystals from Molinello and Gambatesa, and 0.351 Å for the crystal from Fianel. The unit-cell parameter reported by Basso (1987) for palenzonaite from the Molinello mine is similar to our experimental results, but those of synthetic $NaCa_2Mn^{2+}(V^{5+}O_4)_3$ (12.573 Å; Iishi and Ikuta, 2006; 12.568 Å Nakatsuka *et al*., 2004*a*) are slightly larger than the natural samples. The smaller cell dimensions in natural palenzonaite are related to partial substitution of tetrahedral As^{5+} (ionic radius, r = 0.34 Å) and Si^{4+} (r = 0.26 Å) for V^{5+} (r = 0.36 Å). The increase in the unit-cell size with increasing Mn^{2+} content in synthetic $NaCa_2Mg(As^{5+}O_4)_3$ (berzeliite) – $NaCa_2Mn^{2+}(As^{5+}O_4)_3$ (manganberzeliite) reported by (Ito, 1968), is also consistent with our results. The differences in the unit-cell parameters between palenzonaite (Mn^{2+} dominant at *Y* and V^{5+} dominant at *Z*) and manganberzeliite (Mn^{2+} dominant at *Y* and As^{5+} dominant at *Z*) can be explained by the cation distribution at the tetrahedral site. The unit-cell parameters decrease in the order palenzonaite > manganberzeliite > berzeliite.

The sizes of the YO_6 octahedra and ZO_4 tetrahedra increase as the mean ionic radii of the central elements increase (Fig. 2*a*,*b*; R^2 = 0.96 for *Y* and 0.88 for *Z*). There is no correlation between the size of the XO_8 polyhedra and the mean ionic radius of the elements at *X* in our data despite reported increases in <*X*–O> distances in silicate garnets with increasing mean ionic radius (Hawthorne, 1981). However, Na (r = 1.18 Å) and Ca (r = 1.12 Å) in eightfold coordination have similar ionic radii (Shannon, 1976) and the Ca/Na ratio in our samples only varies between 2.00 and 2.85, which corresponds to an increase of 1.136 to 1.140 Å in the mean ionic radius. The distorted square antiprism at *X* in berzeliite is smaller than those in palenzonaite and manganberzeliite (Fig. 2*c*). As a result of the low average charge at the *X* site, the XO_8 polyhedra in these garnet

TABLE 6. Site occupancies for palenzonaite, berzeliite and manganberzeliite.

	Site	Observed no. e^-	Site occupancy based on EMPA	Calculated no. e^-
Palenzonaite				
Molinello mine, Italy	*X*	17.60	$Ca_{0.74}Na_{0.26}$	17.66
	Y	24.73	$Mn^{2+}_{0.95}V^{3+}_{0.05}$	24.90
	Z	22.51	$V^{5+}_{0.88}As^{5+}_{0.06}Si_{0.06}$	21.86
Gambatesa mine, Italy	*X*	17.60	$Ca_{0.74}Na_{0.26}$	17.66
	Y	24.73	$Mn^{2+}_{1.00}$	25.00
	Z	22.93	$V^{5+}_{0.88}As^{5+}_{0.06}Si_{0.06}$	21.86
Fianel mine, Switzerland	*X*	17.09	$Ca_{0.68}Na_{0.32}$	17.12
	Y	24.20	$Mn^{2+}_{0.98}Mg_{0.02}$	24.74
	Z	27.33	$V^{5+}_{0.58}As^{5+}_{0.41}Si_{0.01}$	27.01
Berzeliite				
Långban, Sweden	*X*	17.30	$Ca_{0.70}Na_{0.30}$	17.30
	Y	13.55	$Mg_{0.86}Mn^{2+}_{0.14}$	13.10
	Z	31.82	$As^{5+}_{0.97}Si(+ P)_{0.03}$	32.43
Montaldo mine, Italy	*X*	17.00	$Ca_{0.67}Na_{0.33}$	17.03
	Y	13.57	$Mg_{0.89}Fe^{2+}_{0.06}Mn^{2+}_{0.05}$	13.49
	Z	32.58	$As^{5+}_{0.97}V^{5+}_{0.03}$	32.70
Manganberzeliite				
Varenche, Italy	*X*	17.00	$Ca_{0.67}Na_{0.33}$	17.03
	Y	22.11	$Mn^{2+}_{0.78}Mg_{0.22}$	22.14
	Z	31.48	$As^{5+}_{0.89}V^{5+}_{0.11}$	31.90
Gozaisho mine, Japan	*X*	17.00	$Ca_{0.67}Na_{0.33}$	17.03
	Y	23.03	$Mn^{2+}_{0.91}Mg_{0.09}$	23.83
	Z	31.78	$As^{5+}_{0.97}V^{5+}_{0.02}Si_{0.01}$	32.28

structures make soft links between more rigid octahedra (*Y*) and tetrahedra (*Z*), although an appropriate Na/Ca ratio at *X* is vital for charge balance. Thus, the volume of the XO_8 polyhedra is not governed by the cation distribution at *X*.

The $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedron

Several silicate minerals with $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra have been reported (Nagashima and Armbruster, 2010, table 10). Such tetrahedral sites can be categorized by the number of bridging apices to other tetrahedral sites (Nagashima and Armbruster, 2010). The $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra in vanadate–arsenate garnets, such as palenzonaite, berzeliite and manganberzeliite, are isolated. There is a positive correlation between <*Z*–O> and the mean ionic radii of the central atoms in the $(As,V,P,Si)O_4$ tetrahedral site (R^2 = 0.87 in Fig. 3).

The stoichiometry puzzle

Schäferite, palenzonaite, berzeliite and manganberzeliite are characterized by a combined substitution in which pentavalent cations in tetrahedral coordination at *Z* are charge balanced by an appropriate ratio of monovalent and divalent Na^+ and Ca^{2+} cations at *X*, and divalent octahedrally coordinated cations at *Y*. This observation poses the following question: why are there no minerals with the garnet structure with pentavalent cations at *Z* and trivalent cations at *Y*, in which charge balance is maintained by univalent Na at *X*? A potential example is $Na_3Al_2(PO_4)_3$. Bond-strength arguments can be ruled out as the only O position in the cubic garnet structure is bonded once to *Z* and *Y* and twice to *X*: $5/4 + 3/6 + 2 \times 1/8 = 2$.

Of the synthetic vanadate garnets (V^{5+} at *Z*), those with Na and Ca at the *X* site predominate (Bayer, 1965). All of the vanadate garnets synthesized by Bayer (1965) at 700 to 750ºC by

solid state reaction, with Ca/Na = 2/1 at *X*, contain divalent cations with ionic radii (Shannon, 1976) between 0.690 Å ($^{VI}Ni^{2+}$) and 0.745 Å ($^{VI}Co^{2+}$) at the *Y* site. Synthetic palenzonaite [$Ca_2NaMn_2(VO_4)_3$] single crystals ($^{VI}Mn^{2+}$ = 0.83 Å) have been grown (Nakatsuka *et al*., 2004*a*) from oxides by the floating zone technique. Thus, the radius of the divalent cations at *Y* in vanadate garnets is generally larger than that of the common octahedrally coordinated trivalent cations in silicate garnets [$r(^{VI}Al^{3+})$ = 0.535 Å, $r(^{VI}Fe^{3+})$ = 0.645 Å]. A second group of vanadate garnets listed by Bayer (1965) contain Ca at *X* and a 1:1 ratio of octahedrally coordinated Li^+ and M^{2+} (Mg, Co, Ni, Cu and Zn) at *Y*. As octahedrally coordinated Li has an ionic radius 0.76 Å (Shannon, 1976), these vanadate garnets are also characterized by rather large mean octahedral radii.

Thilo (1941) reported the synthesis of $Na_3Al_2(PO_4)_3$ with a garnet structure at 500ºC from an Na_3PO_4 and AlP_4O melt. However, these results were questioned by Brunet *et al*. (2006) who synthesized the same compound at 17 GPa and 1400–1600ºC. Garnet-structured $Na_3Al_2(PO_4)_3$ with *a* = 11.579(2) Å has an oxygen position at 0.046(1), 0.045(1), 0.658(1) derived from low quality Rietveld powder refinement (Brunet *et al*., 2006).

As all cation sites in the cubic $Ia\bar{3}d$ garnet structure are fixed at special positions, and all the *Z*–O and *Y*–O distances are symmetrically equivalent, the position of the oxygen atom can be calculated from the known cell dimension

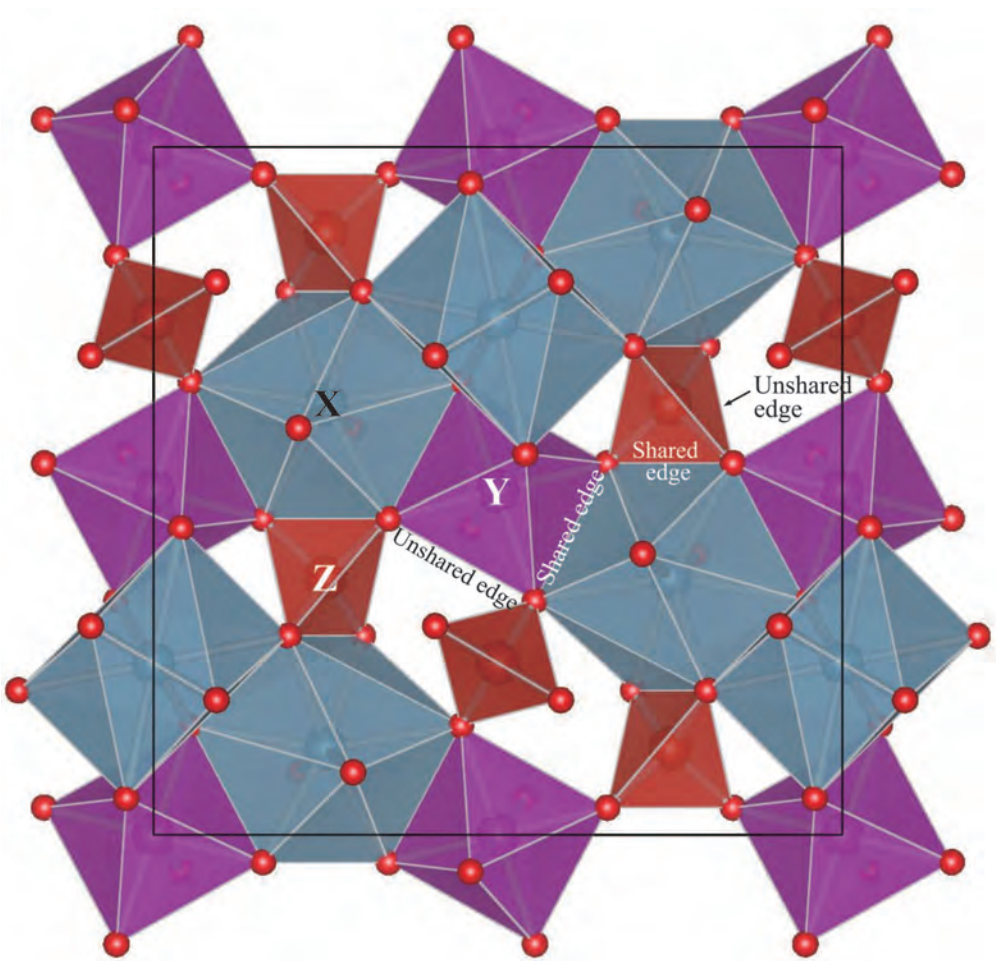

FIG. 1. The crystal structure of palenzonaite (drawn using *VESTA*; Momma and Izumi, 2008).

using P–O and Al–O bond lengths at *Z* and *Y* of P–O = 1.535 Å and Al–O = 1.921 Å, respectively. The calculated oxygen coordinates are 0.0441, 0.0428, 0.6541 which are close to the refined values (Table 7). The resulting Na–O distances at *X* are 2.305 and 2.477 Å, respectively. The corresponding garnet structure is characterized by large angular octahedral distortion (Table 7). The length of the edge shared between the octahedron (*Y*) and distorted square antiprism (*X*) is 2.818 Å, whereas the unshared octahedral edge is 2.612 Å in length. This difference in polyhedral edge length of ~0.2 Å is much larger than pyrope, the most distorted of the common silicate garnets, where the corresponding difference is ~–0.1 Å (Novak and Gibbs, 1971: the shared edge is shorter than the unshared octahedral edge).

Schwarz and Schmidt (1972) reported syntheses of two arsenates with garnet structures: $Na_3Cr_2(AsO_4)_3$ (a = 12.15 Å) between 850 and 900ºC and $Na_3Fe_2(AsO_4)_3$ (a = 12.22 Å) between 600 and 800ºC. Two vanadates: $Na_3Cr_2(VO_4)_3$ (a = 12.29 Å) and $Na_3Sc_2(VO_4)_3$ (a = 12.60 Å), synthesized at 550–600ºC and 750ºC, respectively, were subsequently described (Schwarz and Schmidt, 1975). In the absence of structural data, the oxygen position in the two Cr garnets with tetrahedral AsO_4 and VO_4 can be calculated assuming an octahedral Cr–O distance of 1.99 Å, As–O of 1.693 Å, and V–O of 1.72 Å (Table 7). The differences in the lengths of the shared and unshared octahedral edges are 0.046 Å (arsenate) and 0.068 Å (vanadate), which is considerably smaller than the high-pressure phosphate garnet (and similar to the silicate garnet grossular; Novak and Gibbs, 1971).

If the structures of the synthetic phosphate, arsenate and vanadate garnets which only contain Na at the *X* site are compared with the structures of schäferite, palenzonaite, berzeliite and manganberzeliite, it is clear that the synthetic phases are considerably more distorted than the minerals (Tables 5 and 7). The O–O distances of

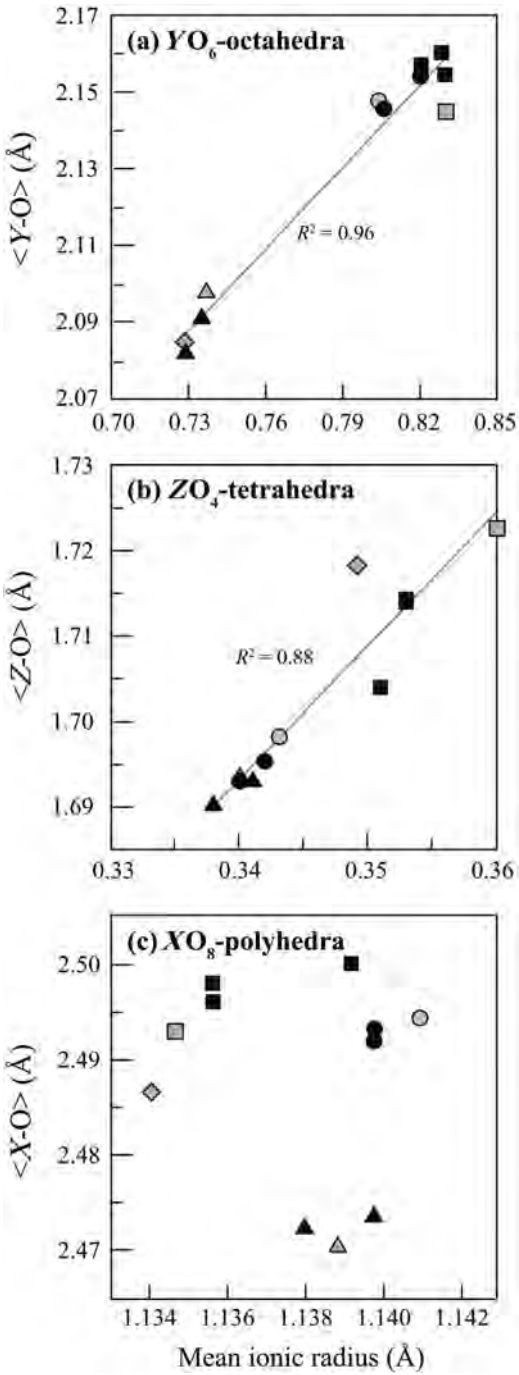

FIG. 2. Variations of (*a*) <*Y*–O>, (*b*) <*Z*–O> and (*c*) <*X*–O> as a function of mean ionic radius. Closed squares represent palenzonaite (this study), closed circles berzeliite (this study), closed circles manganberzeliite (this study), grey squares palenzonaite (Basso, 1987), grey triangles berzeliite (Hawthorne, 1976), grey diamonds schäferite (Krause *et al*., 1999) and grey circles manganberzeliite (Uwe Kolitsch, pers. comm.). Only natural compositions are plotted in this figure. The regression lines are only valid between the data points shown.

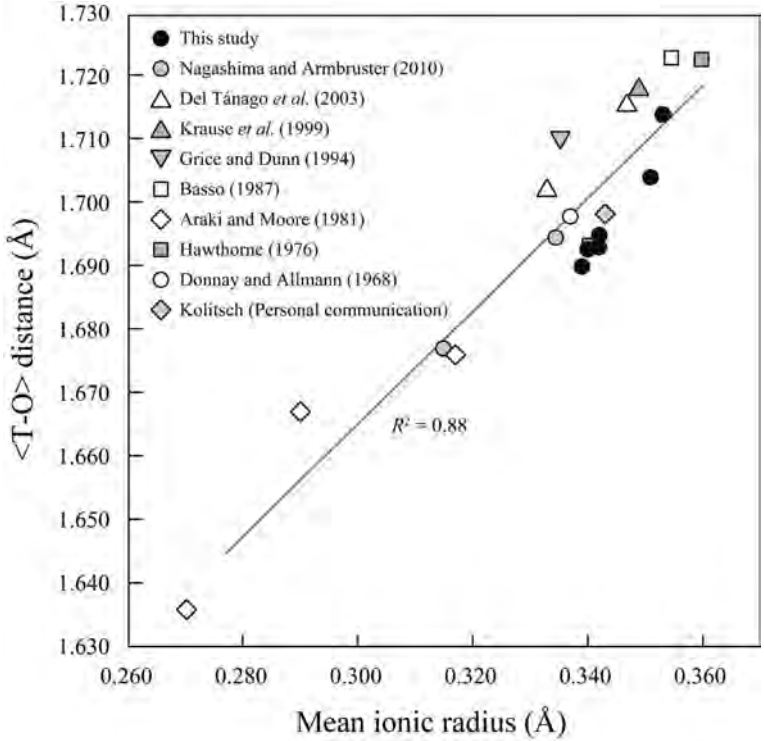

FIG. 3. Variation of <Z–O> distances in none-bridging $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedra as a function of the mean ionic radius of the $(As^{5+},V^{5+},P^{5+},Si^{4+})O_4$ tetrahedron. Only natural specimens are plotted in this figure. The regression line is only valid between the data points shown.

TABLE 7. Calculated crystal structures of garnet group minerals.

Composition		$Na_3Al_2(PO_4)_3$	$Na_3Cr_2(AsO_4)_3$	$Na_3Cr_2(VO_4)_3$
Cell parameter (Å)	*a*	11.580	12.150	12.291
Oxygen position	*x/a*	0.0441	0.0387	0.0388
	y/a	0.0428	0.0480	0.0466
	z/a	0.6541	0.6517	0.6501
Selected bond distances (Å)				
Na–O (×4)		2.305	2.392	2.427
Na–O (×4)		2.477	2.520	2.563
Y–O (×6)		1.921	1.990	1.990
Shared edge		2.818	2.838	2.848
Unshared edge		2.612	2.792	2.780
Δ (shared – unshared)		0.206	0.046	0.068
$\sigma_\theta(oct)^2$*		20.65	0.99	2.12
T–O (×4)		1.535	1.693	1.720
Shared edge		2.432	2.658	2.710
Unshared edge		2.543	2.817	2.866
Δ (shared – unshared)		−0.111	−0.159	−0.156

* Angular distortion parameters are as defined by Robinson *et al*. (1971); $\sigma_\theta(oct)^2 = \Sigma(\theta_i - 90^o)/11$ where θ_i = O–M–O angle.

TABLE 8. The O–O distances of the *Y* and *Z* sites for shared and unshared edges with the *X* distorted square antiprism.

	Y octahedral site			*Z* tetrahedral site			
	Shared edge	Unshared edge	Δ*	Shared edge	Unshared edge	Δ*	
Nat. palenzonaite	3.038(2)	3.063(2)	−0.025	2.669(2)	2.862(2)	−0.193	Molinello mine, Italy
Nat. palenzonaite	3.034(1)	3.059(1)	−0.025	2.671(1)	2.862(1)	−0.191	Gambatesa mine, Italy
Nat. palenzonaite	3.050(2)	3.059(2)	−0.009	2.653(2)	2.844(2)	−0.191	Fianel mine, Switzerland
Nat. palenzonaite	3.015(4)	3.053(4)	−0.038	2.677(4)	2.879(4)	−0.202	Basso (1987)
Syn. $NaCa_2Mn_3(VO_4)_3$	3.038(2)	3.059(2)	−0.021	2.681(2)	2.870(2)	−0.189	Nakatsuka *et al*. (2004*a*)
Nat. schäferite	2.947(2)	2.951(2)	−0.004	2.679(2)	2.867(2)	−0.188	Krause *et al*. (1999)
Syn. $NaCa_2Mg_3(VO_4)_3$	2.951(2)	2.956(2)	−0.005	2.6863(2)	2.871(2)	−0.185	Nakatsuka *et al*. (2003)
Syn. $NaCa_2Zn_3(VO_4)_3$	2.982(4)	2.996(4)	−0.014	2.674(4)	2.864(4)	−0.190	Nakatsuka *et al*. (2004*b*)
Syn. $Na_{0.9}Ca_{2.05}Co_2(VO_4)_3$	2.95(1)	2.95(1)	0.000	2.68(1)	2.87(1)	−0.190	Dukhoskaya and Mill (1974)
Nat. berzeliite	2.961(1)	2.953(1)	0.008	2.630(1)	2.822(1)	−0.192	Långban, Sweden
Nat. berzeliite	2.950(1)	2.939(1)	0.011	2.6360(9)	2.8261(9)	−0.190	Montaldo mine, Italy
Nat. berzeliite	2.967(5)	2.968(5)	−0.001	2.640(5)	2.826(5)	−0.186	Hawthorne (1976)
Nat. manganberzeliite	3.034(1)	3.036(1)	−0.002	2.637(1)	2.832(1)	−0.195	Varenche, Italy
Nat. manganberzeliite	3.044(1)	3.047(1)	−0.003	2.631(1)	2.828(1)	−0.197	Gozaisho mine, Japan
Nat. manganberzeliite	3.035(1)	3.040(1)	−0.005	2.640(1)	2.838(1)	−0.198	Uwe Kolitsch (pers. comm.)

* The Δ value is shared − unshared edge length for the appropriate site.

shared and unshared octahedral edges are listed in Table 8. Increasing the mean ionic radius of the elements at the *X* site has been shown to lengthen shared edges and shorten unshared edges in silicate garnets (Novak and Gibbs, 1971), but this is not observed in the arsenate and vanadate garnets in this study. In palenzonaite, the maximum difference in the refined lengths of the two octahedral edges is 0.025Å (unshared > shared). In manganberzeliite and schäferite the O−O octahedral edges are of almost equal length. The unshared octahedral edge tends to be longer than the shared edge in berzeliite, and the maximum difference is 0.011 Å (shared > unshared).

In the highly condensed garnet structure there are also shared edges between the *Z* tetrahedron and the distorted square *X* antiprism. In silicate garnets (Novak and Gibbs, 1971), the length difference between and the unshared tetrahedral edges (4 ×) and the shared tetrahedral edges (2 ×) varies between −0.257 Å (pyrope) and −0.158 Å (uvarovite). For the octahedron the difference between shared and unshared edges is considerably smaller and varies between 0.099 Å (pyrope) and −0.046 Å (goldmanite). This may indicate that tetrahedral edge distortion is not as critical for the stability of the structure. For arsenate and vanadate garnets the difference between shared and unshared tetrahedral edges varies between −0.19 and −0.20 Å (Table 8), which is within the range observed for silicate garnets (Novak and Gibbs, 1971).

Palenzonaite from manganese deposits in Liguria, the Aosta valley and the Swiss Alps and berzeliite and manganberzeliite from Långban, Varenche and Gozaisho are secondary minerals formed in veins in low-grade metamorphic facies conditions (probably <300ºC). It is inviting to assume that a less distorted arsenate or vanadate garnet structure with larger divalent cations at *Y* charge balanced by a mixture of Na and Ca at *X* would be more stable in these conditions. However, this is highly speculative and there are no reliable estimates for the crystallization temperature of minerals associated with the arsenate or vanadate garnets. Nor are there fluid inclusion studies with results that can be clearly correlated with the formation of the garnets. Matsubara (1975) noted that manganberzeliite can be formed at relatively high fO_2 at low temperatures, and that it is stable over a wide range of metamorphic temperature and redox conditions. In contrast, schäferite from Bellberg in the Eifel district (Krause *et al*., 1999) is almost certainly a high temperature mineral. Synthetic schäferite (Nakatsuka *et al*., 2003) and palenzonaite (Nakatsuka *et al*., 2004*a*) have been synthesized by the floating zone technique from oxide melts at high temperatures. According to Ikuta and Iishi (2006), schäferite and palenzonaite were synthesized at 1100ºC and 850ºC, respectively. The preference of divalent cations for the *Y* site and a ratio of Ca/Na of ~2/1 at the *X* site (reducing structural distortion and providing charge balance) is thus a useful rule which governs the structure and composition of arsenate- and vanadate-bearing garnets, (unless they are formed at extreme pressure). There is no indication in the X-ray diffraction data of a lowering of symmetry from cubic $Ia\bar{3}d$ in spite of the close to 2/1 Ca/Na ratio at the *X* site.

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AsT 0.00499(11) 0.00509(9) 0.00509(9) 0.000 0.000 0.000
Si 0.00499(11) 0.00509(9) 0.00509(9) 0.000 0.000 0.000
O 0.0091(3) 0.0104(3) 0.0078(3) 0.0006(2) -0.0019(3) 0.0013(2)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
;

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NaX O 2.5308(7) 69_656 ?
NaX O 2.5308(7) 52_666 ?
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NaX AsT 3.0863 . ?
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MgY O 2.0908(7) 16 ?
MgY O 2.0908(7) 14 ?
MgY O 2.0908(7) 10 ?
MgY NaX 3.4505 55_556 ?
MgY CaX 3.4505 49 ?
MgY CaX 3.4505 28_444 ?
MgY CaX 3.4505 76 ?
MgY CaX 3.4505 7_554 ?
AsT O 1.6897(7) 17_556 ?
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AsT O 1.6897(7) 42_544 ?
AsT CaX 3.0862 50_656 ?
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O Si 1.6897(7) 17_556 ?
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O MnY 2.0908(7) 11 ?
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O NaX O 91.934(19) 64 69_656 ?
O NaX O 122.846(16) 95_565 69_656 ?
O NaX O 73.53(3) 96_545 69_656 ?
O NaX O 72.99(3) 49_556 69_656 ?
O NaX O 72.99(3) 64 52_666 ?
O NaX O 73.53(3) 95_565 52_666 ?
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MgY O CaX 99.73(3) 11 49_556 ?
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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As As 0.3750 0.0000 0.2500 0.00635(13) Uani 0.044(5) 4 d SP . .
Si Si 0.3750 0.0000 0.2500 0.00635(13) Uani 0.06 4 d SP . .
Mn Mn 0.0000 0.0000 0.0000 0.00949(16) Uani 0.989(3) 6 d SP . .
O O 0.03924(7) 0.05418(7) 0.65829(6) 0.0118(2) Uani 1 1 d . . .

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V 0.0056(2) 0.00672(15) 0.00672(15) 0.000 0.000 0.000
As 0.0056(2) 0.00672(15) 0.00672(15) 0.000 0.000 0.000
Si 0.0056(2) 0.00672(15) 0.00672(15) 0.000 0.000 0.000
Mn 0.00949(16) 0.00949(16) 0.00949(16) -0.00060(9) -0.00060(9) -0.00060(9)
O 0.0126(5) 0.0126(4) 0.0104(4) -0.0006(3) -0.0006(3) -0.0001(3)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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Ca O 2.5381(8) 55_556 ?
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Ca O 2.5381(8) 93_655 ?
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Ca Si 3.1340 50_556 ?
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V Ca 3.1340 50_656 ?
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Mn O 2.1542(8) 32_544 ?
Mn O 2.1542(8) 28_445 ?
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Mn Na 3.5039 49 ?
Mn Na 3.5039 5 ?
Mn Na 3.5039 53 ?
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O As 1.7143(8) 2 ?
O V 1.7143(8) 2 ?
O Mn 2.1542(8) 28_445 ?
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Si O Ca 127.95(4) 2 58_566 ?
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V O Ca 127.95(4) 2 58_566 ?
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_refine_special_details
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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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CaX Ca 0.1250 0.0000 0.2500 0.01099(18) Uani 0.67 4 d SP . .
MnY Mn 0.0000 0.0000 0.0000 0.0093(2) Uani 0.777(7) 6 d SP . .
MgY Mg 0.0000 0.0000 0.0000 0.0093(2) Uani 0.223(7) 6 d SP . .
AsT As 0.3750 0.0000 0.2500 0.00675(9) Uani 0.848(8) 4 d SP . .
VT V 0.3750 0.0000 0.2500 0.00675(9) Uani 0.152(8) 4 d SP . .
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MnY 0.0093(2) 0.0093(2) 0.0093(2) -0.00038(10) -0.00038(10) -0.00038(10)
MgY 0.0093(2) 0.0093(2) 0.0093(2) -0.00038(10) -0.00038(10) -0.00038(10)
AsT 0.00645(14) 0.00690(10) 0.00690(10) 0.000 0.000 0.000
VT 0.00645(14) 0.00690(10) 0.00690(10) 0.000 0.000 0.000
O 0.0114(5) 0.0126(4) 0.0097(4) 0.0008(3) -0.0015(3) 0.0012(3)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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NaX O 2.4416(10) 49_556 ?
NaX O 2.4416(10) 67_656 ?
NaX O 2.5431(10) 55_556 ?
NaX O 2.5431(10) 93_655 ?
NaX O 2.5431(10) 80_455 ?
NaX O 2.5431(10) 70_656 ?
NaX AsT 3.1207 . ?
NaX VT 3.1207 50_556 ?
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MnY O 2.1459(9) 32_544 ?
MnY O 2.1459(9) 28_445 ?
MnY O 2.1459(9) 84_545 ?
MnY O 2.1459(9) 80_455 ?
MnY O 2.1459(9) 76_554 ?
MnY NaX 3.4891 5 ?
MnY NaX 3.4891 57 ?
MnY CaX 3.4891 49 ?
MnY CaX 3.4891 5 ?
MnY CaX 3.4891 53 ?
MnY CaX 3.4891 9 ?
AsT O 1.6953(9) 27_545 ?
AsT O 1.6953(9) 2_554 ?
AsT O 1.6953(9) 90_565 ?
AsT O 1.6953(9) 67_656 ?
AsT CaX 3.1207 50_656 ?
AsT NaX 3.1207 50_656 ?
O VT 1.6953(9) 2 ?
O AsT 1.6953(9) 2 ?
O MgY 2.1459(9) 28_445 ?
O MnY 2.1459(9) 28_445 ?
O NaX 2.4416(10) 49_556 ?
O CaX 2.4416(10) 49_556 ?
O CaX 2.5431(10) 58_566 ?
O NaX 2.5431(10) 58_566 ?

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O NaX O 164.07(4) 90_565 49_556 ?
O NaX O 65.37(4) 76_554 49_556 ?
O NaX O 65.37(4) 90_565 67_656 ?
O NaX O 164.07(4) 76_554 67_656 ?
O NaX O 117.08(4) 49_556 67_656 ?
O NaX O 91.85(3) 90_565 55_556 ?
O NaX O 122.538(19) 76_554 55_556 ?
O NaX O 74.94(4) 49_556 55_556 ?
O NaX O 71.92(4) 67_656 55_556 ?
O NaX O 74.94(4) 90_565 93_655 ?
O NaX O 71.92(4) 76_554 93_655 ?
O NaX O 91.85(3) 49_556 93_655 ?
O NaX O 122.54(2) 67_656 93_655 ?
O NaX O 69.58(4) 55_556 93_655 ?
O NaX O 71.92(4) 90_565 80_455 ?
O NaX O 74.94(4) 76_554 80_455 ?
O NaX O 122.54(2) 49_556 80_455 ?
O NaX O 91.85(3) 67_656 80_455 ?
O NaX O 160.99(4) 55_556 80_455 ?
O NaX O 113.79(4) 93_655 80_455 ?
O NaX O 122.538(19) 90_565 70_656 ?
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O NaX O 71.92(4) 49_556 70_656 ?
O NaX O 74.94(4) 67_656 70_656 ?
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O NaX AsT 147.32(2) 76_554 . ?
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O NaX VT 147.32(2) 67_656 50_556 ?
O NaX VT 99.51(2) 55_556 50_556 ?
O NaX VT 80.49(2) 93_655 50_556 ?
O NaX VT 99.51(2) 80_455 50_556 ?
O NaX VT 80.49(2) 70_656 50_556 ?
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CaX MnY CaX 113.6 49 5 ?
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O MnY CaX 136.25(3) 80_455 53 ?
O MnY CaX 86.09(3) 76_554 53 ?
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CaX MnY CaX 66.4 49 53 ?
CaX MnY CaX 180.0 5 53 ?
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O MnY CaX 86.09(3) 32_544 9 ?
O MnY CaX 133.52(3) 28_445 9 ?
O MnY CaX 43.75(3) 84_545 9 ?
O MnY CaX 93.91(3) 80_455 9 ?
O MnY CaX 46.48(3) 76_554 9 ?
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CaX MnY CaX 113.6 53 9 ?
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O AsT O 102.10(7) 90_565 67_656 ?
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NaX AsT NaX 180.0 . 50_656 ?
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VT O MnY 130.18(5) 2 28_445 ?
AsT O MnY 130.18(5) 2 28_445 ?

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MnY O NaX 98.82(4) 28_445 49_556 ?
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MnY O CaX 98.82(4) 28_445 49_556 ?
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AsT O CaX 127.65(5) 2 58_566 ?
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MnY O CaX 95.79(3) 28_445 58_566 ?
NaX O CaX 100.11(3) 49_556 58_566 ?
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AsT O NaX 127.65(5) 2 58_566 ?
MgY O NaX 95.79(3) 28_445 58_566 ?
MnY O NaX 95.79(3) 28_445 58_566 ?
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 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
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_computing_data_reduction         ?
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_computing_publication_material   ?

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 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0167P)^2^+0.5417P] where P=(Fo^2^+2Fc^2^)/3'
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_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      SHELXL
_refine_ls_extinction_coef        0.00078(8)
_refine_ls_extinction_expression
 'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'
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_refine_ls_number_restraints      0
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_refine_ls_wR_factor_ref          0.0347
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CaX Ca 0.1250 0.0000 0.2500 0.00987(13) Uani 0.67 4 d SP . .
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MnY Mn 0.0000 0.0000 0.0000 0.0084(2) Uani 0.121(5) 6 d SP . .
AsT As 0.3750 0.0000 0.2500 0.00525(7) Uani 0.958(6) 4 d SP . .
VT V 0.3750 0.0000 0.2500 0.00525(7) Uani 0.042(6) 4 d SP . .
O O 0.03893(5) 0.05085(5) 0.65608(5) 0.00876(17) Uani 1 1 d . . .

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CaX 0.00736(19) 0.01113(15) 0.01113(15) 0.00158(13) 0.000 0.000
MgY 0.0084(2) 0.0084(2) 0.0084(2) -0.00021(12) -0.00021(12) -0.00021(12)
MnY 0.0084(2) 0.0084(2) 0.0084(2) -0.00021(12) -0.00021(12) -0.00021(12)
AsT 0.00504(9) 0.00535(8) 0.00535(8) 0.000 0.000 0.000
VT 0.00504(9) 0.00535(8) 0.00535(8) 0.000 0.000 0.000
O 0.0088(3) 0.0100(3) 0.0075(3) 0.0004(2) -0.0017(2) 0.0010(2)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
;

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 _geom_bond_site_symmetry_2
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NaX O 2.4144(7) 49_556 ?
NaX O 2.5332(6) 85_455 ?
NaX O 2.5332(6) 62 ?
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NaX O 2.5332(6) 52_666 ?
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NaX VT 3.0851 65 ?
NaX AsT 3.0851 65 ?
MgY O 2.0819(6) 16 ?
MgY O 2.0819(6) 14 ?
MgY O 2.0819(6) 10 ?
MgY O 2.0819(6) 64 ?
MgY O 2.0819(6) 62 ?
MgY O 2.0819(6) 58 ?
MgY NaX 3.4492 28_444 ?
MgY NaX 3.4492 55_556 ?
MgY CaX 3.4492 49 ?
MgY CaX 3.4492 28_444 ?
MgY CaX 3.4492 76 ?
MgY CaX 3.4492 7_554 ?
AsT O 1.6927(6) 17_556 ?
AsT O 1.6927(6) 42_544 ?
AsT O 1.6927(6) 96_545 ?
AsT O 1.6927(6) 95_565 ?
AsT NaX 3.0851 50_656 ?
AsT CaX 3.0851 50_656 ?
O VT 1.6927(6) 17_556 ?
O AsT 1.6927(6) 17_556 ?
O MnY 2.0819(6) 11 ?
O MgY 2.0819(6) 11 ?
O NaX 2.4144(7) 49_556 ?
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O NaX O 116.90(3) 96_545 49_556 ?
O NaX O 66.17(3) 64 49_556 ?
O NaX O 91.964(17) 95_565 85_455 ?
O NaX O 73.26(2) 96_545 85_455 ?
O NaX O 122.906(14) 64 85_455 ?
O NaX O 73.17(3) 49_556 85_455 ?
O NaX O 73.26(2) 95_565 62 ?
O NaX O 91.964(17) 96_545 62 ?
O NaX O 73.17(3) 64 62 ?
O NaX O 122.906(14) 49_556 62 ?
O NaX O 162.58(3) 85_455 62 ?
O NaX O 122.906(14) 95_565 69_656 ?
O NaX O 73.17(3) 96_545 69_656 ?
O NaX O 91.964(17) 64 69_656 ?
O NaX O 73.26(2) 49_556 69_656 ?
O NaX O 113.01(3) 85_455 69_656 ?
O NaX O 69.82(3) 62 69_656 ?
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O NaX O 122.906(14) 96_545 52_666 ?
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O NaX O 91.964(17) 49_556 52_666 ?
O NaX O 69.82(3) 85_455 52_666 ?
O NaX O 113.01(3) 62 52_666 ?
O NaX O 162.58(3) 69_656 52_666 ?
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O NaX AsT 146.915(15) 64 . ?
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O NaX AsT 81.291(14) 85_455 . ?
O NaX AsT 81.291(14) 62 . ?
O NaX AsT 98.709(14) 69_656 . ?
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O NaX VT 146.914(15) 96_545 65 ?
O NaX VT 33.085(15) 64 65 ?
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AsT NaX VT 180.0 . 65 ?
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CaX MgY CaX 113.6 49 28_444 ?
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O MgY CaX 94.104(18) 14 76 ?
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O MgY CaX 133.106(17) 64 76 ?
O MgY CaX 85.896(18) 62 76 ?
O MgY CaX 136.410(19) 58 76 ?
NaX MgY CaX 180.0 28_444 76 ?
NaX MgY CaX 66.4 55_556 76 ?
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O MgY CaX 46.894(17) 58 7_554 ?
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NaX MgY CaX 180.0 55_556 7_554 ?
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CaX MgY CaX 66.4 28_444 7_554 ?
CaX MgY CaX 113.6 76 7_554 ?
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O AsT O 113.19(2) 17_556 95_565 ?
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O AsT O 102.27(5) 96_545 95_565 ?
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O AsT NaX 128.87(2) 96_545 50_656 ?
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O AsT NaX 128.87(2) 42_544 . ?
O AsT NaX 51.13(2) 96_545 . ?
O AsT NaX 51.13(2) 95_565 . ?
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O AsT CaX 128.87(2) 96_545 50_656 ?
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NaX AsT CaX 180.0 . 50_656 ?
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MnY O MgY 0.0 11 11 ?
VT O NaX 95.78(3) 17_556 49_556 ?
AsT O NaX 95.78(3) 17_556 49_556 ?
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MgY O NaX 99.93(3) 11 49_556 ?
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AsT O CaX 95.78(3) 17_556 49_556 ?
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MgY O CaX 99.93(3) 11 49_556 ?
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VT O CaX 125.61(3) 17_556 53_566 ?
AsT O CaX 125.61(3) 17_556 53_566 ?
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MgY O CaX 96.23(2) 11 53_566 ?
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CaX O CaX 99.55(2) 49_556 53_566 ?
VT O NaX 125.61(3) 17_556 53_566 ?
AsT O NaX 125.61(3) 17_556 53_566 ?
MnY O NaX 96.23(2) 11 53_566 ?
MgY O NaX 96.23(2) 11 53_566 ?
NaX O NaX 99.55(2) 49_556 53_566 ?
CaX O NaX 99.55(2) 49_556 53_566 ?
CaX O NaX 0.0 53_566 53_566 ?

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_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
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_diffrn_reflns_av_sigmaI/netI     0.0233
_diffrn_reflns_limit_h_min        -13
_diffrn_reflns_limit_h_max        10
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_diffrn_reflns_limit_k_max        17
_diffrn_reflns_limit_l_min        -17
_diffrn_reflns_limit_l_max        12
_diffrn_reflns_theta_min          3.98
_diffrn_reflns_theta_max          30.03
_reflns_number_total              245
_reflns_number_gt                 163
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     ?
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 2008)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0263P)^2^+2.7367P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          245
_refine_ls_number_parameters      19
_refine_ls_number_restraints      0
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_refine_ls_R_factor_gt            0.0234
_refine_ls_wR_factor_ref          0.0617
_refine_ls_wR_factor_gt           0.0516
_refine_ls_goodness_of_fit_ref    1.001
_refine_ls_restrained_S_all       1.001
_refine_ls_shift/su_max           0.000
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 _atom_site_type_symbol
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 _atom_site_symmetry_multiplicity
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 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
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V V 0.3750 0.0000 0.2500 0.0074(3) Uani 0.927(9) 4 d SP . .
As As 0.3750 0.0000 0.2500 0.0074(3) Uani 0.008(9) 4 d SP . .
Si Si 0.3750 0.0000 0.2500 0.0074(3) Uani 0.07 4 d SP . .
Mn Mn 0.0000 0.0000 0.0000 0.0111(3) Uani 0.989(5) 6 d SP . .
O O 0.03924(13) 0.05416(14) 0.65842(14) 0.0132(5) Uani 1 1 d . . .

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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Na 0.0106(6) 0.0141(4) 0.0141(4) 0.0016(4) 0.000 0.000
V 0.0076(5) 0.0073(3) 0.0073(3) 0.000 0.000 0.000
As 0.0076(5) 0.0073(3) 0.0073(3) 0.000 0.000 0.000
Si 0.0076(5) 0.0073(3) 0.0073(3) 0.000 0.000 0.000
Mn 0.0111(3) 0.0111(3) 0.0111(3) -0.0005(2) -0.0005(2) -0.0005(2)
O 0.0131(9) 0.0143(10) 0.0122(9) 0.0008(7) 0.0002(8) 0.0000(7)

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;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
;

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 _geom_bond_site_symmetry_2
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Ca O 2.4546(17) 67_656 ?
Ca O 2.4546(17) 90_565 ?
Ca O 2.5401(18) 70_656 ?
Ca O 2.5401(18) 55_556 ?
Ca O 2.5401(18) 80_455 ?
Ca O 2.5401(18) 93_655 ?
Ca V 3.1358(3) . ?
Ca Si 3.1358(3) 50_556 ?
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V O 1.7141(17) 90_565 ?
V O 1.7141(17) 2_554 ?
V O 1.7141(17) 67_656 ?
V Na 3.1358(3) 50_656 ?
V Ca 3.1358(3) 50_656 ?
Mn O 2.1570(17) 36_454 ?
Mn O 2.1570(17) 32_544 ?
Mn O 2.1570(17) 28_445 ?
Mn O 2.1570(17) 84_545 ?
Mn O 2.1570(17) 80_455 ?
Mn O 2.1570(17) 76_554 ?
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Mn Ca 3.5060(3) 57 ?
Mn Na 3.5060(3) 49 ?
Mn Na 3.5060(3) 5 ?
Mn Na 3.5060(3) 53 ?
Mn Na 3.5060(3) 9 ?
O Si 1.7141(17) 2 ?
O As 1.7141(17) 2 ?
O V 1.7141(17) 2 ?
O Mn 2.1570(17) 28_445 ?
O Ca 2.4546(17) 49_556 ?
O Na 2.4546(17) 49_556 ?
O Na 2.5401(18) 58_566 ?
O Ca 2.5401(18) 58_566 ?

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O Ca O 164.46(8) 76_554 67_656 ?
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O Ca O 164.46(8) 49_556 90_565 ?
O Ca O 65.87(8) 67_656 90_565 ?
O Ca O 92.20(5) 76_554 70_656 ?
O Ca O 71.61(6) 49_556 70_656 ?
O Ca O 74.91(8) 67_656 70_656 ?
O Ca O 122.51(3) 90_565 70_656 ?
O Ca O 122.51(3) 76_554 55_556 ?
O Ca O 74.91(8) 49_556 55_556 ?
O Ca O 71.61(6) 67_656 55_556 ?
O Ca O 92.20(5) 90_565 55_556 ?
O Ca O 113.70(8) 70_656 55_556 ?
O Ca O 74.91(8) 76_554 80_455 ?
O Ca O 122.51(3) 49_556 80_455 ?
O Ca O 92.20(5) 67_656 80_455 ?
O Ca O 71.61(6) 90_565 80_455 ?
O Ca O 69.66(8) 70_656 80_455 ?
O Ca O 161.00(8) 55_556 80_455 ?
O Ca O 71.61(6) 76_554 93_655 ?
O Ca O 92.20(5) 49_556 93_655 ?
O Ca O 122.51(3) 67_656 93_655 ?
O Ca O 74.91(8) 90_565 93_655 ?
O Ca O 161.00(8) 70_656 93_655 ?
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O Ca V 80.50(4) 80_455 . ?
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O V Na 128.87(6) 67_656 50_656 ?
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O Mn O 89.54(6) 32_544 28_445 ?
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O Mn O 90.46(6) 32_544 84_545 ?
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O Mn O 90.46(6) 32_544 76_554 ?
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O Mn Ca 46.08(5) 84_545 5 ?
O Mn Ca 43.78(5) 80_455 5 ?
O Mn Ca 93.63(4) 76_554 5 ?

O Mn Ca 43.78(5) 36_454 57 ?
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Ca Mn Na 113.6 5 49 ?
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Ca Mn Na 0.0 5 5 ?
Ca Mn Na 113.6 57 5 ?
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O Mn Na 46.08(5) 36_454 53 ?
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O Mn Na 136.22(5) 80_455 53 ?
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Ca Mn Na 180.0 5 53 ?
Ca Mn Na 66.4 57 53 ?
Na Mn Na 66.4 49 53 ?
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O Mn Na 43.78(5) 84_545 9 ?
O Mn Na 93.63(4) 80_455 9 ?
O Mn Na 46.08(5) 76_554 9 ?
Ca Mn Na 66.4 5 9 ?
Ca Mn Na 180.0 57 9 ?
Na Mn Na 113.6 49 9 ?
Na Mn Na 66.4 5 9 ?
Na Mn Na 113.6 53 9 ?
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Si O V 0.0 2 2 ?
As O V 0.0 2 2 ?
Si O Mn 129.47(9) 2 28_445 ?
As O Mn 129.47(9) 2 28_445 ?
V O Mn 129.47(9) 2 28_445 ?
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As O Ca 95.94(7) 2 49_556 ?
V O Ca 95.94(7) 2 49_556 ?
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As O Na 95.94(7) 2 49_556 ?
V O Na 95.94(7) 2 49_556 ?
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Si O Na 127.99(9) 2 58_566 ?

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As O Na 127.99(9) 2 58_566 ?
V O Na 127.99(9) 2 58_566 ?
Mn O Na 96.22(6) 28_445 58_566 ?
Ca O Na 100.50(6) 49_556 58_566 ?
Na O Na 100.50(6) 49_556 58_566 ?
Si O Ca 127.99(9) 2 58_566 ?
As O Ca 127.99(9) 2 58_566 ?
V O Ca 127.99(9) 2 58_566 ?
Mn O Ca 96.22(6) 28_445 58_566 ?
Ca O Ca 100.50(6) 49_556 58_566 ?
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 'V'  'V'   0.3005   0.5294
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_diffrn_radiation_monochromator   graphite
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_diffrn_measurement_method        ?
_diffrn_detector_area_resol_mean  ?
_diffrn_standards_number          ?
_diffrn_standards_interval_count  ?
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_diffrn_reflns_number             6045
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_diffrn_reflns_av_sigmaI/netI     0.0229
_diffrn_reflns_limit_h_min        -17
_diffrn_reflns_limit_h_max        16
_diffrn_reflns_limit_k_min        -14
_diffrn_reflns_limit_k_max        17
_diffrn_reflns_limit_l_min        -17
_diffrn_reflns_limit_l_max        17
_diffrn_reflns_theta_min          3.98
_diffrn_reflns_theta_max          29.95
_reflns_number_total              244
_reflns_number_gt                 198
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     ?
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 2008)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

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_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0141P)^2^+2.7949P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      none
_refine_ls_extinction_coef        ?
_refine_ls_number_reflns          244
_refine_ls_number_parameters      19
_refine_ls_number_restraints      0
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_refine_ls_R_factor_gt            0.0187
_refine_ls_wR_factor_ref          0.0439
_refine_ls_wR_factor_gt           0.0403
_refine_ls_goodness_of_fit_ref    1.046
_refine_ls_restrained_S_all       1.046
_refine_ls_shift/su_max           0.000
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 _atom_site_type_symbol
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 _atom_site_symmetry_multiplicity
 _atom_site_calc_flag
 _atom_site_refinement_flags
 _atom_site_disorder_assembly
 _atom_site_disorder_group
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V V 0.3750 0.0000 0.2500 0.00854(17) Uani 0.521(9) 4 d SP . .
As As 0.3750 0.0000 0.2500 0.00854(17) Uani 0.460(9) 4 d SP . .
Si Si 0.3750 0.0000 0.2500 0.00854(17) Uani 0.01 4 d SP . .
Mn Mn 0.0000 0.0000 0.0000 0.0122(2) Uani 0.968(4) 6 d SP . .
O O 0.03972(11) 0.05373(11) 0.65883(10) 0.0150(4) Uani 1 1 d . . .

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 _atom_site_aniso_U_22
 _atom_site_aniso_U_33
 _atom_site_aniso_U_23
 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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Na 0.0110(5) 0.0147(3) 0.0147(3) 0.0019(3) 0.000 0.000
V 0.0079(3) 0.00884(19) 0.00884(19) 0.000 0.000 0.000
As 0.0079(3) 0.00884(19) 0.00884(19) 0.000 0.000 0.000
Si 0.0079(3) 0.00884(19) 0.00884(19) 0.000 0.000 0.000
Mn 0.0122(2) 0.0122(2) 0.0122(2) -0.00060(15) -0.00060(15) -0.00060(15)
O 0.0165(7) 0.0153(7) 0.0133(7) 0.0007(5) -0.0007(5) 0.0005(5)

_geom_special_details
;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
;

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 _geom_bond_site_symmetry_2
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Ca O 2.4540(13) 67_656 ?
Ca O 2.4540(13) 49_556 ?
Ca O 2.4540(13) 90_565 ?
Ca O 2.5455(13) 70_656 ?
Ca O 2.5455(13) 55_556 ?
Ca O 2.5455(13) 80_455 ?
Ca O 2.5455(13) 93_655 ?
Ca V 3.1335 . ?
Ca Si 3.1335 50_556 ?
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V O 1.7035(13) 27_545 ?
V O 1.7035(13) 90_565 ?
V O 1.7035(13) 2_554 ?
V O 1.7035(13) 67_656 ?
V Na 3.1336 50_656 ?
V Ca 3.1336 50_656 ?
Mn O 2.1598(13) 76_554 ?
Mn O 2.1598(13) 28_445 ?
Mn O 2.1598(13) 84_545 ?
Mn O 2.1598(13) 36_454 ?
Mn O 2.1598(13) 80_455 ?
Mn O 2.1598(13) 32_544 ?
Mn Ca 3.5034 49 ?
Mn Ca 3.5034 57 ?
Mn Na 3.5034 49 ?
Mn Na 3.5034 5 ?
Mn Na 3.5034 53 ?
Mn Na 3.5034 9 ?
O Si 1.7035(13) 2 ?
O As 1.7035(13) 2 ?
O V 1.7035(13) 2 ?
O Mn 2.1598(13) 28_445 ?
O Ca 2.4540(13) 49_556 ?
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O Ca O 65.44(6) 67_656 90_565 ?
O Ca O 164.46(6) 49_556 90_565 ?
O Ca O 91.95(4) 76_554 70_656 ?
O Ca O 75.15(6) 67_656 70_656 ?
O Ca O 71.68(5) 49_556 70_656 ?
O Ca O 122.45(3) 90_565 70_656 ?
O Ca O 122.45(3) 76_554 55_556 ?
O Ca O 71.68(5) 67_656 55_556 ?
O Ca O 75.15(6) 49_556 55_556 ?
O Ca O 91.95(4) 90_565 55_556 ?
O Ca O 113.94(6) 70_656 55_556 ?
O Ca O 75.15(6) 76_554 80_455 ?
O Ca O 91.95(4) 67_656 80_455 ?
O Ca O 122.45(3) 49_556 80_455 ?
O Ca O 71.68(5) 90_565 80_455 ?
O Ca O 69.49(6) 70_656 80_455 ?
O Ca O 160.82(6) 55_556 80_455 ?
O Ca O 71.68(5) 76_554 93_655 ?
O Ca O 122.45(3) 67_656 93_655 ?
O Ca O 91.95(4) 49_556 93_655 ?
O Ca O 75.15(6) 90_565 93_655 ?
O Ca O 160.82(6) 70_656 93_655 ?
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O Ca O 113.94(6) 80_455 93_655 ?
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O Ca V 80.41(3) 80_455 . ?
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O Ca Si 147.28(3) 67_656 50_556 ?
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O Ca Si 147.28(3) 90_565 50_556 ?
O Ca Si 80.41(3) 70_656 50_556 ?
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O V Ca 51.14(5) 2_554 50_656 ?
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Na V Ca 0.0 50_656 50_656 ?
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Ca V Ca 180.0 50_656 . ?
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O Mn O 89.82(5) 76_554 84_545 ?
O Mn O 90.18(5) 28_445 84_545 ?
O Mn O 90.18(5) 76_554 36_454 ?
O Mn O 89.82(5) 28_445 36_454 ?
O Mn O 180.00(7) 84_545 36_454 ?
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O Mn O 90.18(5) 84_545 32_544 ?
O Mn O 89.82(5) 36_454 32_544 ?
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O Mn Ca 136.17(4) 76_554 49 ?
O Mn Ca 43.83(4) 28_445 49 ?
O Mn Ca 86.17(3) 84_545 49 ?
O Mn Ca 93.83(3) 36_454 49 ?
O Mn Ca 133.72(4) 80_455 49 ?
O Mn Ca 46.28(4) 32_544 49 ?

O Mn Ca 133.72(4) 76_554 57 ?
O Mn Ca 46.28(4) 28_445 57 ?
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O Mn Ca 86.17(3) 80_455 57 ?
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O Mn Na 46.28(4) 32_544 49 ?
Ca Mn Na 0.0 49 49 ?
Ca Mn Na 66.4 57 49 ?
O Mn Na 93.83(3) 76_554 5 ?
O Mn Na 86.17(3) 28_445 5 ?
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Ca Mn Na 113.6 49 5 ?
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Na Mn Na 113.6 49 5 ?
O Mn Na 86.17(3) 76_554 53 ?
O Mn Na 93.83(3) 28_445 53 ?
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O Mn Na 46.28(4) 36_454 53 ?
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O Mn Na 43.83(4) 84_545 9 ?
O Mn Na 136.17(4) 36_454 9 ?
O Mn Na 93.83(3) 80_455 9 ?
O Mn Na 86.17(3) 32_544 9 ?
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Ca Mn Na 180.0 57 9 ?
Na Mn Na 113.6 49 9 ?
Na Mn Na 66.4 5 9 ?
Na Mn Na 113.6 53 9 ?
Si O As 0.0 2 2 ?
Si O V 0.0 2 2 ?
As O V 0.0 2 2 ?
Si O Mn 129.77(7) 2 28_445 ?
As O Mn 129.77(7) 2 28_445 ?
V O Mn 129.77(7) 2 28_445 ?
Si O Ca 96.14(6) 2 49_556 ?
As O Ca 96.14(6) 2 49_556 ?
V O Ca 96.14(6) 2 49_556 ?
Mn O Ca 98.61(5) 28_445 49_556 ?
Si O Na 96.14(6) 2 49_556 ?
As O Na 96.14(6) 2 49_556 ?
V O Na 96.14(6) 2 49_556 ?
Mn O Na 98.61(5) 28_445 49_556 ?
Ca O Na 0.0 49_556 49_556 ?
Si O Na 128.06(7) 2 58_566 ?

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As O Na 128.06(7) 2 58_566 ?
V O Na 128.06(7) 2 58_566 ?
Mn O Na 95.90(5) 28_445 58_566 ?
Ca O Na 100.27(5) 49_556 58_566 ?
Na O Na 100.27(5) 49_556 58_566 ?
Si O Ca 128.06(7) 2 58_566 ?
As O Ca 128.06(7) 2 58_566 ?
V O Ca 128.06(7) 2 58_566 ?
Mn O Ca 95.90(5) 28_445 58_566 ?
Ca O Ca 100.27(5) 49_556 58_566 ?
Na O Ca 100.27(5) 49_556 58_566 ?
Na O Ca 0.0 58_566 58_566 ?

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_diffrn_radiation_source          'fine-focus sealed tube'
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_diffrn_measurement_method        ?
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_diffrn_standards_interval_count  ?
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_diffrn_standards_decay_%         ?
_diffrn_reflns_number             6753
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_diffrn_reflns_av_sigmaI/netI     0.0110
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_diffrn_reflns_limit_k_min        -16
_diffrn_reflns_limit_k_max        17
_diffrn_reflns_limit_l_min        -20
_diffrn_reflns_limit_l_max        19
_diffrn_reflns_theta_min          4.00
_diffrn_reflns_theta_max          35.95
_reflns_number_total              388
_reflns_number_gt                 339
_reflns_threshold_expression      >2\s(I)

_computing_data_collection        ?
_computing_cell_refinement        ?
_computing_data_reduction         ?
_computing_structure_solution     ?
_computing_structure_refinement   'SHELXL-97 (Sheldrick, 2008)'
_computing_molecular_graphics     ?
_computing_publication_material   ?

_refine_special_details
;
 Refinement of F^2^ against ALL reflections.  The weighted R-factor wR and
 goodness of fit S are based on F^2^, conventional R-factors R are based
 on F, with F set to zero for negative F^2^. The threshold expression of
 F^2^ > 2\s(F^2^) is used only for calculating R-factors(gt) etc. and is
 not relevant to the choice of reflections for refinement.  R-factors based
 on F^2^ are statistically about twice as large as those based on F, and R-
 factors based on ALL data will be even larger.
;

_refine_ls_structure_factor_coef  Fsqd
_refine_ls_matrix_type            full
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
 'calc w=1/[\s^2^(Fo^2^)+(0.0120P)^2^+1.6195P] where P=(Fo^2^+2Fc^2^)/3'
_atom_sites_solution_primary      direct
_atom_sites_solution_secondary    difmap
_atom_sites_solution_hydrogens    geom
_refine_ls_hydrogen_treatment     mixed
_refine_ls_extinction_method      SHELXL
_refine_ls_extinction_coef        0.00053(5)
_refine_ls_extinction_expression
 'Fc^*^=kFc[1+0.001xFc^2^\l^3^/sin(2\q)]^-1/4^'
_refine_ls_number_reflns          388
_refine_ls_number_parameters      20
_refine_ls_number_restraints      0
_refine_ls_R_factor_all           0.0175
_refine_ls_R_factor_gt            0.0136
_refine_ls_wR_factor_ref          0.0328
_refine_ls_wR_factor_gt           0.0318
_refine_ls_goodness_of_fit_ref    1.156
_refine_ls_restrained_S_all       1.156
_refine_ls_shift/su_max           0.001
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 _atom_site_symmetry_multiplicity
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 _atom_site_disorder_group
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MnY Mn 0.0000 0.0000 0.0000 0.00945(14) Uani 0.848(5) 6 d SP . .
MgY Mg 0.0000 0.0000 0.0000 0.00945(14) Uani 0.152(5) 6 d SP . .
AsT As 0.3750 0.0000 0.2500 0.00637(7) Uani 0.963(3) 4 d SP . .
O O 0.03973(6) 0.05317(6) 0.65912(6) 0.01104(19) Uani 1 1 d . . .

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 _atom_site_aniso_U_22
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 _atom_site_aniso_U_13
 _atom_site_aniso_U_12
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NaX 0.0085(2) 0.01243(16) 0.01243(16) 0.00168(16) 0.000 0.000
MnY 0.00945(14) 0.00945(14) 0.00945(14) -0.00048(7) -0.00048(7) -0.00048(7)
MgY 0.00945(14) 0.00945(14) 0.00945(14) -0.00048(7) -0.00048(7) -0.00048(7)
AsT 0.00621(11) 0.00645(8) 0.00645(8) 0.000 0.000 0.000
O 0.0112(4) 0.0125(4) 0.0094(3) 0.0007(2) -0.0019(2) 0.0016(3)

_geom_special_details
;
 All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell s.u.'s are taken
 into account individually in the estimation of s.u.'s in distances, angles
 and torsion angles; correlations between s.u.'s in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.
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 _geom_bond_site_symmetry_2
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CaX O 2.4424(8) 67_656 ?
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CaX O 2.4424(8) 90_565 ?
CaX O 2.5446(8) 70_656 ?
CaX O 2.5446(8) 55_556 ?
CaX O 2.5446(8) 80_455 ?
CaX O 2.5446(8) 93_655 ?
CaX AsT 3.1232 . ?
CaX AsT 3.1232 50_556 ?
CaX MnY 3.4919 . ?
MnY O 2.1538(7) 84_545 ?
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MnY O 2.1538(7) 80_455 ?
MnY O 2.1538(7) 76_554 ?
MnY O 2.1538(7) 36_454 ?
MnY O 2.1538(7) 32_544 ?
MnY O 2.1538(7) 28_445 ?
MnY CaX 3.4919 57 ?
MnY NaX 3.4919 49 ?
MnY NaX 3.4919 5 ?
MnY NaX 3.4919 53 ?
MnY NaX 3.4919 9 ?
AsT O 1.6927(7) 27_545 ?
AsT O 1.6927(7) 90_565 ?
AsT O 1.6927(7) 67_656 ?
AsT O 1.6927(7) 2_554 ?
AsT CaX 3.1232 50_656 ?
AsT NaX 3.1232 50_656 ?
O AsT 1.6927(7) 2 ?
O MgY 2.1538(7) 28_445 ?
O MnY 2.1538(7) 28_445 ?
O CaX 2.4424(8) 49_556 ?
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O NaX 2.5446(8) 58_566 ?
O CaX 2.5446(8) 58_566 ?

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O CaX O 75.22(3) 67_656 70_656 ?
O CaX O 71.74(3) 49_556 70_656 ?
O CaX O 122.502(15) 90_565 70_656 ?
O CaX O 122.502(15) 76_554 55_556 ?
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O CaX O 75.22(3) 49_556 55_556 ?
O CaX O 91.78(2) 90_565 55_556 ?
O CaX O 113.89(3) 70_656 55_556 ?
O CaX O 75.22(3) 76_554 80_455 ?
O CaX O 91.78(2) 67_656 80_455 ?
O CaX O 122.502(16) 49_556 80_455 ?
O CaX O 71.74(3) 90_565 80_455 ?
O CaX O 69.58(4) 70_656 80_455 ?
O CaX O 160.71(3) 55_556 80_455 ?
O CaX O 71.74(3) 76_554 93_655 ?
O CaX O 122.502(15) 67_656 93_655 ?
O CaX O 91.78(2) 49_556 93_655 ?
O CaX O 75.22(3) 90_565 93_655 ?
O CaX O 160.71(3) 70_656 93_655 ?
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O CaX O 113.89(3) 80_455 93_655 ?
O CaX AsT 147.414(17) 76_554 . ?
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O MnY CaX 86.09(2) 80_455 57 ?
O MnY CaX 133.52(2) 76_554 57 ?
O MnY CaX 43.74(2) 36_454 57 ?
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O AsT NaX 129.00(3) 67_656 50_656 ?
O AsT NaX 51.00(3) 2_554 50_656 ?
CaX AsT NaX 0.0 50_656 50_656 ?
O AsT CaX 129.00(3) 27_545 . ?
O AsT CaX 51.00(3) 90_565 . ?
O AsT CaX 51.00(3) 67_656 . ?
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NaX AsT CaX 180.0 50_656 . ?
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AsT O MnY 130.02(4) 2 28_445 ?
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MgY O NaX 98.69(3) 28_445 49_556 ?
MnY O NaX 98.69(3) 28_445 49_556 ?

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MnY O NaX 95.65(3) 28_445 58_566 ?
CaX O NaX 100.16(3) 49_556 58_566 ?
NaX O NaX 100.16(3) 49_556 58_566 ?
AsT O CaX 127.90(4) 2 58_566 ?
MgY O CaX 95.65(3) 28_445 58_566 ?
MnY O CaX 95.65(3) 28_445 58_566 ?
CaX O CaX 100.16(3) 49_556 58_566 ?
NaX O CaX 100.16(3) 49_556 58_566 ?
NaX O CaX 0.0 58_566 58_566 ?

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