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DISTINCT DOMAINS IN "GUARINITE" FROM MONTE SOMMA, ITALY: CRYSTAL STRUCTURES AND CRYSTAL CHEMISTRY

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Abstract

"Guarinite" is a typical accessory mineral of the Monte Somma syenite; it belongs to the cuspidine group and displays a domain structure. "Guarinite" contains up to three distinct domains, corresponding to three different ways to connect disilicate groups and walls of octahedra; these may all be simultaneously present in the same crystal. The domains present in the crystals of "guarinite" have cell type I, II and IV, according to the classification scheme proposed for cuspidine-group minerals. Domain IV is the most common, and domain I is the rarest; domain II may occur as the only domain, whereas domain I occurs only in association with domain IV, which invariably predominates. So far, the actual structure of the various domains had not been defined. EPMA and single-crystal structural studies indicate that domain I of "guarinite" displays space group *P*1, with *a* 10.973(2), *b* 10.306(1), *c* 7.367(3) Å, α 90.03(3), β 109.63(3), γ 90.11(2)°, with a crystal-chemical formula $Ca_3(Ca_{0.72}Zr_{0.28})_{\Sigma 1.00}(Zr_{0.86}M_{0.14})_{\Sigma 1.00}(Ca_{0.59}Mn_{0.25}Fe_{0.16})_{\Sigma 1.00}(Na_{1.20}Ca_{0.76})_{\Sigma 1.96}(Si_{1.98}O_7)_2(F_{2.88}O_{1.12})_{\Sigma 4.00}$, where M represents Nb, Ti, Al, Sr, and REE. Domain I is isostructural with hiortdahlite II, and its crystal structure was refined to a final *R* of 0.072. Domain II of "guarinite" displays space group $P12_11$, with *a* 10.836(1), *b* 10.270(1), *c* 7.296(1) Å, β 109.13(3)°, with a crystal-chemical formula $Ca_3Zr(Nb_{0.56}Fe_{0.15}Mn_{0.10}Ti_{0.10}Zr_{0.09})_{\Sigma 1.00}(Ca_{0.72}Mn_{0.18}M_{0.10})_{\Sigma 1.00}(Na_{0.77}Ca_{0.23})_{\Sigma 1.00}(Na_{0.80}Ca_{0.22})_{\Sigma 1.02}(Si_2O_7)_2(O_{2.17}F_{1.83})_{\Sigma 4.00}$, where M represents Al, Mg, Sr and Y. Domain II is isostructural with wöhlerite, and its crystal structure was refined to a final *R* of 0.045. Domain IV of "guarinite" adopts space group *P*1, with *a* 10.970(2), *b* 10.943(2), *c* 7.365(1) Å, α 109.63(2), β 109.65(2), γ 83.39(1)°, with a crystal-chemical formula $Ca_4Zr(Ca_{0.31}Mn_{0.25}Fe_{0.16}Zr_{0.14}M_{0.14})_{\Sigma 1.00}(Na_{1.20}Ca_{0.76})_{\Sigma 1.96}(Si_{1.98}O_7)_2(F_{2.88}O_{1.12})_{\Sigma 4.00}$, where M represents Nb, Ti, Al, Sr and REE. Domain IV is isostructural with hiortdahlite I, and its crystal structure was refined to a final *R* of 0.067. One should note that the refinements of domain I and domain IV (both twinned) have been carried out on the same crystal. EMPA and SEM studies show the presence of chemically homogeneous crystals as well as crystals with distinct chemical zoning due to a wide variation of the major elements Nb, Ca, Na, F, and pointing to the possible coupled substitution $Nb^{5+} + 2Na^+ + O^{2-} \rightleftarrows 3Ca^{2+} + F^-$ as one of the main mechanisms of chemical variation.

Keywords: "guarinite", cuspidine group, domain structure, Monte Somma, Vesuvius, Italy.

Introduction

"Guarinite" is a typical accessory mineral of the Monte Somma syenite, Italy, first described by Guiscardi (1857), who named it after the Italian chemist Giovanni Guarini (1794–1857), Professor at the University of Naples, and who hypothesized that the mineral is a modification of titanite. "Guarinite" was then studied by Krenner (1888), who proposed a relationship with pseudobrookite, and by Zambonini (1902), who classified the mineral in the danburite group. Zambonini & Prior (1909) then proposed an identity of "guarinite" and hiortdahlite on the basis of optical, chemical and crystallographic data. More recently, Merlino & Perchiazzi (1988), in a study of the relationships among minerals of the cuspidine group, pointed out the complexity of the X-ray single-crystal patterns of "guarinite" crystals, which could be explained as due to the overlap of two or three distinct reciprocal lattices. Different crystals showed evidence for the presence of one, two or three reciprocal lattices, with cell type I, II, IV in the nomenclature of Merlino & Perchiazzi (1988). These features point to the presence of a domain structure in the Vesuvian "guarinite". The same domain structure later was reported by Gianfagna *et al.* (1988) in "guarinite" from another Italian locality, the Albano Lake crater.

Our aim in this paper is to describe the domain structure of "guarinite", and to determine the crystal structure of each domain, through combined single-crystal X-ray diffraction (XRD) studies, SEM–EDS observations and electron-microprobe analyses. The crystals examined come from the Monte Somma syenite, S. Vito quarry, Mount Vesuvius area, Italy, where "guarinite" occurs

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as elongate prismatic, translucent yellowish orange crystals, in association with sanidine, sodalite, biotite, amphibole, garnet, leucite, nepheline, magnetite, apatite, monazite, allanite, titanite and zircon (Fulignati *et al.* 2005).

BACKGROUND INFORMATION

The domain structure of "guarinite" is not unexpected, if one takes into account the modular features of minerals belonging to the cuspidine group. As discussed by Merlino & Perchiazzi (1988), the crystal structures of these minerals, with a general formula $X_8(Si_2O_7)_2(O,F)_4$ [where X represents cations with a coordination number ranging from VI to VIII, from the small-radius and high-charge Ti^{4+}, Zr^{4+}, Nb^{5+} to the REE^{3+}, Mn^{2+}, Fe^{2+} and, finally, to the high-radius and low-charge cations Na^+, Ca^{2+}], can be easily described in terms of two different "modules": "walls" of edge-sharing "octahedra" four columns wide and running along **c**, and diorthosilicate groups, which are corner-linked to the walls. Ten topological varieties exist, corresponding to ten distinct ways in which the disilicate groups can be connected to the framework of octahedra; they can be distributed among four types of unit cells, to which four different diffraction patterns correspond, as shown in Figure 1. The distribution of all known minerals of the cuspidine group among the various structural types is reported in Table 1, together with their "topological" and "topochemical" symmetry. The notion of "topological" symmetry was introduced by Smith (1970) to define the symmetry of a structure "when idealized into its most regular shape by movements which leave intact the topologic relationships between nodes". The distributions of cations in the "walls" of the octahedra can lead to a reduction of symmetry, which can be defined, using in our context the term suggested by P.B. Moore (in Smith 1970), a "topochemical" symmetry. As can be seen in Table 1, the same topological symmetry $P12_1/a1$, structure-type 1, can be lowered to different patterns of topochemical symmetries by different patterns of cation distribution.

TABLE 1. TOPOLOGICAL AND TOPOCHEMICAL SYMMETRIES, NATURAL AND SYNTHETIC REPRESENTATIVES OF THE VARIOUS POSSIBLE STRUCTURAL TYPES DISTRIBUTED AMONG THE FOUR KINDS OF UNIT CELL

Type of unit cell	Structure	Topological symmetry	Mineral (topochemical symmetry)	Ref.
I	1	$P12_1/a1$	cuspidine ($P12_1/a1$)	a
			låvenite ($P12_1/a1$)	a
			normandite($P12_1/a1$)	b
			niocalite ($P1a1$)	a
			hiortdahlite II ($P\overline{1}$)	a
			janhaugite ($P12_1/n1$) with $c' = 2c$	a
			$NaCa_2LuSi_2O_7F_2$ ($P12_1/a1$) (synthetic)	c
	5	$P12_1/n1$	$Na_2Ca_2P_2O_7F_2$ ($P12_1/n1$)	d
	2	$Bb11$		
II	8	$P2_111$	wöhlerite ($P2_111$)	a
	9	$P\overline{1}$		
III	6	$P2_1/b11$	baghdadite ($P2_1/b11$)	a, e
			burpalite ($P2_1/b11$)	a, f
	10	$P2_1/n11$		
	7	$P12_11$		
IV	3	$A1a1$		
	4	$P\overline{1}$	hiortdahlite I ($P\overline{1}$)	a

References: a) Merlino & Perchiazzi (1988), b) Perchiazzi *et al.* (2000), c) Fleet & Pan (1995), d) Piotrowski *et al.* (2000), e) Biagioni *et al.* (2010), f) Merlino *et al.* (1990).

In "guarinite", more than one way to connect the disilicate groups to the framework of "octahedra" may be present in the same crystal, and domains may coexist, each domain corresponding to one kind of unit cell.

CHEMICAL COMPOSITION

Qualitative chemical analyses of "guarinite" were performed in energy-dispersive (EDS) mode with a scanning electron microscope on 25 crystals. Images obtained with back-scattered electrons (BSE) show the occurrence of homogeneous and inhomogeneous crystals, these latter displaying an evident discontinuous zoning connected to a variation of the Nb content (Fig. 2). From a compositional point of view, we noticed two distinct chemical groups, corresponding to two distinct amounts of Nb (Fig. 3): one group has a high and variable Nb content (more than 7 wt.%), and the other group has a low and uniform Nb content (about 1 wt.%). Homogeneous crystals display a chemical composition matching one or the other group; zoned crystals display both different chemical compositions in distinct portions of the crystals, with different BSE count-rates: high count-rates correspond to the chemical group with a high amount of Nb, whereas low count-rates correspond to the chemical group with a low amount of Nb.

Niobium is not the only element that varies: analyses show variations involving also Na, Ca, and F. By looking at Figure 3, it seems evident, for both chemical groups, that a direct relation between Nb and Na (Fig. 3a) exists, as well as an inverse relation between Nb and Ca (Fig. 3b), and between Nb and F (Fig. 3c). Therefore, our data point to the combined substitution $Nb^{5+} + 2Na^+ + O^{2-} \rightleftarrows 3Ca^{2+} + F^-$ as one of the main mechanisms of chemical variation in Vesuvian "guarinite" (Fig. 3d).

Quantitative chemical analyses of "guarinite" were done in wavelength-dispersive (WDS) mode by means of a JEOL JXA–8600 electron microprobe. The operating voltage was 15 kV, the beam current was 20 nA, and the beam diameter was 20 μm. As standards, we used kaersutite (Mg, Al, Fe), diopside (Ca, Si), albite (Na), benitoite (Ti), monazite (Ce, La), bustamite (Mn), cubic zirconia (Zr, Y), celestine (Sr), Nb metal (Nb), and fluorite (F). Electron-microprobe data are in agreement

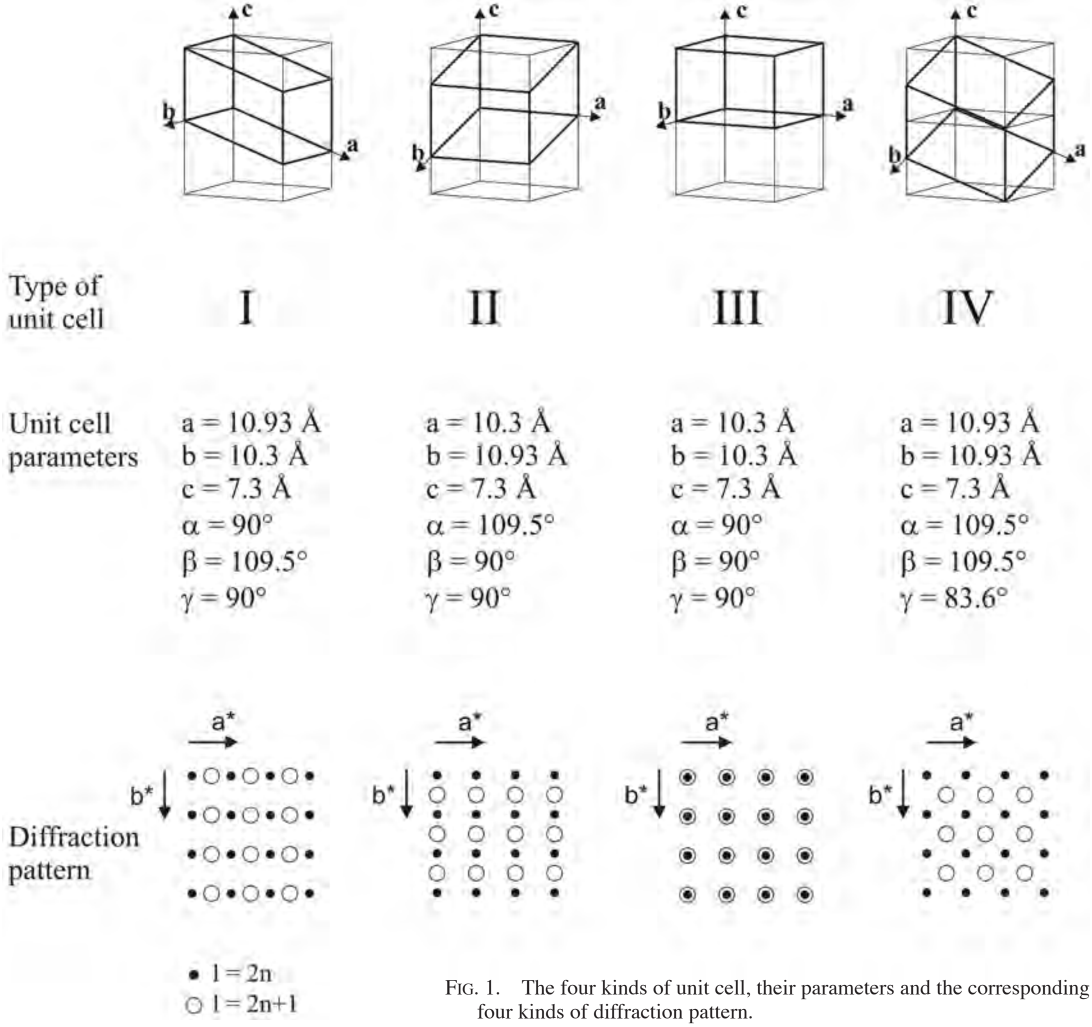

FIG. 1. The four kinds of unit cell, their parameters and the corresponding four kinds of diffraction pattern.

with those obtained in energy-dispersive mode, thus confirming the occurrence of two chemically distinct groups. In Table 2, we report the two mean chemical compositions and ranges, together with the crystal-chemical content, expressed in atoms per formula unit and recalculated on the basis of (O + F) = 18 *apfu*. Table 2 also shows chemical data from the literature for wöhlerite (Mellini & Merlino 1979) and hiortdahlite I (Merlino & Perchiazzi 1985): a close correspondence has been found between the group with high Nb content and wöhlerite, as well as between the group with low Nb content and hiortdahlite I.

PRELIMINARY X-RAY CRYSTALLOGRAPHY

The presence of common structural units variously connected in all the minerals of the cuspidine group can raise severe difficulties in distinguishing the various phases one from the other by means of X-ray powder-diffraction patterns. Only single-crystal investigations can assure the unambiguous identification of these minerals. Therefore, a number of crystals of "guarinite" were examined with the single-crystal Weissenberg method.

Most of the diffraction patterns show the same features already found in a previous crystallographic study on "guarinite" from Albano Lake, Latium, Italy by Gianfagna *et al.* (1988), who maintained that the "diffraction pattern obtained could be explained as due to the overlapping of two or three distinct reciprocal lattices, each corresponding to a particular domain"; on the other hand, there were some crystals whose diffraction patterns match just one reciprocal lattice, thus corresponding to just one domain.

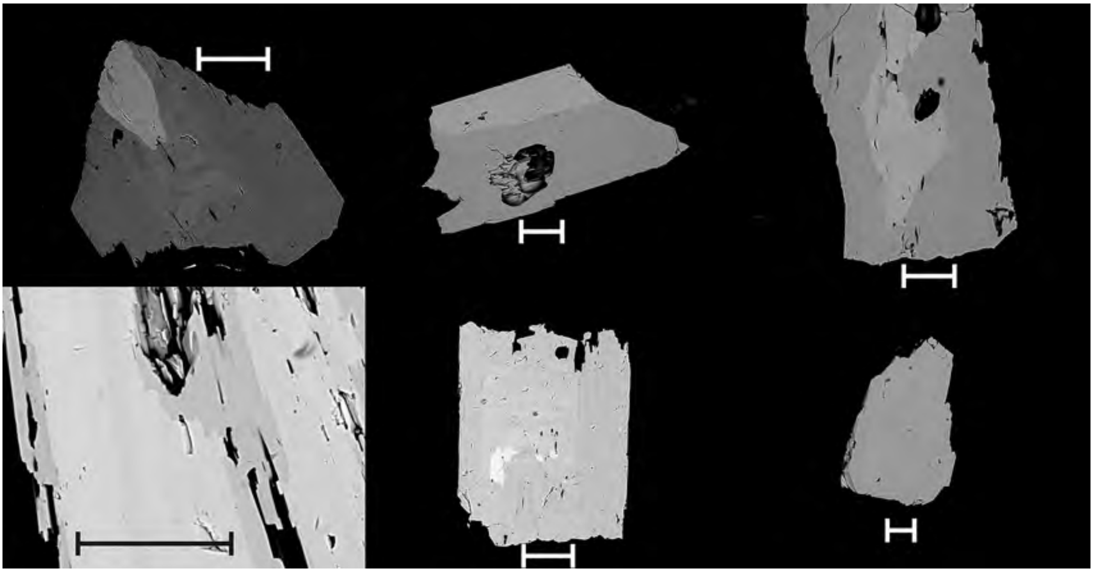

FIG. 2. Back-scattered electron images of "guarinite" from S. Vito, collected with SEM–EDAX equipment. Scale bar 100 μm.

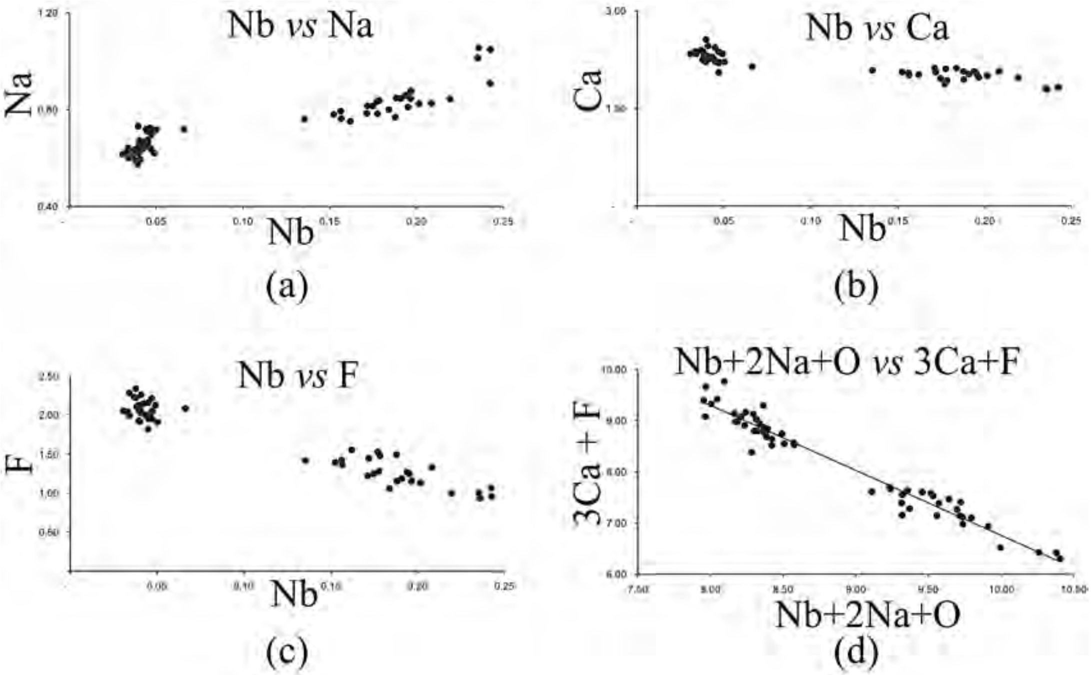

FIG. 3. Plots of correlations (in atoms per formula unit, with O + F = 9) for guarinite from S. Vito. (a) Nb *versus* Na, (b) Nb *versus* Ca, (c) Nb *versus* F, (d) Nb + 2Na + O *versus* 3Ca + F.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF “GUARINITE” FROM S. VITO AND A COMPARISON WITH THE COMPOSITION OF WÖHLERITE AND HIORTDAHLITE I

	“guarinite” with a high Nb content (mean, n = 8)		“guarinite” with a low Nb content (mean, n = 7)		wöhlerite Mellini & Merlino (1979)	hiortdahlite I Merlino & Perchiazzi (1985)
SiO_2 wt.%	29.65	(29.47 - 29.77)	30.38	(29.39 - 30.98)	29.75	32.20
TiO_2	0.96	(0.65 - 1.52)	0.53	(0.47 - 0.59)	1.31	0.30
Al_2O_3	0.18	(0.03 - 0.25)	0.08	(0.03 - 0.13)	-	0.07
MgO	0.18	(0.06 - 0.34)	0.02	(0.00 - 0.04)	0.23	0.09
CaO	28.86	(26.70 - 31.35)	36.41	(35.93 - 37.78)	26.02	29.57
MnO	2.48	(1.86 - 3.28)	2.25	(1.98 - 2.53)	0.90	0.30
FeO	1.34	(0.86 - 1.58)	1.46	(1.12 - 1.64)	1.52	-
Fe_2O_3	-	-	-			0.27
Na_2O	5.99	(5.29 - 6.91)	4.76	(4.64 - 5.22)	7.90	6.85
SrO	0.08	(0.00 - 0.23)	0.09	(0.00 - 0.13)	0.28	0.03
HfO_2	-	-	-			0.27
REE_2O_3	0.12	(0.00 - 0.32)	0.24	(0.11 - 0.53)	-	2.08
Y_2O_3	0.21	(0.00 - 0.65)	0.05	(0.01 - 0.12)	-	3.50
ZrO_2	16.59	(15.72 - 17.55)	17.95	(17.33 - 18.99)	15.26	18.76
Nb_2O_5	9.13	(7.86 - 10.89)	0.94	(0.31 - 1.42)	12.83	0.56
H_2O	-	-	-			0.42
F	4.26	(3.32 - 4.99)	7.02	(6.71 - 7.88)	2.89	6.69
Sum	100.03	(98.54 - 101.77)	102.18	(101.13 - 102.82)	98.89	101.96
O=F	-1.79	(-1.40 - -2.10)	-2.96	(-2.83 - -3.82)	-1.22	-2.81
Total	98.24	(97.04 - 99.78)	99.22	(98.25 - 99.52)	97.67	99.15
Si *apfu*	4.00		3.96		4.00	4.00
Ti	0.10		0.05		0.14	0.03
Al	0.03		0.01		-	0.01
Mg	0.04		-		0.04	0.02
Ca	4.17		5.07		3.74	3.94
Mn	0.28		0.25		0.10	0.03
Fe^{2+}	0.15		0.16		0.16	-
Fe^{3+}	-		-		-	0.03
Na	1.57		1.20		2.06	1.65
Sr	0.01		0.01		-	-
Hf	-		-		-	0.01
REE	-		0.01		-	0.10
Y	0.02		-		0.02	0.19
Zr	1.09		1.14		1.00	1.15
Nb	0.56		0.06		0.78	0.03
H	-		-		-	0.35
F	1.83		2.88		1.23	2.63

These data were acquired with an electron microprobe. The crystal-chemical content, expressed in atoms per formula unit (*apfu*), is recalculated on the basis of (O + F) = 18 *apfu*. The chemical composition and crystal-chemical content of wöhlerite and hiotdahlite I also are reported.

As already pointed out by Merlino & Perchiazzi (1988), the ascription of the diffraction pattern of any crystal under study to one of the four kinds is possible by comparing $hkl_{(2n)}$ and $hkl_{(2n+1)}$ diffraction patterns (Fig. 1), the reflections with an even l value being common to all the patterns, and the reflections with an odd l value being characteristic of each pattern.

The domains present in the crystals of “guarinite” from S. Vito are the same as those found in the “guarinite” from Albano Lake, with cell type I, II, and IV (respectively called domain I, domain II, and domain IV, in the following), according to the classification scheme given in Merlino & Perchiazzi (1988); they are distributed as shown in Table 3.

Domains I and IV are simultaneously present (with domain II absent) in ten out of the twenty-five crystals examined, whereas domains IV, I and II (but with the domain II very faint, almost absent) occur in nine crystals; domain II is present as the only domain in five crystals, and only one crystal (g–9) gave a diffraction pattern consistent with the presence of domains II and IV. Where it is present, domain IV is invariably dominant except in crystal g–9, where domain II is much more important than domain IV.

By comparing the spot chemical data and the Weissenberg crystallographic results obtained on the same crystals, we noticed that crystals showing the presence of domain II only are chemically homogeneous, with composition corresponding to the group with high Nb, *i.e.*, to wöhlerite; the crystals showing the domains IV and I also are homogeneous, with a composition corresponding to the group with low Nb, *i.e.*, to hiortdahlite

I; crystals showing the simultaneous occurrence of the three domains are zoned and display both distinct chemical compositions.

STRUCTURE REFINEMENTS

One crystal in which domain II occurs as the only domain and two crystals in which domains IV and I are simultaneously present were selected among the various crystals of "guarinite" from S. Vito examined.

The intensity data for domain II were collected with a Bruker P4 four-circle diffractometer using Mo$K\alpha$ radiation (λ = 0.71703 Å). The measured reflections were corrected for Lorentz, polarization and absorption factors. This last correction was made according to the method of North *et al.* (1968). The unit-cell parameters reported in Table 4 were determined by the least-squares method based on the angular parameters of 30 reflections in the range $18° \le 2\theta \le 30°$. In Table 4 and Figure 4b, the cell parameters for domain II and wöhlerite and their standard space-group, $P2_1$, are referred to a cell orientation with **a** and **b** interchanged with respect to the orientation that was assumed in Figure 1 and in Table 1, in order to plainly discuss the common features and the metrical relationships in the whole group of compounds.

TABLE 3. OCCURRENCE AND DISTRIBUTION OF DOMAINS IN THE CRYSTALS OF "GUARINITE" EXAMINED FROM S. VITO

crystal	domains	crystal	domains
g-1	IV > I	g-14	IV > I
g-2	IV > I > II	g-15	IV > I
g-3	IV > I	g-16	IV > I
g-4	IV > I	g-17	IV > I
g-5	IV > I > II	g-18	IV > I > II
g-6	IV > I > II	g-19	II
g-7	IV > I > II	g-20	II
g-8	IV > I > II	g-21	IV > I
g-9	II > IV	g-22	IV > I
g-10	II	g-23	IV > I
g-11	IV > I > II	g-24	II
g-12	IV > I > II	g-25	II
g-13	IV > I > II		

According to Merlino & Perchiazzi (1988), who reported wöhlerite as the unique natural representative for structural types with unit-cell type II (Table 1), the structure was tentatively refined in the space group $P2_1$ starting from the atom coordinates reported in Mellini & Merlino (1979) for wöhlerite. Initially, the structure was refined isotropically to $R = 0.06$, thus validating the starting structural model. Subsequently, the occupancy factors at the eight octahedral sites were refined, and the anisotropic displacement parameters were included, which made it possible to obtain an R factor of 0.045 for 2435 reflections with $F_o > 4\sigma(F_o)$. Taking into account the EMP data and following the indications obtained in the first stages of the refinement, we inferred mixed occupancies of the Nb site by niobium and manganese, of the Ca(2) site by calcium and iron, of the Na(1) and Na(2) sites by sodium and calcium, and full occupancies of Ca(1), Ca(3), Ca(4) sites by calcium, and of the Zr site by zirconium. The final coordinates, together with the refined occupancies and displacement parameters of all atoms, are reported in Table 5.

One crystal with the domains I and IV was mounted on an Ital Structure automatic four-circle diffractometer, and data were collected using Mo$K\alpha$ radiation. In order to find reflections corresponding to each domain, an orientation photograph was taken with the crystal rotating about the **c** axis. In the orientation photograph, we noticed a regular alternation of strong and weak reflections along reciprocal lattice planes with the l index odd. Assuming that the stronger and the weaker reflections belong to the major domain IV and to the minor domain I, respectively, we determined both the unit cells using the reflections with an even l index common to both domains, plus the stronger reflections with odd l index for the domain IV and the weaker reflections with an odd l index for the domain I.

The resulting unit-cell parameters of both domains I and IV were refined by the least-squares method on the basis of the angular parameters of 40 reflections in

TABLE 4. UNIT-CELL PARAMETERS AND SPACE GROUPS FOR THE VARIOUS DOMAINS OF "GUARINITE" FROM S. VITO AND FOR WÖHLERITE, HIORTDAHLITE II, HIORTDAHLITE I

	Domain II (a)	wöhlerite (b)	Domain I (a)	hiortdahlite II (c)	Domain IV (a)	hiortdahlite I (d)
a (Å)	10.836(1)	10.823(3)	10.973(2)	11.012(6)	10.970(2)	11.015(1)
b (Å)	10.270(1)	10.244(3)	10.306(1)	10.342(3)	10.943(2)	10.941(1)
c (Å)	7.296(1)	7.290(2)	7.367(3)	7.359(3)	7.365(1)	7.353(3)
α (°)	90.0	90.0	90.03(3)	89.92(2)	109.63(2)	109.35(1)
β (°)	109.13(1)	109.00(4)	109.63(3)	109.21(5)	109.65(2)	109.88(1)
γ (°)	90.0	90.0	90.11(2)	90.06(3)	83.39(1)	83.43(1)
Space group	$P2_1$	$P2_1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$

References: (a) this study, (b) Mellini & Merlino (1979), (c) Merlino & Perchiazzi (1987), (d) Merlino & Perchiazzi (1985).

the range 18° ≤ 2θ ≤ 30°. They are reported in Table 4; as can be seen in the table, they correspond to the unit cells of hiortdahlite II (Merlino & Perchiazzi 1987) and hiortdahlite I (Merlino & Perchiazzi 1985), respectively. Then, the intensity data for both the domains I and IV were collected, and the measured reflections were corrected for Lorentz, polarization and absorption factors. This last correction was made according to the method of North *et al.* (1968).

Because of the simultaneous presence of the two domains, the intensity values of the common reflections, namely those with an even l index, were tentatively scaled for both the data collections until we obtained a good initial reliability-factor R; the scale factors were 0.63 for domain IV and 0.37 for domain I.

Following Merlino & Perchiazzi (1988), who reported hiortdahlite I as the unique natural representative for structural types with unit-cell type IV (Table 1), the structure of domain IV of "guarinite" was tentatively refined in the space group $P\overline{1}$ starting from the coordinates of atoms reported in Merlino & Perchiazzi (1985) for hiortdahlite I. Initially, the structure was refined isotropically to R = 0.09, thus validating the starting structural model. Subsequently, the occupancy factors at the eight "octahedral" sites were refined, and the anisotropic thermal parameters were included,

TABLE 5. FINAL COORDINATES, OCCUPANCIES AND ATOMIC DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN DOMAIN II OF "GUARINITE"

site	*x*	*y*	*z*	occupancy	U_{eq}
Ca(1)	0.3469(3)	0.2965(4)	0.5526(4)	Ca	0.019(1)
Nb	0.1299(1)	0.0521(1)	0.1897(2)	$Nb_{0.57}Mn_{0.43}$	0.014(1)
Zr	0.3427(1)	0.2868(1)	0.0535(2)	Zr	0.012(3)
Ca(2)	0.1460(2)	0.6817(2)	0.1986(4)	$Ca_{0.82}Fe_{0.18}$	0.012(1)
Ca(3)	0.3693(2)	0.9104(3)	0.0554(5)	Ca	0.017(1)
Ca(4)	0.1531(2)	0.6803(3)	0.6995(4)	Ca	0.014(1)
Na(1)	0.1216(4)	0.0675(6)	0.6909(7)	$Na_{0.77}Ca_{0.23}$	0.021(2)
Na(2)	0.3681(4)	0.9142(5)	0.5514(8)	$Na_{0.80}Ca_{0.20}$	0.020(2)
Si(1)	0.0808(3)	0.3713(3)	0.1980(5)	Si	0.012(1)
Si(2)	0.0724(3)	0.3632(3)	0.6358(6)	Si	0.012(1)
Si(3)	0.4374(3)	0.6112(4)	0.5625(5)	Si	0.012(1)
Si(4)	0.4319(3)	0.6107(4)	0.1231(6)	Si	0.012(1)
O(1)	0.0065(9)	0.2360(9)	0.1164(15)	O	0.019(2)
O(2)	-0.0181(8)	0.2386(8)	0.6213(15)	O	0.016(2)
O(3)	0.0078(9)	0.4998(10)	0.0912(15)	O	0.024(2)
O(4)	0.0169(9)	0.4969(10)	0.6944(14)	O	0.022(2)
O(5)	0.2324(8)	0.3699(9)	0.2070(15)	O	0.020(2)
O(6)	0.2211(8)	0.3323(9)	0.7754(13)	O	0.017(2)
O(7)	0.4871(9)	0.4690(9)	0.6486(14)	O	0.019(2)
O(8)	0.4607(9)	0.4603(9)	0.0772(15)	O	0.019(2)
O(9)	0.4744(8)	0.2341(9)	0.3201(14)	O	0.016(2)
O(10)	0.4664(9)	0.2148(9)	0.9148(13)	O	0.018(2)
O(11)	0.2852(8)	0.6371(10)	0.5156(15)	O	0.023(2)
O(12)	0.2855(8)	0.6669(9)	0.0197(15)	O	0.019(2)
O(13)	0.2461(8)	0.1132(9)	0.0365(15)	O	0.023(2)
O(14)	0.2283(9)	0.1135(9)	0.4503(16)	O	0.025(2)
F(15)	0.2382(7)	0.8866(7)	0.7445(12)	F	0.018(2)
O(16)	0.2178(8)	0.8880(9)	0.2273(15)	O	0.018(2)
O(17)	0.0865(9)	0.3886(9)	0.4241(15)	O	0.028(2)
O(18)	0.5268(8)	0.1214(9)	0.6404(15)	O	0.022(2)

The estimated standard deviation on the occupancies of the atoms in the Nb site is ~0.02; in the Ca(2), Na(1) and Na(2) sites, it is ~0.03.

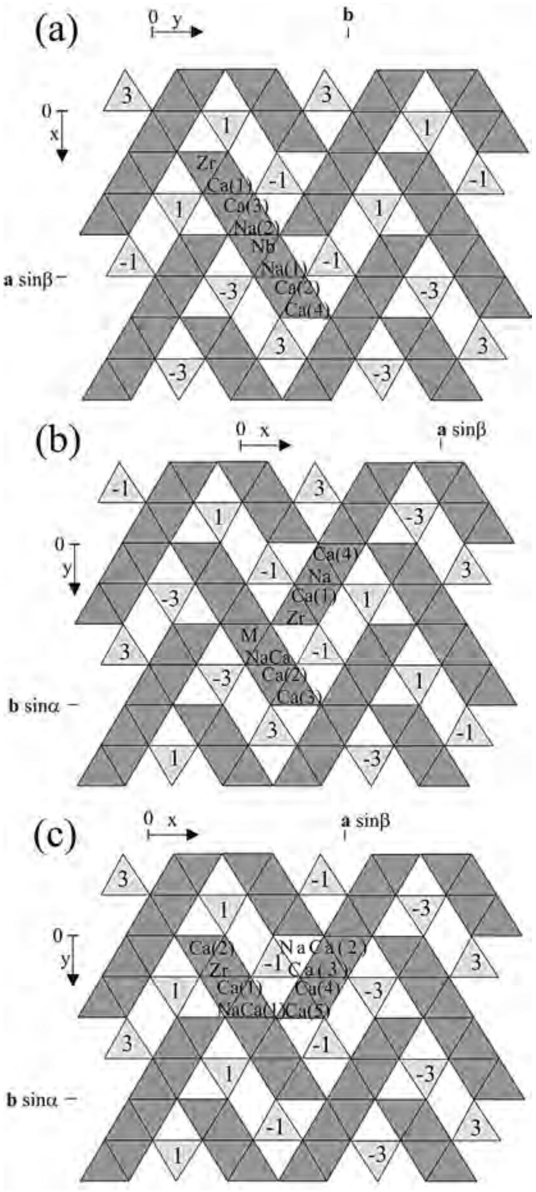

FIG. 4. Schematic view of "octahedra" in the crystal structures of domain II (a), domain IV (b), and domain I (c) in "guarinite", as seen along [001]. The walls of "octahedra" run along **c**, and the disilicate groups are oriented parallel to the **c** axis. Each disilicate group is connected to three walls; following Merlino & Perchiazzi (1988), the positions of the Si_2O_7 groups are indicated by giving the heights of the bridging oxygen atoms of the Si_2O_7 groups in $c/8$ units, with respect to a plane normal to **c** and passing through the origin. The distributions of the cations in the independent walls of "octahedra"also are reported.

which made it possible to obtain an *R* factor of 0.067 for 3293 reflections with $F_o > 4\sigma(F_o)$. Taking into account the EMP data and following the indications obtained in the first stages of the refinement, we inferred mixed occupancies by calcium and sodium at the Ca(1) site, by manganese, calcium and zirconium at the *M* site (fixing the Mn occupancy to 0.41), by sodium and calcium at the NaCa site, and full occupancies by calcium at the Ca(2), Ca(3), Ca(4) sites, by sodium at the Na site, and by zirconium at the Zr site. The final coordinates, together with the refined occupancies and displacement parameters of all atoms, are reported in Table 6.

With regards to domain I of the "guarinite" from S. Vito, we tentatively refined it starting from the structural models of all the representatives, among the types with unit cell I, that are not affected by doubling of axes (Table 1), namely cuspidine (space group $P2_1/a$; Saburi *et al.* 1977), niocalite (space group *Pa*; Mellini 1982), hiortdahlite II (space group $P\bar{1}$; Merlino & Perchiazzi 1987), and the type-5 structure (space group $P2_1/n$; Piotrowski *et al.* 2000). By comparing the results of these preliminary refinements, the structural model of hiortdahlite II was chosen: it showed not only the best initial *R* factor (0.11 for hiortdahlite II model *versus* 0.18 for cuspidine model, 0.26 for niocalite model and 0.21 for type-5 structure model), but also more reliable values for the Si–O distances and for the displacement parameters of bridging oxygen atoms of the disilicate groups (it is worth noting that the position of these oxygen atoms is indicative of the various structural types).

TABLE 6. FINAL COORDINATES, OCCUPANCIES AND ATOMIC DISPLACEMENT PARAMETERS (Å²) OF ATOMS IN DOMAIN IV OF "GUARINITE"

site	*x*	*y*	*z*	occupancy	U_{eq}
Ca(1)	0.3119(3)	0.4032(3)	0.2269(8)	$Ca_{0.72}Na_{0.28}$	0.018(1)
Ca(2)	0.1943(2)	0.9033(2)	0.4224(7)	Ca	0.017(1)
Ca(3)	0.1928(2)	0.8994(2)	0.9189(7)	Ca	0.015(1)
Ca(4)	0.4240(2)	0.1283(2)	0.8912(7)	Ca	0.016(1)
Zr	0.2943(2)	0.4028(1)	0.7187(3)	Zr	0.016(1)
M	0.0669(2)	0.6259(2)	0.4756(6)	$Mn_{0.41}Ca_{0.40}Zr_{0.19}$	0.021(1)
Na	0.4223(4)	0.1222(5)	0.3995(15)	Na	0.020(1)
NaCa	0.0773(3)	0.6244(4)	0.9610(9)	$Na_{0.60}Ca_{0.40}$	0.014(1)
Si(1)	0.6229(3)	0.3315(3)	0.8153(6)	Si	0.012(1)
Si(2)	0.6208(3)	0.3295(3)	0.3765(6)	Si	0.014(1)
Si(3)	0.1268(4)	0.1832(4)	0.2435(6)	Si	0.016(1)
Si(4)	0.1251(3)	0.1846(3)	0.8103(6)	Si	0.014(1)
O(1)	0.6208(9)	0.3575(10)	0.6078(18)	O	0.029(2)
O(2)	0.1404(12)	0.2188(10)	0.0505(24)	O	0.043(3)
O(3)	0.4861(9)	0.2639(9)	0.2253(18)	O	0.020(2)
O(4)	0.1604(10)	0.0370(8)	0.7226(29)	O	0.030(2)
O(5)	0.7378(7)	0.2307(8)	0.8624(25)	O	0.024(2)
O(6)	0.1459(11)	0.0308(9)	0.2190(29)	O	0.032(2)
O(7)	0.1156(9)	0.4816(10)	0.6511(20)	O	0.023(2)
O(8)	0.7489(9)	0.2465(10)	0.3589(26)	O	0.031(3)
O(9)	-0.0168(10)	0.2352(11)	0.7038(24)	O	0.033(3)
O(10)	0.2431(10)	0.2732(10)	0.8399(16)	O	0.024(2)
O(11)	0.3627(12)	0.5246(11)	0.6137(18)	O	0.030(2)
O(12)	0.4773(9)	0.2897(9)	0.7818(18)	O	0.020(2)
O(13)	0.2460(10)	0.2689(10)	0.4305(15)	O	0.023(2)
O(14)	-0.0132(8)	0.2398(9)	0.2604(23)	O	0.025(2)
O(15)	0.3389(10)	0.5245(9)	0.0159(16)	O	0.023(2)
F(16)	0.3913(7)	-0.0070(7)	0.0604(24)	F	0.029(2)
F(17)	0.3914(8)	-0.0094(7)	0.5675(22)	F	0.027(2)
F(18)	0.1124(7)	0.5030(7)	0.1921(22)	F	0.026(2)

The estimated standard deviation on the occupancies of the atoms in Ca(1) and NaCa sites are ~0.03.

Therefore, starting from the atom coordinates reported in Merlino & Perchiazzi (1987) for hiortdahlite II, the structure was refined isotropically to an initial reliability *R* factor of 0.11. As a subsequent step, the occupancy factors at the eight "octahedral" sites were refined, and the anisotropic displacement parameters were included, which made it possible for us to obtain an *R* factor of 0.072 for 4790 reflections with $F_o > 4\sigma(F_o)$. Taking into account the EMPA data and following the indications obtained in the first stages of the refinement, we inferred mixed occupancies by calcium and sodium at the Ca(2) and NaCa(2) sites, by calcium and zirconium at the Ca(3) site, by calcium and manganese at the Ca(5) site, by sodium and calcium at the NaCa(1) site, and full occupancies by calcium at the Ca(1) and Ca(4) sites. The final coordinates, together with the refined occupancies and displacement parameters of all atoms, are reported in Table 7.

In Table 8, we report information on the data collections and details of the refinements for the three domains. All the structural calculations were executed by means of the SHELXL–97 software (Sheldrick 1997).

Note that all the crystals examined in our structural study were strongly affected by twinning, on (100) with [001] as twin axis for all the three domains. We introduced the TWIN option of SHELXL–97 (Sheldrick 1997) in the least-squares refinement: the results indicate a volume ratio of ~ 0.50 : 0.50 for domains IV and I, and of ~ 0.85 : 0.15 for domain II. Tables of anisotropic thermal parameters have been deposited (Table A1). The tables of structure factors for domain II (Table A2), domain I (Table A3), domain IV (Table A4) have also been deposited. These tables are available from the Depository of Unpublished data, on the Mineralogical Association of Canada website [document "Guarinite" CM50_531].

STRUCTURAL DETAILS OF THE VARIOUS DOMAINS IN "GUARINITE"

The crystal structures of the domains II, IV, and I of "guarinite" from S. Vito are represented in terms of octahedra and tetrahedra in Figures 4a, 4b, and 4c, respectively; the drawings are somewhat idealized, as all the cation polyhedra are drawn as regular octahedra, although the actual coordination number ranges from six to eight.

As members of the cuspidine group, these structures can be described as built up by walls of large edge-sharing coordination-polyhedra four columns wide and running along [001], and diorthosilicate groups corner-linked to the walls. The peculiar features of the diorthosilicate groups are essentially the same in all the three distinct structures: thus they will be discussed once in general terms suitable for the different domains. On the other hand, the structures of the various domains differ in the features of the walls of "octahedra", which will be presented separately for the three structures. In order to obtain a clearer comparison with the structural models, the various sites in the walls of "octahedra" for domain II, IV, and I of "guarinite" have been denoted as the corresponding sites in wöhlerite (Mellini & Merlino 1979), in hiortdahlite I (Merlino & Perchiazzi 1985), and in hiortdahlite II (Merlino & Perchiazzi 1987), respectively, except for the *Y* site of hiortdahlite II, which is here called Ca(5) in view of the lack of yttrium and the dominant presence of calcium.

Diorthosilicate groups

The main geometrical features of the diorthosilicate groups are given in Table 9. Average and individual distances, as well as Si–O–Si angles, for domains II, IV, and I are very close to those of the structural models, namely wöhlerite (Mellini & Merlino 1979), hiortdahlite I (Merlino & Perchiazzi 1985), and hiortdahlite II (Merlino & Perchiazzi 1987), respectively. The Si–O–Si angles, ranging from 151.17° to 162.92°, are in agreement with the values found in the other phases of the cuspidine group, such as cuspidine (155.4°; Saburi *et al.* 1977), normandite (163.5°; Perchiazzi *et al.* 2000), wöhlerite (159.8° and 149.5°; Mellini & Merlino 1979), hiortdahlite II (176.7° and 162.8°; Merlino & Perchiazzi 1987), and hiortdahlite I (161.0° and 157.0°; Merlino & Perchiazzi 1985). Bond-valence calculations, reported in Tables 10, 11 and 12, were calculated according to the parameters reported by Brese & O'Keeffe (1991). In the calculations, we assumed the site occupancies for cations and anions derived from structural refinements, and reported in Tables 5, 6, 7. It can be seen that all the sums reaching the anions deviate less than 10%, except for the case of O(14) site of domain II, which shall be discussed in the following section. It can also be noticed that in every domain, the bridging oxygen atoms [O(17) and O(18) in domain II, O(1) and O(2) in domain IV, O(1) and O(8) in domain I] are invariably overbonded. A similar overbonding of the bridging oxygen atoms has also been observed in other members of the cuspidine group (Mellini 1981, Merlino *et al.* 1990, Perchiazzi *et al.* 2000). As stated by Mellini (1981), the systematic

TABLE 7. FINAL COORDINATES, OCCUPANCIES AND ATOMIC DISPLACEMENT PARAMETERS (Å^2) OF ATOMS IN DOMAIN I OF "GUARINITE"

site	*x*	*y*	*z*	occupancy	U_{eq}
Ca(1)	0.4247(2)	0.3708(2)	0.8430(5)	Ca	0.018(1)
Ca(2)	0.3090(2)	0.0964(3)	0.5291(6)	$Ca_{0.71}Na_{0.29}$	0.019(1)
Ca(3)	0.9333(2)	0.1264(2)	0.8472(4)	$Ca_{0.71}Zr_{0.29}$	0.021(1)
Ca(4)	0.8039(2)	0.3972(2)	0.5270(5)	Ca	0.015(1)
Zr	0.2953(1)	0.0973(1)	0.0262(2)	Zr	0.020(1)
Ca(5)	0.8091(2)	0.4049(2)	0.0258(4)	$Ca_{0.55}Mn_{0.45}$	0.015(1)
NaCa(1)	0.4207(4)	0.3791(4)	0.3378(10)	$Na_{0.74}Ca_{0.26}$	0.024(1)
NaCa(2)	0.9227(3)	0.1239(3)	0.3220(6)	$Ca_{0.59}Na_{0.41}$	0.015(1)
Si(1)	0.6231(3)	0.1679(3)	0.2221(4)	Si	0.011(1)
Si(2)	0.6203(3)	0.1711(3)	0.6582(4)	Si	0.011(1)
Si(3)	0.1293(3)	0.3140(3)	0.2284(4)	Si	0.012(1)
Si(4)	0.1221(3)	0.3185(3)	0.6590(4)	Si	0.010(1)
O(1)	0.6210(8)	0.1460(9)	0.4404(18)	O	0.030(2)
O(2)	0.7389(7)	0.2676(8)	0.2380(18)	O	0.025(2)
O(3)	0.7471(8)	0.2578(9)	0.7677(17)	O	0.025(2)
O(4)	0.6629(9)	0.0229(8)	0.1711(13)	O	0.021(2)
O(5)	0.6371(10)	0.0280(10)	0.7371(14)	O	0.025(2)
O(6)	0.4792(8)	0.2105(8)	0.0913(13)	O	0.016(2)
O(7)	0.4846(8)	0.2361(8)	0.6409(17)	O	0.021(2)
O(8)	0.1397(11)	0.2807(8)	0.4524(17)	O	0.037(2)
O(9)	0.2470(8)	0.2261(8)	0.2137(11)	O	0.016(2)
O(10)	0.2411(9)	0.2297(9)	0.7998(13)	O	0.023(2)
O(11)	0.1581(9)	0.4657(7)	0.1971(21)	O	0.025(2)
O(12)	0.1475(10)	0.4677(8)	0.6876(20)	O	0.029(2)
O(13)	0.9885(7)	0.2636(8)	0.0937(17)	O	0.022(2)
O(14)	0.9816(8)	0.2621(10)	0.6420(20)	O	0.029(3)
O(15)	0.1147(8)	0.0182(8)	0.9465(21)	O	0.023(2)
F(16)	0.6080(6)	0.4937(6)	0.9361(14)	F	0.017(1)
F(17)	0.3911(7)	0.5112(7)	0.5818(18)	F	0.025(2)
F(18)	0.8880(7)	0.0023(7)	0.5828(18)	F	0.028(2)

The estimated standard deviation on the occupancies of the atoms at the Ca(3) site is ~0.01; at Ca(2), Ca(5), NaCa(1) and NaCa(2) sites, it is ~0.03.

TABLE 8. CRYSTAL DATA AND REFINEMENT DETAILS FOR THE THREE STRUCTURALLY DEFINED DOMAINS OF "GUARINITE"

	Domain II	Domain IV	Domain I
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.836(2)	10.970(4)	10.973(2)
b (Å)	10.270(2)	10.943(5)	10.306(1)
c (Å)	7.296(1)	7.365(5)	7.367(3)
α (°)	89.99(1)	109.63(5)	90.03(3)
β (°)	109.13(2)	109.65(5)	109.63(3)
γ (°)	90.00(1)	83.39(4)	90.11(2)
Density (g/cm^3)	3.41	3.22	3.21
Cell volume (Å^3)	767.10(13)	784.25(55)	784.70(25)
Z	2	2	2
Radiation type (wavelength)	Mo*K*α (0.71073 Å)	Mo*K*α (0.71073 Å)	Mo*K*α (0.71073 Å)
Crystal size (mm)	0.28 × 0.18 × 0.08	0.22 × 0.16 × 0.12	0.22 × 0.16 × 0.12
Scan mode	θ-2θ	θ-2θ	θ-2θ
Scan width	± 0.57° (in θ)	± 0.57° (in θ)	± 0.57° (in θ)
Scan speed	2°/min	2°/min	2°/min
θ range (°)	4 - 49.95 (in 2θ)	4 – 59.99 (in 2θ)	4 – 69.99 (in 2θ)
Reflection ranges	$-1 \leq h \leq 12$ $-12 \leq k \leq 12$ $-7 \leq l \leq 8$	$-14 \leq h \leq 14$ $-14 \leq k \leq 14$ $0 \leq l \leq 9$	$-16 \leq h \leq 16$ $-16 \leq k \leq 16$ $0 \leq l \leq 11$
R_{int}	0.0276	0.059	0.0373
Reflections collected	2906	3293	4810
Reflections unique	2495	3293	4810
Reflections observed	2435	3293 with $F_o > 4\sigma F_o$	4790
Absorption correction: Ψ-scan on	12 reflections	3 reflections	3 reflections
Data / restraints / parameters	2435 / 1 / 286	3293 / 0 / 277	4810 / 0 / 283
Goodness of fit	1.098	1.189	1.154
Final *R* indices [$F_o > 4\sigma(F_o)$]	R_1 = 0.0450 wR_2 = 0.1291	R_1 = 0.0670 wR_2 = 0.1852	R_1 = 0.0720 wR_2 = 0.1946
Largest difference peak, hole (*e*/Å^3)	1.19 –0.88	1.45 –1.59	2.54 –2.83

overbonding of the bridging oxygen atoms may be due to the use of a correlation between bond distance and bond strength that does not take into account other parameters like bond angles and mutual screening among atoms.

Walls of "octahedra" in the structure of domain II

The crystal structure of domain II of "guarinite" is represented in Figure 4a in terms of octahedra and tetrahedra: actually, the Ca(1), Na(1) and Na(2) sites are eight-fold coordinated, and the Ca(3) site is seven-fold coordinated; however, they were drawn as octahedra to obtain a clearer view of the structure. In this structure, the walls are characterized by a non-centrosymmetric distribution of cations and are related by 2_1 screw axes parallel to the [010] direction. The distribution of the cations in the walls is presented in Figure 5, drawn with the program ATOMS (Dowty 1995).

Bond distances for the eight independent "octahedral" cation sites, labeled Ca(1), Ca(2), Ca(3), Ca(4), Nb, Zr, Na(1), Na(2), are reported in Table 13, together with their average values: these latter values are in close agreement with the values calculated for the proposed site-occupancies on the basis of the effective ionic radii.

In domain II of "guarinite", as in wöhlerite (Mellini & Merlino 1979), the Ca(1), Ca(3) and Ca(4) sites are completely occupied by calcium cations, the Ca(2) site is occupied by calcium with minor substitution by iron (which could represent also other transition elements of the fourth series like manganese and titanium), and the Zr site is fully occupied by zirconium. However, the Na(1) and Na(2) sites present a minor substitution of calcium for sodium, whereas in wöhlerite, they are fully

TABLE 9. SELECTED DISTANCES (Å) AND ANGLES FOR THE DIORTHOSILICATE GROUPS IN THE VARIOUS DOMAINS OF "GUARINITE"

	Domain II		Domain IV		Domain I	
Si(1)	- O(3)	1.603(10)	- O(5)	1.603(8)	- O(2)	1.606(7)
	- O(1)	1.618(9)	- O(12)	1.628(10)	- O(6)	1.611(8)
	- O(5)	1.623(9)	- O(1)	1.639(13)	- O(1)	1.632(13)
	- O(17)	1.640(11)	- O(15)^{III}	1.640(11)	- O(4)	1.637(9)
	average	1.621	average	1.628	average	1.622
Si(2)	- O(2)	1.594(9)	- O(3)	1.594(10)	- O(5)	1.573(10)
	- O(4)	1.613(10)	- O(8)	1.602(11)	- O(7)	1.600(9)
	- O(17)	1.622(11)	- O(11)^{III}	1.602(11)	- O(3)	1.621(8)
	- O(6)	1.631(9)	- O(1)	1.627(13)	- O(1)	1.627(13)
	average	1.615	average	1.607	average	1.605
Si(3)	- O(11)	1.594(9)	- O(6)	1.617(10)	- O(9)	1.611(8)
	- O(7)	1.610(10)	- O(14)	1.613(10)	- O(13)^{VII}	1.616(8)
	- O(9)^{III}	1.645(9)	- O(13)	1.640(11)	- O(11)	1.626(8)
	- O(18)^{III}	1.652(12)	- O(2)^{I}	1.650(16)	- O(8)	1.652(12)
	average	1.626	average	1.630	average	1.626
Si(4)	- O(12)	1.623(8)	- O(4)	1.580(10)	- O(12)	1.565(8)
	- O(10)^{III}	1.623(9)	- O(9)	1.617(11)	- O(14)^{VII}	1.611(9)
	- O(8)	1.632(10)	- O(10)	1.619(11)	- O(8)	1.645(13)
	- O(18)^{III}	1.638(11)	- O(2)^{I}	1.634(16)	- O(10)	1.649(9)
	average	1.629	average	1.613	average	1.618
	Si(1)-O(17)-Si(2)	162.92°	Si(1)-O(1)-Si(2)	160.37°	Si(1)-O(1)-Si(2)	162.89°
	Si(3)-O(18)-Si(4)	151.17°	Si(3)-O(2)-Si(4)	152.53°	Si(3)-O(8)-Si(4)	152.25°

Operators generating equivalent atoms

I.	x, y, z-1	I.	x, y, z+1	I.	x, y, z-1
II.	x, y+1, z	II.	-x, -y+1, -z+1	II.	-x+1, -y+1, -z+1
III.	-x+1, y+1/2, -z+1	III.	-x+1, -y+1, -z+1	III.	-x+1, -y+1, -z+2
IV.	x, y, z+1	IV.	x, y-1, z	IV.	x+1, y, z
V.	-x, y+1/2, -z	V.	x, y-1, z-1	V.	-x+1, -y, -z+1
VI.	-x, y+1/2, -z+1	VI.	x, y, z-1	VI.	x-1, y, z-1
VII	-x+1, y+1/2, -z	VII.	-x+1, -y+1, -z+2	VII.	x-1, y, z
VIII.	x, y-1, z	VIII.	x, y+1, z	VIII.	-x+2, -y, -z+1
IX.	-x, y-1/2, -z	IX.	-x+1, -y, -z+1	IX.	-x+1, -y, -z+2
X.	-x, y-1/2, -z+1	X	-x+1, -y, -z+2	X.	-x+2, -y, -z+2
XI.	x, y-1, z+1	XI.	x, y+1, z+1	XI.	x, y, z+1
XII.	-x+1, y-1/2, -z	XII.	-x, -y+1, -z+2	XII.	x+1, y, z+1
XIII.	-x+1, y-1/2, -z+1			XIII.	-x+1, -y, -z
XIV.	x, y+1, z-1			XIV.	-x+1, -y+1, -z

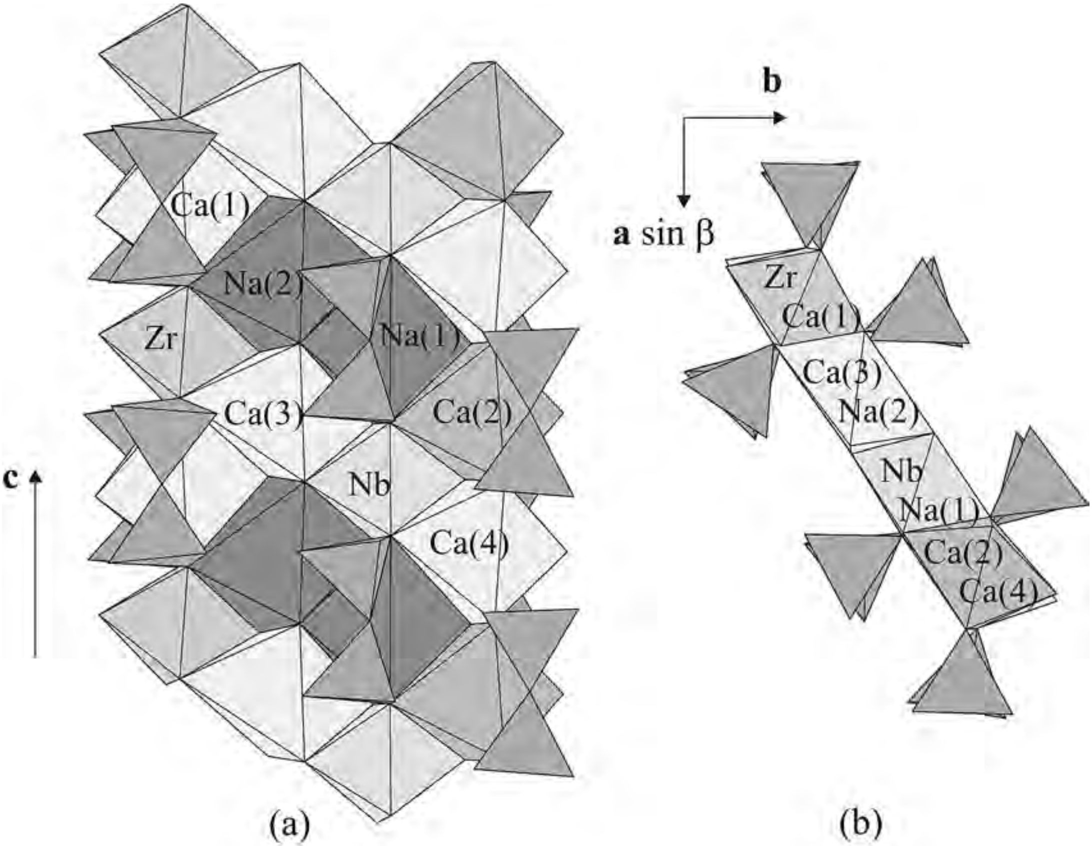

FIG. 5. Drawings of the crystal structure of domain II of "guarinite". (a) The wall of octahedra as seen along [110]; (b) the wall of octahedra as seen along [001].

occupied by sodium: the presence of calcium results in a smaller average distance for Na(1) and Na(2) sites with respect to the corresponding sites in wöhlerite [2.560 and 2.528 Å in domain II of "guarinite", and 2.577 and 2.584 Å in wöhlerite, for Na(1) and Na(2) sites, respectively]. As indicated by the results of the chemical analysis and structural refinement, the Nb site is occupied by Nb and by elements of the first transition series (and also by minor Zr); a mixed occupancy of $Nb_{0.57}$ and $Mn_{0.43}$ was refined, representing a scattering factor value of ~34 electrons, which compares with the value of ~35 electrons derived for the Nb site from EPM data (see Table 2 and considerations below). The actual occupancy of the Nb site may be estimated as $Nb_{0.57}(Mn,Fe)_{0.25}(Ti,Zr)_{0.18}$.

Figures 5a and 5b clearly show the connection between the walls of the polyhedra and the diorthosilicate groups: as in wöhlerite, in the two inner columns of the walls of "octahedra", Si_2O_7 groups link only to one edge of the sodium polyhedra in the outer columns, whereas on one side, two Si_2O_7 groups link to two edges of the Ca(1) polyhedron, and on the other side, both the regularly alternating polyhedra, namely Ca(2) and Ca(4), have one Si_2O_7 group clinging to an edge, on opposite parts of the wall.

In the bond-valence balance (Table 10), no significant discrepancies are found between the sum of the valences reaching each cation and the values calculated from occupancies, and the valence sums reaching the anions deviate less than 10% from the ideal value, except for O(14), which is an anion not linked to the Si_2O_7 groups, suggesting a possible replacement of oxygen by fluorine at this site. This substitution could possibly be related with the concomitant occupancy by divalent cations at the Nb site and by sodium in Na(1) and Na(2) sites, which contribute to the charge balance of the O(14) site.

Taking into account all these considerations, the crystal-chemical formula of domain II that results from the structural study is Ca_3 Zr [$Nb_{0.57}$

TABLE 10. BOND-VALENCE SUMS (*vu*) FOR DOMAIN II IN "GUARINITE"

	Ca(1)	Nb	Zr	Ca(2)	Ca(3)	Ca(4)	Na(1)	Na(2)	Si(1)	Si(2)	Si(3)	Si(4)	Σv_c
O(1)		0.33		0.27		0.19			1.02				1.81
O(2)				0.40		0.32	0.32			1.08			2.12
O(3)		0.44		0.32			0.15		1.06				1.97
O(4)		0.51				0.32	0.07			1.03			1.93
O(5)	0.22		0.70						1.00				1.92
O(6)	0.26		0.68				0.06			0.98			1.98
O(7)	0.42				0.42			0.15			1.04		2.03
O(8)			0.54		0.31			0.08				0.98	1.91
O(9)	0.18		0.69					0.18			0.95		2.00
O(10)	0.15		0.71		0.16							1.00	2.02
O(11)				0.32		0.40		0.06			1.08		1.86
O(12)				0.37	0.16	0.40						1.00	1.93
O(13)		0.63	0.74		0.27		0.18						1.82
O(14)	0.45	0.78					0.20	0.16					1.59
F(15)					0.32	0.30	0.27	0.20					1.09
O(16)		0.88		0.43	0.33			0.22					1.86
O(17)	0.10						0.07		0.96	1.01			2.14
O(18)	0.19							0.10			0.93	0.96	2.18
Σv_a	1.97 (2.00)	3.57 (3.71)	4.06 (4.00)	2.11 (2.00)	1.97 (2.00)	1.93 (2.00)	1.32 (1.23)	1.15 (1.20)	4.04 (4.00)	4.10 (4.00)	4.00 (4.00)	3.94 (4.00)	

Parameters taken from Brese & O'Keeffe (1991). Σv_c and Σv_a gives the sum of the valences reaching each anion and cation, respectively, together with the values calculated from occupancies (in parentheses).

TABLE 11. BOND-VALENCE SUMS (*vu*) FOR DOMAIN IV IN "GUARINITE"

	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Zr	*M*	Na	NaCa	Si(1)	Si(2)	Si(3)	Si(4)	Σv_c
O(1)	0.18								0.96	1.01			2.15
O(2)	0.16							0.09			0.93	0.98	2.16
O(3)	0.36			0.39			0.12			1.08			1.95
O(4)		0.38	0.36	0.08								1.13	1.95
O(5)		0.30	0.33					0.23	1.06				1.92
O(6)		0.44	0.33				0.04				1.03		1.84
O(7)					0.80	0.45 0.36		0.23					1.84
O(8)		0.20	0.34			0.32				1.06			1.92
O(9)		0.37				0.39		0.11				1.02	1.89
O(10)	0.16			0.31	0.61							1.01	2.09
O(11)	0.16				0.72					1.06			1.94
O(12)				0.34	0.46		0.09		0.99				1.88
O(13)	0.12				0.71		0.21				0.96		2.00
O(14)			0.35			0.42		0.22			1.02		2.01
O(15)	0.24				0.70			0.06	0.96				1.96
F(16)			0.32	0.34 0.25			0.16						1.07
F(17)		0.35		0.30			0.21 0.18						1.04
F(18)	0.26					0.29		0.19 0.16					0.90
Σv_a	1.64 (1.72)	2.04 (2.00)	2.03 (2.00)	2.01 (2.00)	4.00 (4.00)	2.23 (2.38)	1.01 (1.00)	1.29 (1.40)	3.97 (4.00)	4.21 (4.00)	3.94 (4.00)	4.14 (4.00)	

Parameters taken from Brese & O'Keeffe (1991). Σv_c and Σv_a gives the sum of the valences reaching each anion and cation, respectively, together with the values calculated from occupancies (in parentheses).

TABLE 12. BOND-VALENCE SUMS (*vu*) FOR DOMAIN I IN "GUARINITE"

	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Zr	Ca(5)	NaCa(1)	NaCa(2)	Si(1)	Si(2)	Si(3)	Si(4)	Σv_c
O(1)		0.16							0.98	0.99			2.13
O(2)				0.30		0.24		0.26	1.05				1.85
O(3)			0.34	0.23		0.30				1.01			1.88
O(4)		0.24			0.69			0.07	0.97				1.97
O(5)		0.17			0.65					1.15			1.97
O(6)	0.32				0.44		0.09		1.04				1.89
O(7)	0.42	0.34					0.14			1.07			1.97
O(8)		0.17						0.10			0.93	0.95	2.15
O(9)		0.18			0.63		0.23				1.03		2.07
O(10)	0.30	0.12			0.67							0.94	2.03
O(11)				0.32		0.40	0.07				1.03		1.82
O(12)				0.41		0.26						1.18	1.85
O(13)			0.49			0.28		0.20			1.00		1.97
O(14)			0.46	0.39				0.14				1.04	2.03
O(15)			0.54 0.39		0.77			0.28					1.98
F(16)	0.32 0.31					0.27	0.19						1.09
F(17)	0.26			0.35			0.24 0.18						1.03
F(18)		0.28	0.34					0.21 0.17					1.00
Σv_a	1.93 (2.00)	1.66 (1.71)	2.56 (2.58)	2.00 (2.00)	3.85 (4.00)	1.75 (2.00)	1.14 (1.26)	1.43 (1.59)	4.04 (4.00)	4.22 (4.00)	3.99 (4.00)	4.11 (4.00)	

Parameters taken from Brese & O'Keeffe (1991). Σv_c and Σv_a gives the sum of the valences reaching each anion and cation, respectively, together with the values calculated from occupancies (in parentheses).

$(Mn,Fe)_{0.25}(Ti,Zr)_{0.18}]_{\Sigma 1.00}$ $[Ca_{0.82}(Fe,Mn)_{0.18}]_{\Sigma 1.00}$ $(Na_{0.77}Ca_{0.23})_{\Sigma 1.00}$ $(Na_{0.80}Ca_{0.20})_{\Sigma 1.00}$ $(Si_2O_7)_2$ $(O_{2.50}F_{1.50})_{\Sigma 4.00}$, which is in good agreement with the formula obtained from an EMP study: Ca_3 Zr $(Nb_{0.56}Fe_{0.15}Mn_{0.10}Ti_{0.10}Zr_{0.09})_{\Sigma 1.00}$ $(Ca_{0.72}Mn_{0.18}M_{0.10})_{\Sigma 1.00}$ $(Na_{0.77}Ca_{0.23})_{\Sigma 1.00}$ $(Na_{0.80}Ca_{0.22})_{\Sigma 1.02}$ $(Si_2O_7)_2$ $(O_{2.17}F_{1.83})_{\Sigma 4.00}$, where *M* represents Al, Mg, Sr, and Y.

Walls of "octahedra" in the structure of domain IV

The crystal structure of domain IV of "guarinite" is represented in Figure 4b in terms of octahedra and tetrahedra: actually, Ca(1) and NaCa sites are eightfold coordinated, whereas the Ca(4) site is seven-fold coordinated. In this structure, two structurally different walls of polyhedra are present, both of them presenting a centrosymmetric distribution of cations.

Bond distances for the eight independent "octahedral" cation sites, labeled Ca(1), Ca(2), Ca(3), Ca(4), Zr, *M*, Na, NaCa, are reported in Table 14, together with their average values, which closely agree with the values calculated for the proposed site-occupancies on the basis of the effective ionic radii.

As in hiortdahlite I (Merlino & Perchiazzi 1985), the Ca(2), Ca(3) and Ca(4) sites are completely occupied by calcium cations, the Zr site is occupied by zirconium, the Na site is occupied by sodium, and the NaCa site is occupied by sodium and calcium in domain IV of "guarinite" from S.Vito. However, the Ca(1) site is occupied by calcium with minor substitution of sodium for calcium, whereas in hiortdahlite I, it is fully occupied by calcium: the presence of a minor amount of sodium does not change the average distance with respect to the corresponding site in hiortdahlite I (2.520 Å in domain IV of "guarinite", 2.524 Å in hiortdahlite I). The *M* site was refined as if it were occupied by manganese, calcium and zirconium, representing a scattering factor value of ~26 electrons, which compares with the value of ~27 electrons derived for *M* site from EPM data (see Table 2 and considerations below). Taking into account that in the refinement procedure, the manganese amount could represent also iron and titanium, the *M* site in domain IV of "guarinite" is not different from the *M* site in hiortdahlite I, assumed to be occupied by zirconium, titanium, calcium, manganese and iron (Merlino & Perchiazzi 1985).

The distribution of the cations in the two structurally different walls of polyhedra is presented in Figure 6, drawn with the program ATOMS (Dowty 1995). In one wall, Ca(1) and Zr polyhedra regularly alternate in the outer columns, whereas Na and Ca(4) polyhedra regularly alternate in the inner columns; two Si_2O_7 groups link to two edges of the Ca(1) polyhedron in the outer columns, and one Si_2O_7 group links to one edge of the

TABLE 13. SELECTED DISTANCES (Å) FOR THE LARGE COORDINATION-POLYHEDRA IN DOMAIN II OF "GUARINITE"

Ca(1)	- O(14)	2.262(10)	Nb (Nb$_{0.57}$ Mn$_{0.43}$)	- O(16)$^{\mathrm{VIII}}$	1.911(9)
	- O(7)	2.289(10)		- O(14)	1.955(10)
	- O(6)	2.468(10)		- O(13)	2.037(11)
	- O(5)	2.533(10)		- O(4)$^{\mathrm{X}}$	2.110(10)
	- O(18)	2.574(10)		- O(3)$^{\mathrm{IX}}$	2.171(10)
	- O(9)	2.595(10)		- O(1)	2.275(10)
	- O(10)	2.669(10)		average	2.076 (2.091*)
	- O(17)	2.828(11)			
	average	2.527 (2.515*)	Ca(2) (Ca$_{0.82}$ Fe$_{0.18}$)	- O(16)	2.244(9)
				- O(2)$^{\mathrm{VI}}$	2.277(10)
Zr	- O(13)	2.051(9)		- O(12)	2.304(10)
	- O(10)$^{\mathrm{I}}$	2.063(9)		- O(11)	2.355(10)
	- O(5)	2.071(9)		- O(3)	2.362(11)
	- O(9)	2.072(9)		- O(1)$^{\mathrm{V}}$	2.416(10)
	- O(6)$^{\mathrm{I}}$	2.078(9)		average	2.326 (2.333*)
	- O(8)	2.167(9)			
	average	2.084 (2.093*)	Ca(4)	- F(15)	2.291(8)
				- O(11)	2.303(10)
Ca(3)	- F(15)$^{\mathrm{I}}$	2.261(8)		- O(12)$^{\mathrm{IV}}$	2.311(10)
	- O(7)$^{\mathrm{III}}$	2.291(9)		- O(4)	2.385(10)
	- O(16)	2.381(10)		- O(2)$^{\mathrm{VI}}$	2.394(10)
	- O(8)$^{\mathrm{VII}}$	2.401(10)		- O(1)$^{\mathrm{VI}}$	2.578(10)
	- O(13)$^{\mathrm{II}}$	2.453(10)		average	2.377 (2.369*)
	- O(12)	2.644(10)			
	- O(10)$^{\mathrm{III}}$	2.645(9)	Na(2) (Na$_{0.80}$ Ca$_{0.20}$)	- F(15)	2.311(10)
	average	2.439 (2.442*)		- O(16)	2.407(11)
				- O(9)$^{\mathrm{III}}$	2.483(10)
Na(1) (Na$_{0.77}$ Ca$_{0.23}$)	- F(15)$^{\mathrm{VIII}}$	2.208(9)		- O(14)$^{\mathrm{II}}$	2.509(11)
	- O(2)	2.266(10)		- O(7)$^{\mathrm{III}}$	2.532(12)
	- O(14)	2.443(12)		- O(18)$^{\mathrm{II}}$	2.679(11)
	- O(13)$^{\mathrm{IV}}$	2.484(11)		- O(8)$^{\mathrm{III}}$	2.778(11)
	- O(3)$^{\mathrm{X}}$	2.537(11)		- O(11)$^{\mathrm{III}}$	2.969(12)
	- O(4)$^{\mathrm{X}}$	2.813(11)		average	2.584 (2.507*)
	- O(17)$^{\mathrm{X}}$	2.815(12)			
	- O(6)	2.914(12)			
	average	2.560 (2.535*)			

The average values calculated for the proposed site-occupancies on the basis of the effective ionic radii given by Shannon & Prewitt (1969) are marked with asterisks.

Na polyhedron in the inner columns. In the other wall, Ca(2) and Ca(3) polyhedra, both chelated by one Si_2O_7 group on opposite sides, regularly alternate in the outer columns, whereas the *M* and NaCa polyhedra regularly alternate in the inner columns with one Si_2O_7 group linked to one edge of the NaCa polyhedron.

In the bond-valence balance (Table 11), no significant discrepancies are found between the sum of the valences reaching each cation and the values calculated from the assumed occupancies; among the anions not linked to the Si_2O_7 groups, the monovalent character of F(16), F(17), and F(18) is confirmed, whereas the low sum of the valences reaching the O(7) site suggests a possible replacement of oxygen by fluorine. In fact, with the cation distribution determined in the refinement procedure for the mixed-occupancy sites, the charge balance is restored if the O(7) site is occupied by 0.72 oxygen and 0.28 fluorine atoms.

Taking into account all these considerations, the crystal-chemical formula of domain IV that results from the structural study is $(Ca_{3.72}Na_{0.28})_{\Sigma 4.00}Zr[Ca_{0.40}(Mn,Fe)_{0.30}(Zr,Ti)_{0.30}]_{\Sigma 1.00}(Na_{1.60}Ca_{0.40})_{\Sigma 2.00}(Si_2O_7)_2(F_{3.28}O_{0.72})_{\Sigma 4.00}$, which is in close agreement with the formula obtained from the EMPA study: $Ca_4Zr(Ca_{0.31}Mn_{0.25}Fe_{0.16}Zr_{0.14}M_{0.14})_{\Sigma 1.00}(Na_{1.20}Ca_{0.76})_{\Sigma 1.96}(Si_{1.98}O_7)_2(F_{2.88}O_{1.12})_{\Sigma 4.00}$, where *M* represents Nb, Ti, Al, Sr and REE.

Walls of "octahedra" in the structure of domain I

Figure 7 gives a schematic view for the crystal structure of domain I of "guarinite" from S. Vito, drawn with the program ATOMS (Dowty 1995), with coordination polyhedra drawn as regular octahedra: actually, the Ca(2) and NaCa(2) sites are eight-fold coordinated, whereas the NaCa(1) site is seven-fold coordinated, but, as in the preceding cases, they were drawn as octahedra in order to obtain a clearer view of the structure. As regards the connections between Si_2O_7 groups and walls of octahedra, the crystal structure of domain I of "guarinite", isostructural with hiortdahlite II, is closely similar to those of janhaugite (Annehed *et al.* 1985), cuspidine, låvenite, normandite and niocalite: all these structures present the same topological symmetry, $P2_1/a$, which is the ideal symmetry obtained whatever the cationic population in all the "octahedral" sites. As discussed in Merlino & Perchiazzi (1988), in this topological symmetry, the centrosymmetric walls of

TABLE 14. SELECTED DISTANCES (Å) FOR THE LARGE COORDINATION-POLYHEDRA IN DOMAIN IV OF "GUARINITE"

Ca(1) (Ca$_{0.72}$ Na$_{0.28}$)	- F(18)	2.304(8)	Ca(2)	- F(17)$^{\mathrm{VIII}}$	2.228(8)
	- O(3)	2.304(9)		- O(6)$^{\mathrm{VIII}}$	2.274(17)
	- O(15)	2.460(11)		- O(4)$^{\mathrm{VIII}}$	2.328(18)
	- O(1)$^{\mathrm{III}}$	2.566(11)		- O(9)$^{\mathrm{II}}$	2.339(11)
	- O(11)	2.598(13)		- O(5)$^{\mathrm{III}}$	2.416(16)
	- O(2)	2.602(12)		- O(8)$^{\mathrm{III}}$	2.556(14)
	- O(10)$^{\mathrm{VI}}$	2.607(12)		average	2.357 (2.365*)
	- O(13)	2.717(11)			
	average	2.520 (2.506*)	Ca(4)	- F(16)$^{\mathrm{IX}}$	2.282(8)
				- F(17)	2.285(13)
Ca(3)	- F(16)$^{\mathrm{XI}}$	2.268(8)		- O(3)$^{\mathrm{I}}$	2.318(12)
	- O(4)$^{\mathrm{VII}}$	2.341(18)		- F(16)$^{\mathrm{I}}$	2.353(14)
	- O(14)$^{\mathrm{II}}$	2.353(9)		- O(12)	2.371(12)
	- O(8)$^{\mathrm{III}}$	2.366(17)		- O(10)	2.402(10)
	- O(5)$^{\mathrm{VII}}$	2.381(13)		- O(4)	2.884(11)
	- O(6)$^{\mathrm{XI}}$	2.382(18)		average	2.414 (2.410*)
	average	2.349 (2.365*)			
			M (Mn$_{0.41}$ Ca$_{0.40}$ Zr$_{0.19}$)	- O(7)$^{\mathrm{II}}$	2.193(11)
Zr	- O(7)	2.019(10)		- O(14)$^{\mathrm{II}}$	2.223(14)
	- O(11)	2.061(11)		- O(9)$^{\mathrm{II}}$	2.242(14)
	- O(13)	2.065(10)		- F(18)	2.253(14)
	- O(15)$^{\mathrm{I}}$	2.068(11)		- O(7)	2.273(14)
	- O(10)	2.121(10)		- O(8)$^{\mathrm{III}}$	2.317(11)
	- O(12)	2.228(10)		average	2.250 (2.241*)
	average	2.094 (2.037*)			
			NaCa (Na$_{0.60}$ Ca$_{0.40}$)	- F(18)$^{\mathrm{II}}$	2.362(9)
Na	- F(17)$^{\mathrm{IX}}$	2.247(9)		- F(18)$^{\mathrm{I}}$	2.403(14)
	- F(17)	2.304(16)		- O(5)$^{\mathrm{VII}}$	2.429(10)
	- F(16)	2.349(17)		- O(7)	2.434(13)
	- O(13)	2.389(10)		- O(14)$^{\mathrm{II}}$	2.444(15)
	- O(3)	2.594(15)		- O(9)$^{\mathrm{XII}}$	2.686(16)
	- O(12)	2.701(14)		- O(2)$^{\mathrm{II}}$	2.770(13)
	average	2.431 (2.365*)		- O(15)$^{\mathrm{I}}$	2.897(12)
				average	2.553 (2.519*)

The average values calculated for the proposed site-occupancies on the basis of the effective ionic radii given by Shannon & Prewitt (1969) are marked with asterisks.

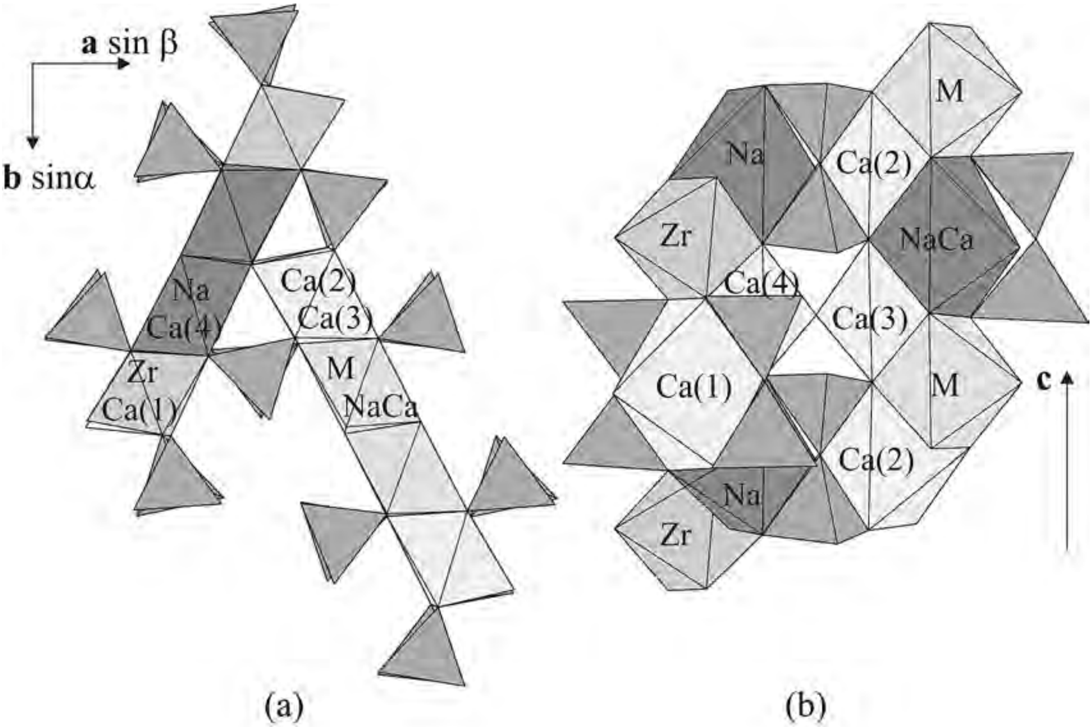

FIG. 6. Drawings of the crystal structure of domain IV of "guarinite". (a) The walls of octahedra as seen along [001]; (b) structural slab as seen along [010], drawn between $x \approx 0$ and $x \approx 5/4$, $y \approx 0$ and $y \approx 3/4$ of Figure 4b.

octahedra are repeated through *a* glides in the [100] direction. The real symmetry of the various phases depends on the distribution of cations in the walls of the octahedra. Cuspidine has a space group $P2_1/a$, as only calcium cations occupy the walls. Låvenite and normandite also adopt space group $P2_1/a$: various cations are distributed in the octahedral sites, but their distribution is still centrosymmetric. Niocalite adopts space group *Pa*: the distribution of Ca and Nb cations in the walls is no longer centrosymmetric, but successive walls in the [100] direction are still symmetry-related through *a* glides. Janhaugite adopts space group $P2_1/n$ with a double *c* parameter: the centrosymmetric walls consist of inner columns of alternating Mn and Na polyhedra, and outer columns characterized by the sequence Na–Ti–Mn–Ti–Na…, with a translation period every fifth polyhedron. The walls are related to each other in the [100] direction through *n* glides. For hiortdahlite II and domain I of "guarinite", the space group is $P\overline{1}$: the inversion centers in each wall are preserved, but the walls are no longer related through the *a* glide perpendicular to **b**.

Bond distances for the eight independent "octahedral" cation sites, labeled Ca(1), Ca(2), Ca(3), Ca(4), Zr, Ca(5), NaCa(1), NaCa(2), are reported in Table 15, together with their average values: these latter values are in agreement with the corresponding values calculated for the proposed site-occupancies on the basis of the effective ionic radii.

As in hiortdahlite II (Merlino & Perchiazzi 1987), the Ca(1) and Ca(4) sites are completely occupied by calcium cations, the Zr site is occupied by zirconium, and the NaCa(1) and NaCa(2) sites are occupied by sodium and calcium in domain I of "guarinite" from S. Vito. However, in hiortdahlite II, the Ca(2) site is fully occupied by calcium, whereas in domain I of "guarinite", it is occupied by calcium with minor replacement by sodium; the presence of a minor amount of sodium does not change the average distance (2.514 Å) with respect to the corresponding sites in hiortdahlite II (2.516 Å). In hiortdahlite II, the Ca(3) site hosts calcium and yttrium, whereas in domain I of "guarinite", it is occupied by calcium and zirconium, with no significant difference in the average distance (2.288 Å in hiortdahlite II, 2.261 Å in domain I of "guarinite"). Moreover, in hiortdahlite II, the *Y* site is occupied by yttrium and sodium with an average distance 2.296 Å, whereas the corresponding site in domain I of "guarinite", Ca(5), was refined as occupied by calcium and manganese, which also includes iron and titanium, with an average distance 2.339 Å. The different occupancy of the Ca(3) and Ca(5) sites in domain I of "guarinite", with respect to the corresponding sites in hiortdahlite II, is in keeping with the chemical data, which reveal an absence of yttrium in "guarinite" (see Table 1), whereas in hiortdahlite II, yttrium is 4.12 wt.% (Aarden & Gittins 1974).

The distribution of the cations in the two structurally different walls of polyhedra is presented in Figures 4c and 7. In one wall, the Ca(2) and Zr polyhedra regularly alternate in the outer columns, whereas NaCa(1) and Ca(1) polyhedra regularly alternate in the inner columns; as can be seen in Figure 7, two Si_2O_7 groups link to two edges of the Ca(2) polyhedron in the outer columns, and one Si_2O_7 group links to one edge of the NaCa(1) polyhedron in the inner columns. In the other wall, Ca(4) and Ca(5) polyhedra regularly alternate in the outer columns, with two Si_2O_7 groups linked to two edges of the Ca(4) polyhedron, whereas Ca(3) and NaCa(2) polyhedra regularly alternate in the inner columns, with one Si_2O_7 group linked to one edge of the NaCa(2) polyhedron. By looking at Table 15, we conclude that the Si_2O_7 groups are connected to the larger polyhedra present in each column.

In the bond-valence balance (Table 12), no significant discrepancies are found between the sum of the valences reaching each cation and the values calculated from occupancies; the divalent character of the Ca(5) site is confirmed. With respect to the four anions not linked to the diorthosilicate groups, the proposed monovalent character of F(16), F(17), F(18) is confirmed, as well as the divalent character of O(15). Taking into account these latter considerations, the crystal-chemical formula of domain I that results from the structural study is $(Ca_{2.71}Na_{0.29})_{\Sigma 3.00}$ $(Ca_{0.71}Zr_{0.29})_{\Sigma 1.00}Zr_{1.00}[Ca_{0.55}(Mn,Fe)_{0.45}]_{\Sigma 1.00}$ $(Na_{1.15}Ca_{0.85})_{\Sigma 2.00}$ $(Si_2O_7)_2$ F_3O, which is in good agreement with the formula that may be obtained from the EMPA study: $Ca_3(Ca_{0.72}Zr_{0.28})_{\Sigma 1.00}(Zr_{0.86}M_{0.14})_{\Sigma 1.00}(Ca_{0.59}Mn_{0.25}Fe_{0.16})_{\Sigma 1.00}(Na_{1.20}Ca_{0.76})_{\Sigma 1.96}$ $(Si_{1.98}O_7)_2$ $(F_{2.88}O_{1.12})_{\Sigma 4.00}$, where M represents Nb, Ti, Al, Sr, and the REE.

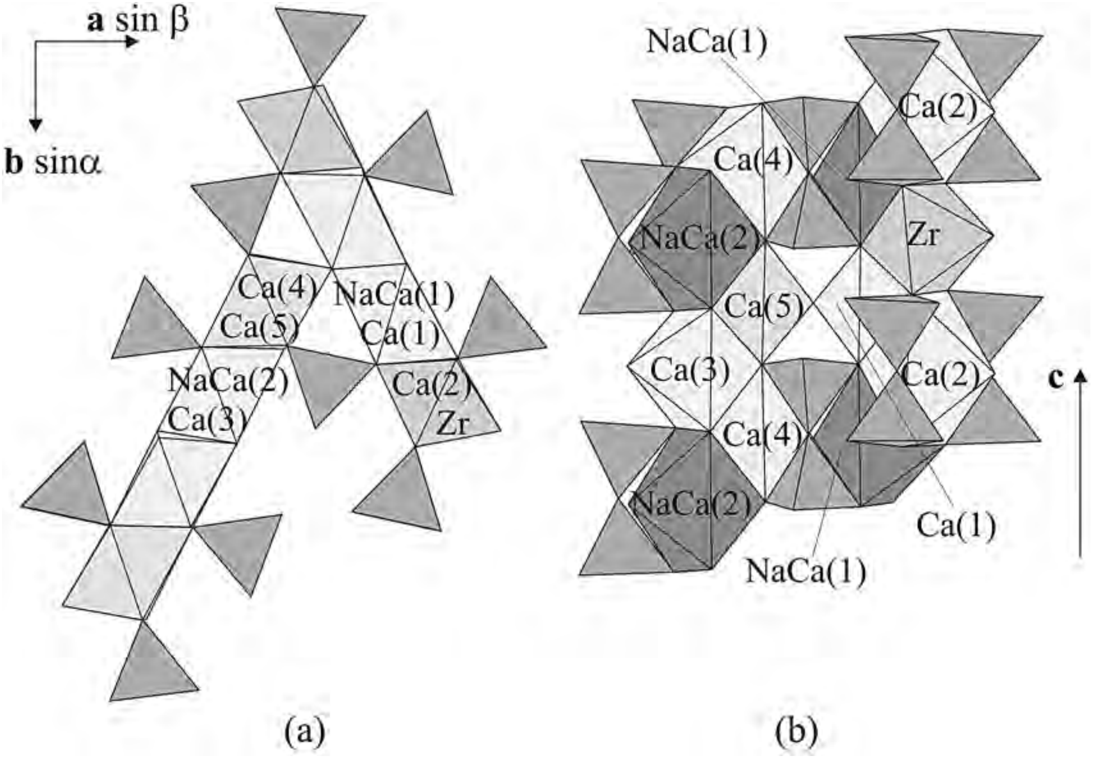

FIG. 7. Drawings of the crystal structure of domain I of "guarinite". (a) The walls of octahedra as seen along [001]; (b) structural slab as seen along [010], drawn between $x \approx -1/4$ and $x \approx 1$, $y \approx 1/4$ and $y \approx 5/4$ of Figure 4c.

TABLE 15. SELECTED DISTANCES (Å) FOR THE LARGE COORDINATION-POLYHEDRA IN DOMAIN I OF "GUARINITE"

Ca(1)	- F(16)	2.262(10)	Ca(2)	- F(18)^{V}	2.275(7)
	- F(16)^{III}	2.274(6)	(Ca$_{0.71}$	- O(7)	2.321(8)
	- O(7)	2.288(11)	Na$_{0.29}$)	- O(4)^{V}	2.456(9)
	- F(17)	2.337(12)		- O(9)	2.568(9)
	- O(6)^{XI}	2.388(9)		- O(5)^{V}	2.575(11)
	- O(10)	2.415(9)		- O(8)	2.585(11)
	average	2.327 (2.345*)		- O(1)^{V}	2.603(10)
				- O(10)	2.724(11)
				average	2.514 (2.500*)
Ca(3)	- O(15)^{IV}	2.185(9)	Ca(4)	- F(17)^{II}	2.229(7)
(Ca$_{0.71}$	- O(13)^{XI}	2.218(10)		- O(12)^{II}	2.300(13)
Zr$_{0.29}$)	- F(18)	2.241(12)		- O(14)	2.315(10)
	- O(14)	2.250(12)		- O(11)^{II}	2.394(13)
	- O(15)^{IX}	2.312(13)		- O(2)	2.409(13)
	- O(3)	2.358(10)		- O(3)	2.518(10)
	average	2.261 (2.287*)		average	2.361 (2.365*)
Zr	- O(15)^{I}	2.036(8)	Ca(5)	- O(11)^{XIV}	2.236(13)
	- O(4)^{XIII}	2.075(9)	(Ca$_{0.55}$	- F(16)^{I}	2.275(7)
	- O(10)^{I}	2.083(9)	Mn$_{0.45}$)	- O(3)^{I}	2.345(12)
	- O(5)^{V}	2.096(10)		- O(13)	2.365(8)
	- O(9)	2.108(8)		- O(12)^{II}	2.394(12)
	- O(6)	2.237(8)		- O(2)	2.418(9)
	average	2.106 (2.100*)		average	2.339 (2.284*)
NaCa(1)	- F(17)^{II}	2.250(8)	NaCa(2)	- F(18)^{VIII}	2.352(8)
(Na$_{0.74}$	- F(16)^{II}	2.339(11)	(Na$_{0.41}$	- O(15)^{V}	2.382(12)
Ca$_{0.26}$)	- F(17)	2.363(13)	Ca$_{0.59}$)	- O(2)	2.412(9)
	- O(9)	2.402(9)		- F(18)	2.429(12)
	- O(7)	2.570(12)		- O(13)	2.498(12)
	- O(6)	2.741(11)		- O(14)	2.641(13)
	- O(11)	2.860(10)		- O(8)^{IV}	2.766(11)
	average	2.504 (2.464*)		- O(4)	2.882(10)
				average	2.545 (2.499*)

The average values calculated for the proposed site-occupancies on the basis of the effective ionic radii given by Shannon & Prewitt (1969) are marked with asterisks.

CONCLUSIONS

"Guarinite" crystals from the Monte Somma syenite show a domain structure, with the simultaneous presence of up to three distinct domains. Referring to the cell types of Merlino & Perchiazzi (1988), domains with cell type I, II, IV were identified. The crystal structure of each domain has been defined through combined single-crystal XRD studies, EMP analyses, and determinations of their structure. The domain I of "guarinite" is isostructural with hiortdahlite II; the absence of yttrium results in a site occupied by calcium and manganese instead of yttrium and sodium. The domains II and IV of "guarinite" are isostructural with wöhlerite and hiortdahlite I, respectively, without any significant difference. On this basis, "guarinite" cannot be considered a valid mineralogical species.

It is worth noticing that this work partially confirms the results of an old study carried on by Zambonini & Prior (1909), who realized a relationship between "guarinite" and hiortdahlite. The distinction between hiortdahlite I and II had not yet been defined, and the mineral at that time called hiortdahlite corresponds to the phase now called hiortdahlite I, isostructural with domain IV, which corresponds to the most common domain in the Vesuvian "guarinite" in our material.

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