

Vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$, a new natural calcium aluminum nesosilicate

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Abstract

Vuagnatite, $\text{CaAl}(\text{OH})\text{SiO}_4$, occurs with prehnite, hydrogrossular, vesuvianite, and chlorite in rodingitic dykes from an ophiolitic zone in the Taurus Mountains, southwest Turkey. The name is for Professor Marc Vuagnat, of the Department of Mineralogy of the University of Geneva, Switzerland. Electron microprobe analysis has shown the uniform distribution of major elements and the absence of other components. X-ray powder diffraction data are from Gandolfi and Hägg-Guinier cameras. The crystal system is orthorhombic, and the cell parameters are: $a = 7.055(6)$, $b = 8.542(7)$, and $c = 5.683(5)$ Å. The space group is $P2_12_12_1$. Vuagnatite is isotypic with conichalcite, $\text{CaCu}(\text{OH})\text{AsO}_4$. Prominent X-ray diffractions occur at 2.993, 2.635, 2.517, 2.391, and 2.453 Å. Crystals are generally anhedral, varying in size between 0.03 and 0.5 mm. The measured density is 3.20–3.25 g/cc, the calculated density being 3.42 g/cc. This difference is due to difficulties in getting material free of inclusions. The refractive indices are: $\alpha = 1.700$, $\beta = 1.725$, $\gamma = 1.730$; optically negative, $2V = 48^\circ$. The crystallization of vuagnatite is related to metasomatic processes of rodingitization.

Introduction

This new silicate was discovered by one of us (H. Sarp) while carrying out a mapping and petrological study in southwest Turkey. The mineral occurs in an ophiolitic zone in the Taurus Mountains, in the "Vilâyet" of Burdur, 600 m northeast of Bögürtlencik Tepe about 10 km northeast of Doğanbaba ($37^\circ 36.5'$ N, $29^\circ 44.5'$ E). Vuagnatite is associated with other calcium silicates (prehnite, hydrogrossular, vesuvianite) in thin rodingitic dykes as a replacement product of primary plagioclase. Crystals are generally anhedral and are intimately intergrown with the other calcium silicates and chlorite. The mineral is named in honor of Professor Marc Vuagnat, of the University of Geneva, in recognition of his work spanning some twenty-five years in the field of ophiolites. The name and the mineral have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. The recommended pronunciation is VÜÄNYÄTAIT (English form) or VÜÄNYÄTÎT (French form). Type material is preserved at the Department of Mineralogy of the University of Geneva, Switzerland.

Occurrence and coexisting minerals

Vuagnatite occurs in dykes (2–15 cm thick, occasionally 50 cm) of pegmatitic anorthositic gabbro, cross-cutting harzburgite–serpentinites and affected by partial or complete rodingitization. In fresh or slightly serpentinized harzburgites, these dykes, not affected by any transformation, show the following mineralogical composition: anorthite (90–95% An), orthopyroxene, clinopyroxene, and sometimes xenoliths of olivine, chromite and pyroxene. Chilled margins have never been observed, indicating injection into a still-hot host rock. In some dykes affected by a partial rodingitization (mineralogical composition: anorthite, prehnite, hydrogrossular, thomsonite, pyroxenes), vuagnatite appears in thin veinlets in association with prehnite and hydrogrossular or with prehnite, hydrogrossular, thomsonite, zoisite, and calcite. In such dykes two other interesting mineral associations may also occur: hydrogrossular, pyroaurite–hydrotalcite, tremolite, clinochlore; and hydrogrossular, tremolite, clinochlore, septechlorites.

Among over one-hundred more fully rodingitized dykes studied in thin sections, vuagnatite has been recognized in two, in which it occurs as a replacement product of plagioclase as mentioned above. It has the following two main parageneses: prehnite, vuagna-

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tite, hydrogrossular, relict pyroxenes, tremolite, clinocllore; hydrogrossular, vuagnatite, vesuvianite, clinocllore. The margins of these rodingitized dykes are chloritized with clinocllore as the only essential component. Rodingitic dykes of fine-grained gabbro-diabase also cross the ultramafites. Of later origin than those of anorthositic gabbro, they always show chilled margins. Vuagnatite has not been found in these later dykes.

The diameter of crystals of vuagnatite varies between 0.03 and 0.5 mm. No alteration has been ob-

served, but inclusions of associated minerals (especially clinocllore, vesuvianite, hydrogrossular) are very common (Sarp, 1976).

Chemical composition

Since vuagnatite is very rare and contains numerous minute inclusions of associated minerals, it has been impossible to obtain an amount of pure vuagnatite large enough for conventional quantitative chemical analysis. Qualitative and quantitative measurements were made on two thin sections coated with

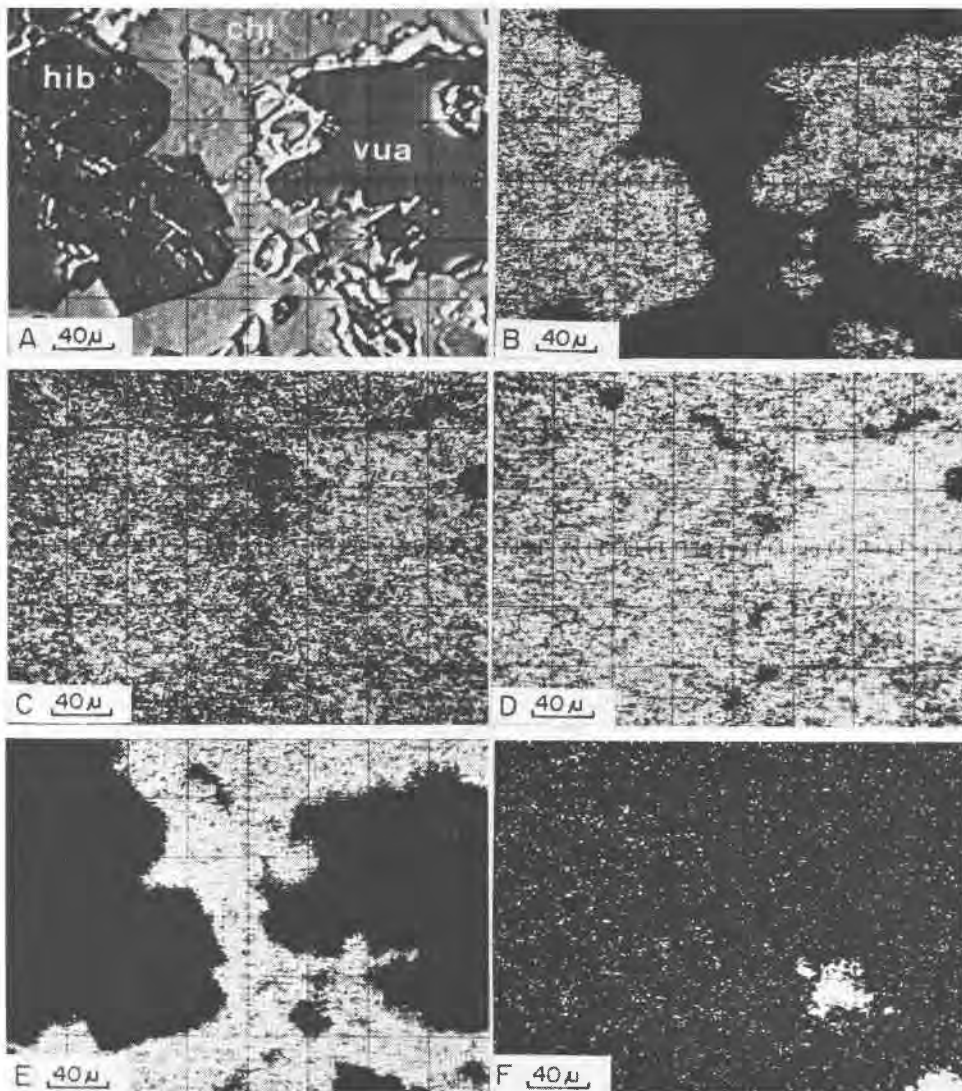


FIG. 1. Electron microprobe scanning images. A: Absorbed electrons image (25 kV-50nA) showing vuagnatite (vua) associated with hydrogrossular (hib) and chlorite (chl); the lightest areas correspond to cracks and holes. B-F: X-ray images (15 kV-50nA). B: Calcium. C: Silicon. D: Aluminum. E: Magnesium. F: Iron.

Ni, with an ARL EMX-SM electron microprobe X-ray analyzer.

Qualitative analysis

Wavelength scans on several grains were made by means of Pb stearate, RbAP, ADP, and LiF analyzing crystals with an excitation potential of 15 kV. Such measurements demonstrated that Ca, Si, Al, and O were the only major elements. Numerous profiles across a great number of grains have shown the uniform distribution of these elements, which is confirmed by the quantitative results. By reference to standards, the complete absence of detectable C (standards: graphite and aragonite), Na (standard: jadeite), Mg (standard: periclase), Fe (standard: Fe), and F and Cl (standard: apatite) has been demonstrated. K (standard: adularia), Mn (standard: Mn), P (standard: apatite), and Ti (standard: Ti) have been detected as trace elements. Electron microprobe scanning images are shown in Figure 1.

Quantitative analysis

The following experimental conditions were used. Excitation potential: 8 kV (to minimize the absorption effects); sample current (measured on brass): 150 nA; counts (in number large enough for good counting statistics) stopped by a constant digitized beam current; spectral lines-analyzing crystal-standards for major elements: CaK α -LiF-wollastonite, SiK α -ADP-wollastonite, AlK α -ADP-synthetic corundum, OK α -RbAP-synthetic corundum (on one grain only; on other grains by difference); number of measurement points: more than one-hundred chosen in six grains. Corrections for instrumental and matrix effects were made following procedures contained in computer program MAGIC IV described by J. W.

TABLE 2. Crystal data for vuagnatite

Crystal system	: orthorhombic
Unit cell parameters*	: $a = 7.055 \pm 0.006 \text{ \AA}$ $b = 8.542 \pm 0.007 \text{ \AA}$ $c = 5.683 \pm 0.005 \text{ \AA}$ $V = 342.5 \pm 0.5 \text{ \AA}^3$
Space group	: $P2_1^2 2_1$ Z (formula units) = 4
Optical Properties	
Refractive indices	: $\alpha = 1.700 \pm 0.001$ $\beta = 1.725 \pm 0.001$ $\gamma = 1.730 \pm 0.001$ $\gamma - \alpha = 0.030$
Optical orientation**	: $\alpha = c, \beta = b, \gamma = a$ O.A.P. (010)
Optical axial angle**	: $2 V_\alpha = 48^\circ$
Acute bisectrix	: α
Dispersion	: $r < v$, very strong
Colour	: colourless
Pleochroism	: none
Extinction	: parallel or symmetrical
Elongation	: negative
Cleavage	: none observed
Twinning	: none observed
Physical Properties	
Density _{calc}	: 3.42 g/cc
Density _{meas} ***	: 3.20 - 3.25 g/cc (with mineral as free as possible from clinocllore inclusions)
Colour	: white (in grain under binocular)
Luster	: vitreous
* From X-ray powder and single crystal diffraction data, errors based on 3σ	
** Confirmed on a Charles Supper spindle stage	
*** Measured by suspension in Clerici liquor-distilled water	

Colby, Bell Telephone Laboratories, Inc., Allentown, Pennsylvania.

The results, in weight percent, are given in Table 1 with the values of the 2σ limits, atomic ratios, and for

TABLE 1. Electron microprobe chemical analyses of vuagnatite in weight percent

	1*	2**	3	4	5	6	2σ + limits	Atom $\dagger\dagger$ ratios	Theoretical CaAl(OH)SiO ₄	
SiO ₂	33.59	32.50	32.65	32.54	32.39	33.10	± 0.24	Si 1.000	34.10	SiO ₂
Al ₂ O ₃	27.76	27.27	27.32	27.06	27.00	27.15	± 0.28	Al 0.980	28.95	Al ₂ O ₃
CaO	31.52	31.31	31.61	31.45	31.29	31.08	± 0.15	Ca 1.025	31.83	CaO
H ₂ O	-	-	-	-	-	-	-	-	5.12	H ₂ O
Total	92.87	91.08	91.58	91.05	90.68	91.33			100.00	Total
* Grain 1: Mean of 25 measurement points										
** Grains 2-6: Mean of 16 measurement points										
\dagger Calculated with the 105 measurement points										
$\dagger\dagger$ Calculated after the mean of the values obtained on each grain										

comparison, theoretical $\text{CaAl}(\text{OH})\text{SiO}_4$. The atomic ratios give a 1:1:1 proportion for Ca, Al, and Si. The presence of (OH) was first suspected by the behavior of the mineral under the microprobe beam and is supported by low summation of the oxides. The

formula $\text{CaAl}(\text{OH})\text{SiO}_4$ with one (OH) group is confirmed by crystal structure analysis (Mc Near *et al.*, 1976). The experimental values are a little low for Ca, Si, and especially for Al, but we have no direct evidence for more than one (OH) group. The deficiency

TABLE 3. Comparison of observed and calculated power diffraction data of vuagnatite

hkl	d_{obs}^*	d_{calc}^\dagger	I_{obs}^*	I_{calc}^\dagger	$I_{\text{calc}}^{\dagger\dagger}$	hkl	d_{obs}^*	d_{calc}^\dagger	I_{obs}^*	I_{calc}^\dagger	$I_{\text{calc}}^{\dagger\dagger}$
110	5.44	5.44	15	14.4	3.6	241	1.739			2.1	6.3
011		4.73		0.2	2.2	023	1.732			3.7	3.3
101		4.43		0.3	0.5	331	1.726	1.727	10	21.5	23.8
020		4.27		1.4	2.0	410	1.727			0.2	0.3
111	3.94	3.93	40	30.6	45.0	042	1.71	1.707	25	13.0	18.1
120		3.65		0.5	2.0	401	1.685			0.1	0.0
200	3.53	3.53	25	17.1	10.7	123	1.682			0.1	0.0
021		3.41		3.8	2.0	203	1.669			11.2	11.5
210		3.26		1.4	1.9	322	1.665	1.668	10	0.6	0.9
121		3.07		0.3	1.0	150	1.660			0.6	0.0
201	2.993	2.997	100	100.0	100.0	142	1.659			0.1	2.4
002	2.84	2.842	30	26.9	24.3	411	1.653			1.5	1.7
211		2.828		4.6	1.2	213	1.638			0.7	0.4
220	2.72	2.720	5	7.3	9.5	051	1.632	1.636	30	4.1	1.3
012		2.696		1.1	1.3	420	1.630			20.5	24.4
130	2.635	2.640	70	51.2	64.5	151	1.594			5.1	7.6
102		2.636		0.0	1.7	340	1.581			1.3	0.5
031		2.546		0.0	2.3	033	1.577			0.1	0.3
112	2.517	2.519	60	65.9	55.6	421	1.567			0.2	0.1
221	2.453	2.453	50	50.2	50.3	223	1.555			4.9	5.0
131	2.391	2.395	60	52.1	41.4	133	1.539			11.3	8.7
022		2.366		1.3	0.2	250	1.538			0.0	0.0
310		2.267		0.0	0.4	242	1.537			7.2	5.1
122		2.243		10.8	7.8	332	1.528	1.529	30	37.9	39.5
230	2.212	2.216	40	38.4	24.2	341	1.523			0.9	0.2
202		2.213		8.1	8.5	430	1.499			0.1	0.3
301		2.173		0.8	0.6	402	1.499		10	13.0	11.4
212	2.14	2.142	40	39.2	44.8	251	1.484			0.7	0.5
040		2.136		0.5	4.4	412	1.476			1.2	0.3
311		2.106		2.8	0.7	303	1.475			1.0	0.3
231	2.07	2.064	15	0.9	1.1	052	1.464			0.0	0.1
320		2.060		9.5	3.6	313	1.454			0.8	1.0
140	2.04	2.044	10	13.1	10.3	431	1.450			4.3	0.6
032		2.011		1.6	0.7	233	1.440			0.8	0.0
041		1.999		0.0	0.1	152	1.434		10	24.3	19.0
222	1.96	1.965	15	12.6	14.3	060	1.424			3.2	2.4
321		1.937		3.5	0.2	004	1.421		10	16.4	16.1
132	1.93	1.934	40	16.7	9.3	043	1.417			0.8	0.4
141		1.923		6.3	8.7	422	1.414			0.6	1.2
013		1.849		0.4	1.5	014	1.402			0.0	0.1
103		1.830		2.0	0.3	160	1.396			0.3	0.0
240		1.827		2.7	3.0	323	1.394			0.4	0.1
330		1.813		0.6	3.4	104	1.393			0.1	0.1
302		1.812		0.4	0.3	510	1.392			4.2	5.0
113	1.77	1.789	10	9.5	8.0	143	1.38	1.389	10	0.3	0.5
312		1.772		9.9	10.3	350	1.382			6.2	5.0
400	1.767	1.764	15	11.1	10.3						
232		1.747		5.1	0.7						

* d_{obs} in Å and I_{obs} (visually estimated) are from Gandolfi and Hägg-Guinier patterns made with $\text{CuK}\alpha$ rad. ($\lambda = 1.5418$ Å)

† d_{calc} in Å and I_{calc} ($I = m \cdot LP \cdot F^2$) are from refined parameters of vuagnatite (McNear, Vincent and Parthé, 1976)

†† I_{calc} are based on conicalcrite atomic parameters ($B = 0.5 \text{ \AA}^2$ for all atoms)

may possibly be explained by weak instability under the electron beam. Trace element contents are approximately: K: ~1000 ppm irregularly distributed (probably submicroscopic phyllosilicate inclusions), Mn: ~400 ppm, Ti and P: ~120 ppm.

X-ray crystallography

The X-ray powder pattern of vuagnatite has been established using Gandolfi and Hägg-Guinier cameras. The mineral is orthorhombic with space group $P2_12_12_1$. The structure determination (Mc Near *et al.*, 1976) shows that vuagnatite is a nesosilicate isotypic with conichalcite, $\text{CaCu}(\text{OH})\text{AsO}_4$ (Qurashi and Barnes, 1963).

The unit cell constants and the X-ray powder diffraction data are given respectively in Tables 2 and 3. In Table 3 the $d_{\text{calc}}\dagger$ and $I_{\text{calc}}\dagger$ values are based on the refined cell and atomic parameters of vuagnatite measured on a Philips PW-1100 computer-controlled four-circle diffractometer using $\text{MoK}\alpha$ rad. ($\lambda = 0.71069 \text{ \AA}$). The parameters (scattering factors, anomalous dispersion, *etc.*) required for the structure refinement were used in the powder pattern calculation (Yvon *et al.*, 1969). A second calculation ($I_{\text{calc}}\dagger\dagger$) with vuagnatite cell parameters but conichalcite atomic parameters shows the similarity in structures of vuagnatite and conichalcite.

A stereoscopic view of the structure (Fig. 3), plotted using the program ORTEP-ORNL-3794, (John-

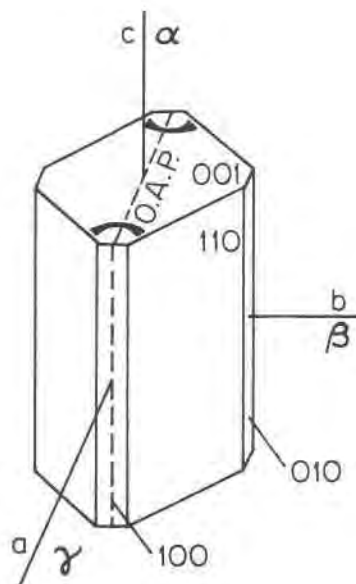


FIG. 2. Single crystal habit of vuagnatite with the main forms and position of optical elements.

son, 1970), shows that Al octahedra are linked by edges to form chains parallel to c . The Si tetrahedra link three octahedral chains: two by sharing corners and the third by a hydrogen bond. The Ca atoms are in eightfold coordination, and link these chains yielding a dense compact structure. A more detailed de-

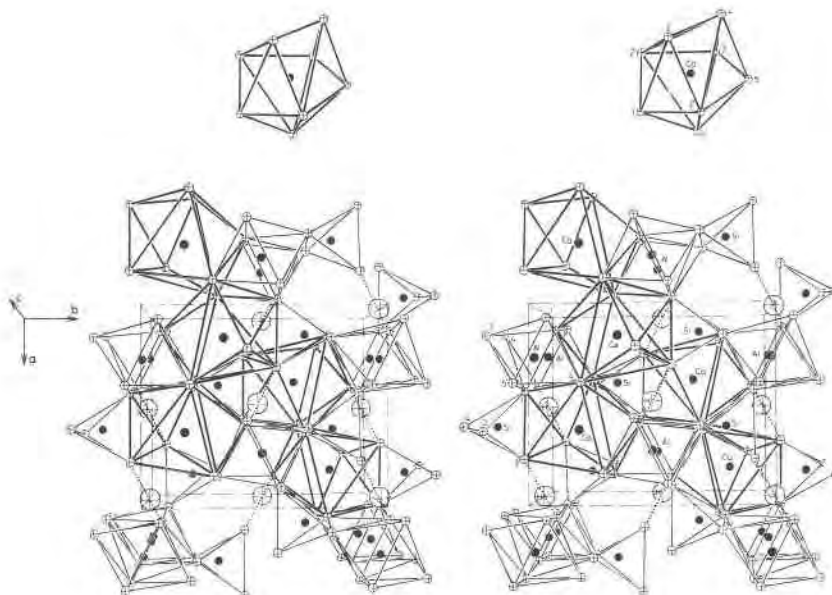


FIG. 3. Stereoscopic view down the c axis of the structure and of a Ca polyhedron of vuagnatite. The spheres represent 75 percent probability surfaces (Johnson, 1970).

scription will be found in the accompanying article (Mc Near *et al.*, 1976).

Crystal morphology

Vuagnatite appears most often in anhedral crystals varying in size between 0.03 and 0.5 mm. Sometimes, however, when intergrown in prehnite, very small subhedral or even euhedral sections (rectangular, rhombic, and 6-sided) may be observed. Such sections are the basis for Figure 2 which represents the probable habit of the mineral: prismatic, elongated parallel to *c* with {110}, {001}, {100}, and {010} as dominant forms. Rare minor forms are present, perhaps prisms {0*kl*} or {*h0l*} or disphenoids, but they are too poorly developed to be indexed and drawn.

Physical and optical properties

Vuagnatite is white with a vitreous luster when observed under the stereomicroscope. In thin sections it is colorless. The measured density, 3.20–3.25 g/cc, determined by suspension method in a mixture of Clerici solution and distilled water, is always significantly lower than the calculated density; difficulties in getting material completely free of associated inclusions, especially of clinocllore, may explain the difference.

The optical properties have been determined under polarizing microscope in thin sections and, for the determination of the indices of refraction, in grain mounts. The refractive index liquids were quite fresh, values were checked by refractometer, and the measurements were done at a stabilized room temperature. The optical data, especially the optical orientation and the optic axial angle, have also been measured with the aid of a spindle stage during optical preorientation for single crystal X-ray diffraction methods. These properties are given in Table 2.

Genesis

The crystallization of vuagnatite is due to metasomatic processes of rodingitization related to serpentinization phenomena. This new mineral is a member of the typical calc-silicate suite of minerals which appear as replacement products of primary plagioclase in rodingitic rocks, of which hydrogrossular, prehnite, zoisite, clinzoisite, diopside, and vesuvianite are the most common. The formation of these rodingitic rocks has been described by many authors, *e.g.* Marshall (1911), Coleman (1966), and Vuagnat (1967).

According to the observed mineral assemblages and by comparison with regional metamorphic para-

geneses, vuagnatite crystallizes in the conditions of the prehnite–pumpellyite facies. From the data of Coombs *et al.* (1959, 1970), Coleman (1966), Strens (1968), Liou (1971), and O'Brien and Rodgers (1973) on the stability fields of mineral assemblages of this facies and particularly on the behavior of prehnite and hydrogrossular, a maximum pressure of about 3 kbar and a maximum temperature of about 450°C may be estimated for the parageneses of the rodingites described here. In these limits the stability field of vuagnatite is certainly much more limited, this mineral being only sometimes observed.

An occurrence of vuagnatite in rodingites of Guatemala will be described elsewhere.

Acknowledgments

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