Bull. Natn. Sci. Mus., Ser. C (Geol.), 3 (2), June 22, 1977

The Occurrence of Vuagnatite from Shiraki, Toba, Mie Prefecture, Japan

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Introduction

In 1972 the first author collected very pale blue tiny lenses in pectolite veinlets cutting serpentinite exposed in a quarry at Shiraki, Toba, Mie Prefecture. But its X-ray powder study was inconclusive due to the absence of any identical X-ray powder pattern in literatures. Now it has turned out to be vuagnatite ($CaAlSiO_4(OH)$), a new mineral from Turkey described by Sarp, Bertrand and Mc Near (1976). After this find, the occurrence of this mineral have been reported from Guatemala and California (McNear *et al.*, 1976; Pabst *et al.*, 1976).

Here the wet chemical and spectroscopic analyses, X-ray powder pattern, some physical and optical properties are reported together with the brief discussion about the formation possibly favored by a lower temperature, higher pressure and silica-undersaturated condition.

The authors extend their sincere thanks to Professor Kozo Nagashima, Department of Chemistry, University of Tsukuba, for his wet chemical and spectroscopic analyses. They are also greatly indebted to Dr. Halil Sarp, Université de Genève, for his information about the original vuagnatite and to Professor Adolf Pabst, University of California, for his supply of some mineralogical data on the Californian material.

Occurrence

In eastern part of the Shima Peninsula, Mie Prefecture, many ultrabasic and basic rocks are exposed along faults of ENE-WSW direction intruding Paleozoic and Mesozoic sedimentary rocks (Yamagiwa, 1957).

The vuagnatite-bearing specimens are from a serpentinite quarry at Shiraki, Toba (Fig. 1), where serpentinite is intersected by a number of veinlets of various dimensions and of various mineralogical constituents including pectolite, chlorite, aragonite, prehnite, hydrogrossular, natrolite, xonotlite, vesuvianite, calcite, hydromagnesite, artinite, coalingite, a hydrotalcite-like mineral and stevensite in the order of approximate frequency (Suzuki *et al.*, 1976; Matsubara *et al.*, 1976).

Vuagnatite occurs as veinlets less than 5 mm wide or as small lenses less than 15mm

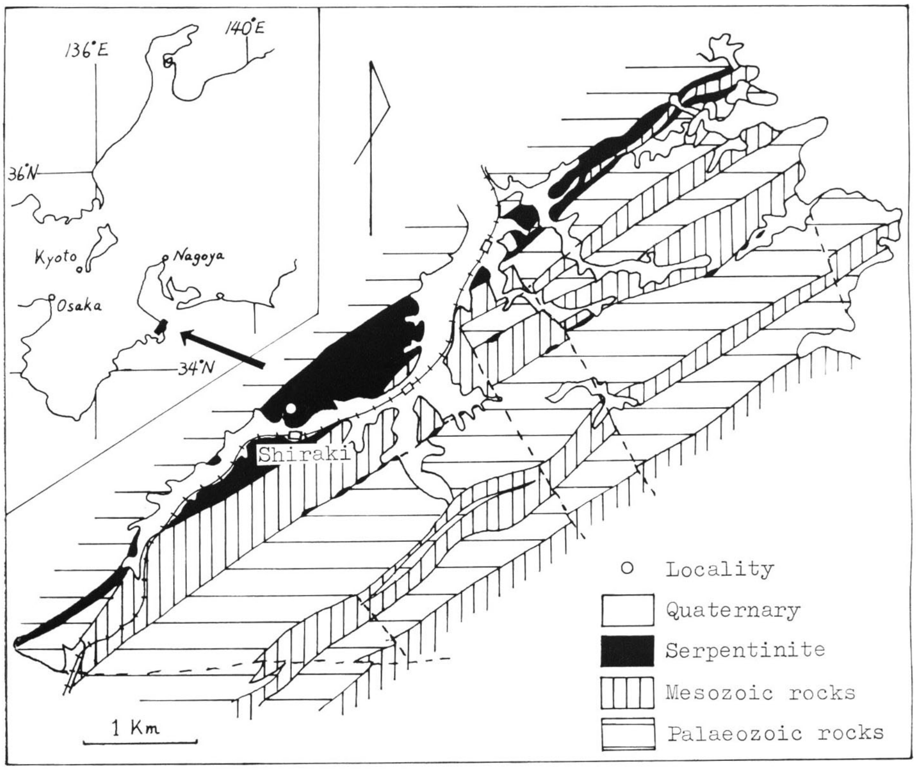

Fig. 1. Geologic sketch map of the adjacent area of vuagnatite locality (white circle). After YAMAGIWA (1957) with the authors' minor corrections.

long in pectolite veinlets, which are aggregates of coarser cleavable platelets or of minute fibers. Under the microscope, the vuagnatite veinlets and lenses consist of aggregate of subhedral to euhedral inclusion-free grains reaching 1 mm across (Fig. 2), which occasionally display crystal faces including m(110), a(100), b(010), c(001), and p(111) under the electron microscope (Fig. 3). In a few vugs developed among vuagnatite grains, fibers of pectolite growing on vuagnatite penetrate well-developed otcahedra (Fig. 4). Seeing from the external shape and the chemical natures of the associated minerals, this might be hydrogrossular or its pseudomorph.

Apart from pectolite veinlets, no vuagnatite has been found at this locality irrespective of the development of many veinlets composed of such minerals compositionally similar to vuagnatite as prehnite and hydrogrossular. Calcite and aragonite are found to be in direct contact with vuagnatite in hand specimens and in thin sections, although they are admittedly of later formation than vuagnatite.

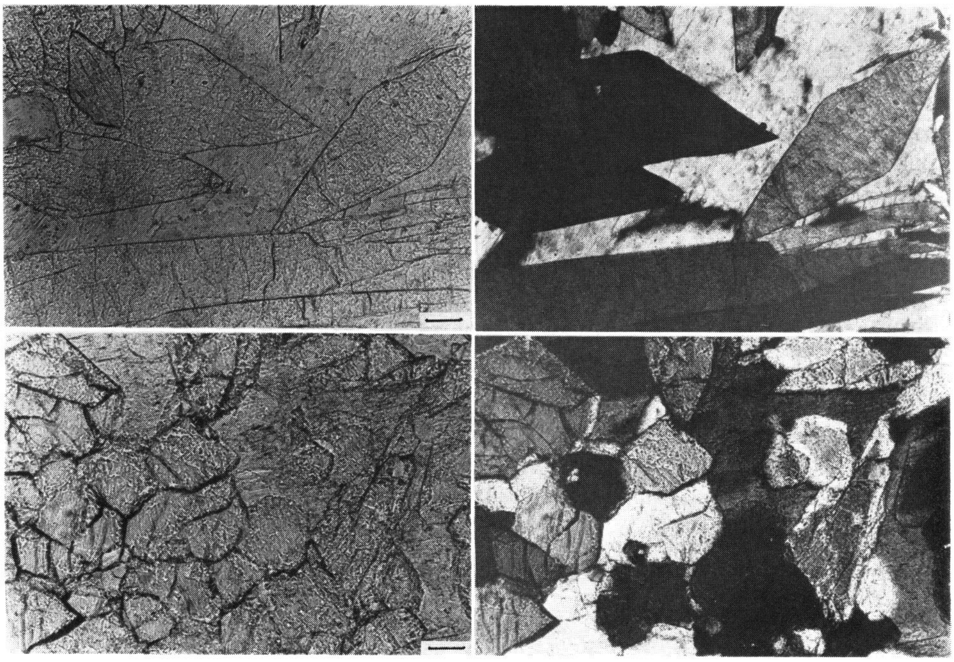

Fig. 2. Photomicrographs of vuagnatite (scale 0.05 mm).
Upper: Euhedral crystals in pectolite. One polar (left) and crossed polars (right).
Lower: Aggregate of subhedral grains in association with pectolite. One polar (left) and crossed polars (right).

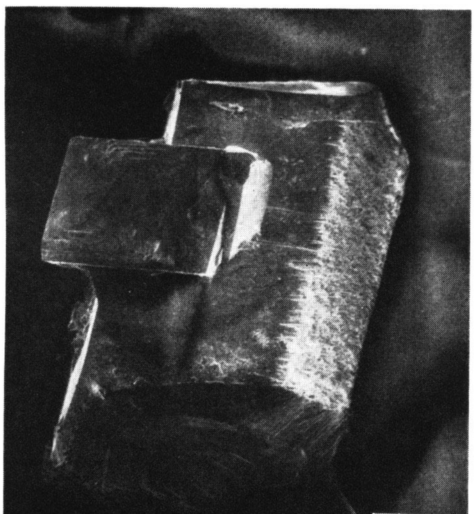

Fig. 3. Scanning electron micrograph of vuagnatite crystals (scale 0.05 mm).

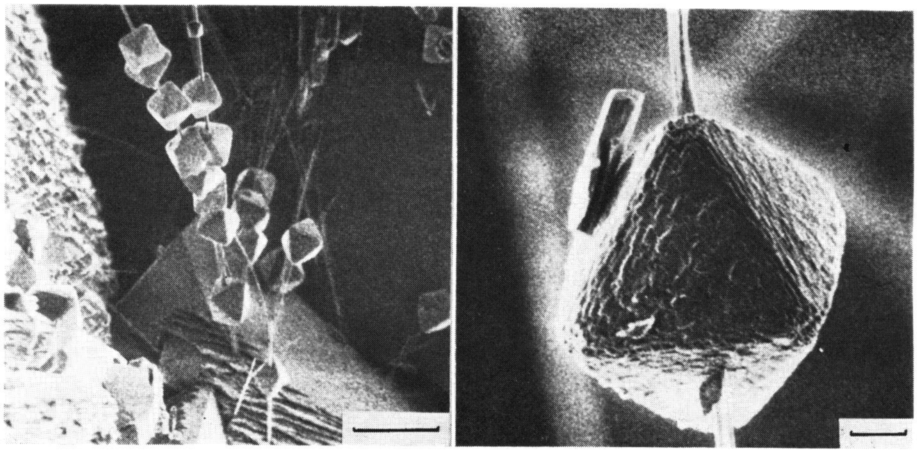

Fig. 4. Scanning electron micrographs of undetermined octahedral crystals spitted by fiber-like pectolite on vuagnatite (scale: left 0.05 mm; right 0.005 mm).

Physical and Optical Properties

Vuagnatite is very pale blue, very pale yellowish brown or rarely very pale pink in color, and transparent to translucent with vitreous luster. Cleavage is not observed both in hand specimen and in thin section. MOHS' hardness is about 7½ and the massive aggregate is very tough in the mortar. Density measured by BERMAN microbalance is 3.36 g/cm^3.

It is colorless in thin section with parallel extinction and negative elongation. It is optically biaxial negative with 2V about 50°, $r<v$ very strong. Refractive indices are $\alpha=1.702(2)$, $\beta=1.725(2)$, $\gamma=1.730(2)$ by the immersion method and the optic plane is parallel to {010}.

In Table 1 these properties are compared with those of the original material.

Chemical Analyses

Wet chemical analysis was made by Professor KOZO NAGASHIMA for about 2 grams of very pale blue material purified by hand-picking and heavy liquid separation. As given in Table 2, the analysis leads to the empirical formula $Ca_{0.999}(Al_{0.995}Fe^{3+}_{0.002})_{\Sigma 0.997}Si_{1.000}O_{3.980}(OH)_{1.069}$ on the basis of Si=1, which is very close to $CaAlSiO_4(OH)$. Spectroscopic analysis by him detected traces of Na, Mg, K, Mn and Sr.

X-ray Powder Study

X-ray powder pattern of a part of analysed material was obtained by diffractometer method employing Cu/Ni radiation (Table 3). That of the pale yellowish brown material is actually identical with that of the studied one.

Table 1. Crystallographic, physical and optical properties of vuagnatites from Turkey and Shiraki

	Turkey	Shiraki
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$
unit cell constants	$a_0=7.055$ (6)Å	$a_0=7.052$ (5)Å
	$b_0=8.542$ (7)Å	$b_0=8.534$ (5)Å
	$c_0=5.683$ (5)Å	$c_0=5.680$ (5)Å
Z	4	4
color	white	very pale blue
		very pale yellowish brown
		very pale pink
luster	vitreous	vitreous
cleavage	none	none
density (g/cm^3)	3.20–3.25 (meas.)	3.36 (meas.)
	3.42 (calc.)	3.44 (calc.)
hardness (Mohs)		$7\frac{1}{2}$
color in thin section	colorless	colorless
extinction	parallel	parallel
sign of elongation	negative	negative
optic sign	negative	negative
optic axial angle	48°	about 50°
dispersion	$r<v$, very strong	$r<v$, very strong
refractive indices	$\alpha=1.700$ (1)	$\alpha=1.702$ (2)
	$\beta=1.725$ (1)	$\beta=1.725$ (2)
	$\gamma=1.730$ (1)	$\gamma=1.730$ (2)

Table 2. Wet chemical analysis of vuagnatite (NSM M–21621) from Shiraki, Mie Prefecture. (Analyst: K. NAGASHIMA)

	wt. %	molecular quotient	metal number	metal number (basis Si=1)	theoretical figure
SiO_2	34.30	0.5709	0.5709	1	34.11
Al_2O_3	28.95	0.2839	0.5679	0.995	28.94
Fe_2O_3	0.11	0.0007	0.0014	0.002	
CaO	31.97	0.5701	0.5701	0.999	31.83
$H_2O(\pm)$	5.50	0.3053	0.6106	1.069	5.12
Total	100.83%				100.00%

Consideration of the Formation

Compared with known hydrous calcium aluminum silicates with the same Ca/Al ratio as vuagnatite in their ideal formulae, this mineral is less siliceous than prehnite and more siliceous than bicchulite as given by the following formulae which accompany the figures of molar volume of respective component for forthcoming discussion:

Table 3. X-ray powder data for vuagnatites from Turkey (1) and Shiraki (2), Mie Prefecture

1.		2.				
d(Å)	I	d(Å)	I	Qobs	Qcal	hkl
5.44	15	5.437	16	0.0338	0.0338	101
3.94	40	3.922	40	0.0650	0.0648	111
3.53	25	3.523	17	0.0806	0.0804	200
		3.409	6	0.0860	0.0859	012
		3.259	4	0.0942	0.0941	201
		3.074	8	0.1058	0.1060	112
2.993	100	2.996	100	0.1114	0.1114	210
2.84	30	2.841	40	0.1239	0.1240	020
2.72	5	2.720	10	0.1352	0.1353	202
2.635	70	2.638	75	0.1437	0.1437	103
					0.1441	120
2.517	60	2.518	90	0.1577	0.1578	121
2.453	50	2.452	60	0.1663	0.1663	212
2.391	60	2.393	75	0.1746	0.1747	113
		2.241	18	0.1991	0.1990	122
2.212	40	2.214	75	0.2040	0.2040	203
					0.2044	220
2.14	40	2.142	55	0.2180	0.2181	221
		2.106	3	0.2255	0.2257	311
2.07	15	2.060	16	0.2356	0.2350	213
					0.2359	302
2.04	10	2.042	22	0.2398	0.2398	104
		2.010	3	0.2475	0.2476	023
1.96	15	1.964	15	0.2592	0.2593	222
1.93	40	1.933	25	0.2676	0.2677	123
		1.825	6	0.3002	0.3001	204
		1.789	10	0.3124	0.3128	131
1.77	10	1.770	15	0.3190	0.3187	321
1.767	15	1.763	12	0.3217	0.3217	400
		1.746	8	0.3280	0.3280	223
1.726	10	1.727	25	0.3353	0.3354	401
					0.3356	313
1.707	25	1.706	22	0.3436	0.3437	024
1.665	10	1.668	17	0.3594	0.3594	230
1.632	30	1.630	25	0.3764	0.3766	402
		1.593	7	0.3941	0.3944	115
		1.553	8	0.4146	0.4143	232
		1.538	20	0.4228	0.4227	133
		1.536	18	0.4239	0.4237	205
1.528	30	1.527	40	0.4289	0.4286	323
1.50	10	1.498	10	0.4456	0.4457	420
		1.475	3	0.4596	0.4594	421
1.44	10	1.449	5	0.4763	0.4763	413
1.43	10	1.433	35	0.4870	0.4874	125
		1.420	18	0.4959	0.4959	040
1.38	10	1.381	10	0.5243	0.5243	305
		1.374	5	0.5297	0.5297	141
		1.359	3	0.5415	0.5414	404
		1.354	5	0.5455	0.5454	116
		1.342	8	0.5553	0.5553	315
		1.309	10	0.5836	0.5836	333
		1.285	15	0.6056	0.6057	216
		1.251	15	0.6390	0.6384	126
					0.6396	143
		1.234	4	0.6567	0.6573	513
		1.196	6	0.6991	0.6987	226
		1.154	10	0.7509	0.7503	523
		1.152	10	0.7535	0.7534	514
		1.121	6	0.7958	0.7950	150
		1.106	5	0.8175	0.8176	440
		1.082	12	0.8542	0.8538	307
		1.071	6	0.8718	0.8725	442
		1.068	6	0.8767	0.8772	227

1.	2.
a_0=7.055(6)Å	a_0=7.052(5)Å
c_0=5.683(5)Å	b_0=5.680(5)Å
b_0=8.542(7)Å	c_0=8.534(5)Å

$$Ca_2Al_2Si_3O_{10}(OH)_2 = 2CaAlSiO_4(OH) + SiO_2$$

prehnite	vuagnatite	quartz
233 Å^3	170.88 Å^3	37.68 Å^3

$$2CaAlSiO_4(OH) = Ca_2Al_2SiO_7 \cdot H_2O + SiO_2$$

vuagnatite	bicchulite	quartz
170.88 Å^3	172.12 Å^3	37.68 Å^3

Since prehnite is found in the same mode of occurrence as that of vuagnatite in this quarry, it is highly probable that there is an overlapping area in pressure-temperature stability ranges of the two minerals, although the aggregate of vuagnatite plus quartz has smaller molar volume than prehnite. Thus the formation of vuagnatite was obviously favored by silica deficient condition. MC NEAR *et al.* (1976) showed that vuagnatite has a dense atomic packing and SARP *et al.* (1976) considered the original vuagnatite as a product of rodingitization derived from replacement of plagioclase under the conditions of prehnite-pumpellyite facies. This may be also evident due to the comparison with bicchulite, which corresponds compositionally to a low silica derivative of vuagnatite. As shown above the molar volume of bicchulite is larger than that of vuagnatite irrespective of the subtraction of one molecule of SiO_2 (as quartz), indicating bicchulite to have an open structure. At Fuka, one of the original localities of bicchulite, this mineral is considered as one of the retrograde skarn minerals (HENMI *et al.*, 1973), and the occurrence of prehnite is also found as veinlets cutting skarns at the locality (HENMI *et al.*, 1976). This suggests that vuagnatite might have not been formed under the surrounding condition of retrograde skarn formation at Fuka, where lower pressure and decreasing temperature condition impeded the formation of vuagnatite.

The validity of these discussions are to be confirmed after the synthesis of vuagnatite and configuration of its stability range. The authors believe that vuagnatite is not so rare but rather common mineral in altered ultrabasic to basic rocks and their schistose derivatives. Anyway this will be explained by synthetic works in the system CaO–Al_2O_3–SiO_2–H_2O under lower temperature and higher pressure condition, which may require prolonged treatment of prepared mixtures of desired composition.

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