

Baghdadite from the Akagane Mine, Iwate Prefecture, Japan

Satoshi Matsubara and Ritsuro Miyawaki

Department of Geology, National Science Museum, 3–23–1
Hyakunincho, Shinjuku-ku, Tokyo, 169–0073 Japan

Abstract Baghdadite from the Akagane mine, Iwate Prefecture, is found as minute accicular crystal groups in garnet-vesuvianite skarn. This is the second occurrence of this mineral in the world. The representative chemical analysis by EPMA gave SiO_2 28.82, TiO_2 0.98, ZrO_2 27.80, CaO 41.71, total 99.31 wt.%, yielding the empirical formula $\text{Ca}_{3.07}(\text{Zr}_{0.93}\text{Ti}_{0.05})_{\Sigma 0.98}\text{Si}_{1.98}\text{O}_9$ on the basis of $\text{O}=9$. The X-ray powder diffraction data by a Gandolfi camera are indexed on monoclinic cell with $a=10.37$ (2), $b=10.19$ (2), $c=7.35$ (1) Å, $\beta=91.05$ (5)°.

Key words : baghdadite, perovskite, Akagane mine, skarn

Introduction

Baghdadite is a calcium zirconium silicate of cuspidine group, $\text{Ca}_3\text{Zr}[\text{O}_2|\text{Si}_2\text{O}_7]$, and uniquely reported from Dupezeh mountain, near Hero Town, Qala-Dizeh region, Iraq. It was associated with åkermanite, perovskite, grossular, schorlomite, Zr-schorlomite, monticellite, wollastonite, fassaite and foshagite (Al-Hermezi *et al.*, 1986). Baghdadite is considered as a product by a reaction between wollastonite and calcite in country rock and zirconia in the intrusive igneous liquid under high-temperature condition.

During mineralogical survey for the material from the Sakae ore deposit of the Akagane mine, the authors have recognized colorless accicular mineral in garnet-vesuvianite skarn. The X-ray and chemical studies have proved it to be baghdadite as the second occurrence in the world.

Occurrence

The Akagane mine is located at about 18 km E of Mizusawa station, Tohoku Line, JR Railway Co. In the Akagane mine area Carboniferous pyroclastic and sedimentary rocks (greenstone and limestone) are cut by igneous intrusions (quartz porphyry, porphyrite, gabbro, granite and granodiorite). The ore body and skarn of the Sakae ore deposit are developed at limestone along the contact zone of gabbro (Aisawa, 1966). At Sakae ore deposit such high-temperature type skarn minerals as tilleyite, foshagite and bicchulite have been found (Bunno *et al.*, 1975; Nambu *et al.*,

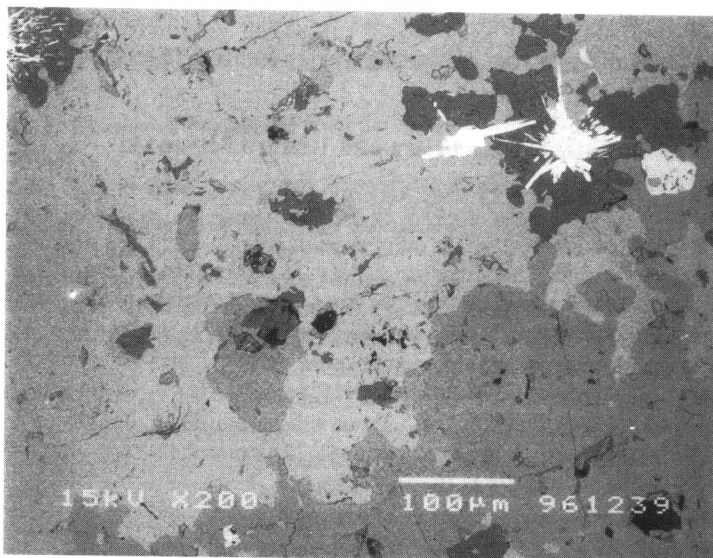


Fig. 1. Back-scattered electron image of the assemblage of baghdadite (bright), perovskite (light gray), garnet (gray), vesuvianite (dark gray), and wollastonite and/or calcite (dark).

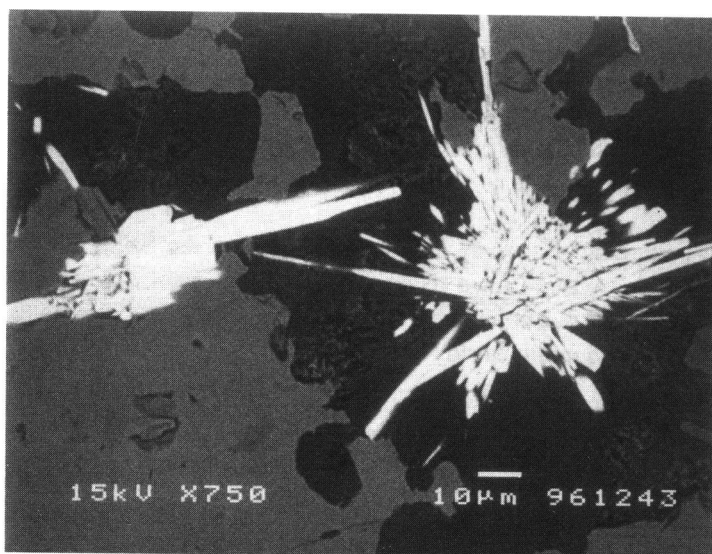


Fig. 2. Back-scattered electron image of accicular crystal groups of baghdadite (bright) in association with garnet (gray), and wollastonite and/or calcite (dark).

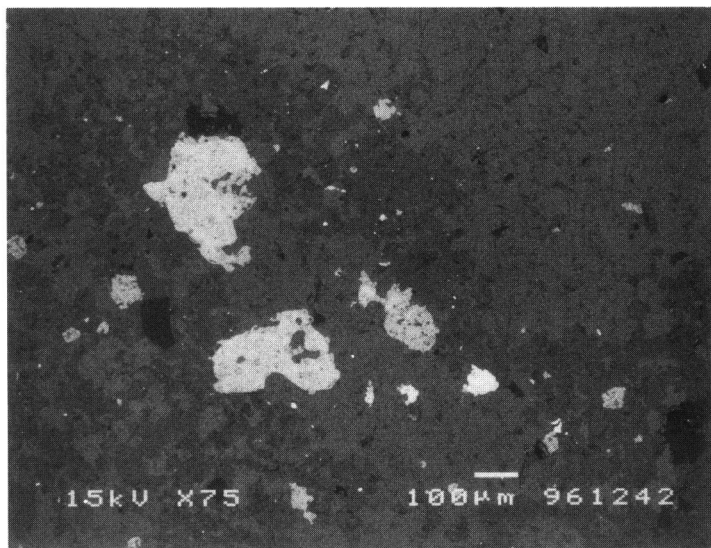


Fig. 3. Back-scattered electron image of anhedra grains of perovskite (light gray) in association with vesuvianite, garnet and baghdadite (bright: very minute aggregates).

1975). The studied skarn is yellowish green massive, and includes blackish brown granular garnets under 10 mm in diameter. The granular garnet is rich in Ti and sometimes has the component of schorlomite. The massive part is composed of anhedra grossular, vesuvianite, wollastonite, and calcite with accessory perovskite, silician sulfatite apatite, and baghdadite (Fig. 1). Baghdadite occurs as spotted aggregates of acicular to minute prismatic crystals under 0.1 mm in length (Fig. 2). Under the binocular the aggregates is feebly visible as colorless spots. Perovskite is found near by baghdadite as anhedra grains and the size is under 0.5 mm (Fig. 3). No ore minerals such as chalcopyrite, pyrrhotite and magnetite are observed in the studied material.

Chemical Composition

Chemical analyses were made using Link Systems energy dispersive X-ray spectrometer (QX-2000) for Si, Ti, Zr, Al, Fe, Mg, Mn, Ca, K, Na, P and S. The contents of Al, Fe, Mg, Mn, K, Na, P and S in baghdadite were under the detected limit. Standard materials and detailed analytical procedure have been reported by Yokoyama *et al.* (1993). In Table 1 the figures of the representative analysis of baghdadite from the Akagane mine is compared with that from Iraq (Al-Hermezi *et al.*, 1986). The empirical formula is $\text{Ca}_{3.07}(\text{Zr}_{0.93}\text{Ti}_{0.05})_{\Sigma 0.98}\text{Si}_{1.98}\text{O}_9$ on the basis of O=9. The range of Zr/(Zr+Ti) varies 0.98 to 0.88. The representative chemical compositions of the associ-

Table 1. Chemical analyses for baghdadite from the Akagane mine and Iraq. 1: representative analysis of baghdadites from the Akagane mine. 2: atomic number of No. 1 on the basis of O=9. 3: average analysis of baghdadite from Iraq (Al-Hermezi *et al.*, 1986). 4: atomic number of No. 3 on the basis of O=9.

Wt.%	1	2	3	4
SiO ₂	28.82	1.98	29.26	1.98
ZrO ₂	27.80	0.93	27.00	0.89
TiO ₂	0.98	0.05	2.11	0.11
Fe ₂ O ₃ *	n.d.		0.11	0.01
Al ₂ O ₃	n.d.		0.03	0
MgO	n.d.		0.05	0
CaO	41.71	3.07	41.44	3.01
Na ₂ O	n.d.		0.02	0
Total	99.31		100.02	

*: total iron, n.d.: not detected

Table 2. Chemical analyses of grossular, schorlomite, vesuvianite, perovskite and apatite from the Akagane mine.

Wt.%	grossular	schoromite	vesuvianite	perovskite	apatite
SiO ₂	35.72	27.58	34.80	n.d.	11.50
ZrO ₂	n.d.	0.67	n.d.	n.d.	n.d.
TiO ₂	2.08	13.68	0.73	58.98	n.d.
Fe ₂ O ₃ *	13.97	17.60	4.81	n.d.	n.d.
Al ₂ O ₃	11.52	6.65	18.18	n.d.	n.d.
MgO	n.d.	0.36	0.98	n.d.	n.d.
CaO	36.32	33.08	36.67	40.42	55.07
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	14.41
SO ₃	n.d.	n.d.	n.d.	n.d.	13.98
Total	99.61	99.62	96.17	99.40	94.96

*: total iron, n.d.: not detected

ated minerals such as grossular, schorlomite, vesuvianite, perovskite and apatite are given in Table 2.

X-ray Study

The X-ray powder diffraction data were obtained by a Gandolfi camera (diameter=114.6 mm) using Cu/Ni radiation. This is a mixture of the diffraction patterns of grossular and baghdadite with subordinate vesuvianite as given in Table 3, in which those of the original baghdadite were compared. The calculated unit cell parameters

Table 3. X-ray powder diffraction data for baghdadite. 1: baghdadite from the Akagane mine. Diffraction peaks with indices are for baghdadite and those with symbols at remarks column are enhanced due to the admixed garnet (G) and vesuvianite (V). Diffraction peaks without indices are for garnet and vesuvianite. 2: baghdadite from Iraq (Al-Hermezi *et al.*, 1986.).

1					2		
h k l	d _{calc.}	d _{obs.}	I	remarks	h k l	d	I
					1 1 0	7.30	45
					0 1 1	5.94	5
					1 1 $\bar{1}$	5.21	5
					0 2 1	4.20	10
					1 2 1	3.88	10
					0 1 2	3.46	5
					2 2 $\bar{1}$	3.29	5
1 3 0	3.23	3.23	30		1 3 0	3.23	80
2 0 $\bar{2}$	3.02	3.02	60		2 0 $\bar{2}$	3.04	75
2 0 2	2.97	2.97	90	G+V	2 0 2	2.98	85
					2 1 $\bar{2}$	2.90	5
1 2 $\bar{2}$	2.88	2.87	50		3 2 0, 2 1 2	2.88	70
3 2 0	2.86						
2 3 0	2.84						
		2.78	20	V			
		2.66	100	G			
		2.55	30	G			
1 3 $\bar{2}$	2.43	2.44	60	G	0 3 2	2.50	20
		2.34	40	G	1 3 $\bar{2}$, 3 1 2, } 3 3 0, 1 3 2 }	2.43	35
					2 4 0, 3 2 $\bar{2}$	2.29	10
					3 2 2	2.25	10
					4 2 1, 2 4 $\bar{1}$	2.20	5
		2.18	60	G			
2 2 $\bar{3}$	2.04	2.04	20		2 1 0, 3 3 $\bar{2}$	2.04	5
5 1 0, 3 3 $\bar{2}$	2.03	2.03	20		3 3 2	2.02	15
4 3 $\bar{1}$	1.992	1.993	15				
		1.937	70	G	1 5 0, 3 1 $\bar{3}$	1.987	10
					2 5 0	1.895	5
0 0 4	1.837	1.835	50		0 0 4	1.842	30
					4 3 $\bar{2}$	1.819	15
0 1 4	1.810	1.811	10				
3 4 $\bar{2}$	1.799	1.809	15				

Table 3. (Continued).

1					2		
h k l	d _{calc.}	d _{obs.}	I	remarks	h k l	d	I
					4 3 2	1.795	25
0 5 2	1.782	1.782	15		0 5 2, 0 3 0, } 5 1 2	1.778	5
2 0 4	1.722	1.722	25	G	5 2 $\bar{2}$	1.724	30
1 2 4	1.700	1.701	15		5 3 2	1.702	40
1 6 0	1.676	1.675	10			1.6765	8
		1.655	45	G			
		1.595	70	G		1.6070	5
						1.5945	5
						1.5617	8
						1.5502	8
1 6 $\bar{2}$	1.527	1.526	15			1.5380	8
3 6 0	1.524						
4 0 $\bar{4}$	1.512	1.513	15				
		1.493	40	G		1.4966	5
1 4 $\bar{4}$	1.478	1.478	13				
		1.469	15	G			
		1.433	13	G		1.4591	5
		1.410	10	G		1.4430	5
5 2 $\bar{4}$	1.339	1.341	35			1.3485	8
		1.335	50	G		1.3367	8
		1.303	30	G		1.3227	8
		1.272	25	G			

for the present material with refer to the original result (Al-Hermezi *et al.*, 1986) are $a=10.37$ (2), $b=10.19$ (2), $c=7.35$ (1) Å, $\beta=91.05$ (5)°, $V=776.5$ Å³. These are very close to those from Iraq, $a=10.42$ (2), $b=10.16$ (2), $c=7.36$ (1) Å, $\beta=91.1$ °, $V=779.0$ Å³ (Al-Hermezi *et al.*, 1986), and to those of synthetic material, $a=10.361$, $b=10.152$, $c=7.379$ Å, $\beta=90.72$ °, $V=776.1$ Å³ (ICDD 39-195).

Discussion

In skarn and metamorphosed crystalline limestone and/or dolomite from Japan Ca–Ti–Zr minerals are rather rare. Baghdadite and related minerals are plotted on Ca–Ti–Zr–Si diagram (Fig. 4). Zirconolite and baddeleyite assemblage without silicate minerals is known in dolomitic marble from the Neichi mine, Iwate Prefecture (Kato & Matsubara, 1991). Such oxides as calzirtite, baddeleyite, and perovskite, and

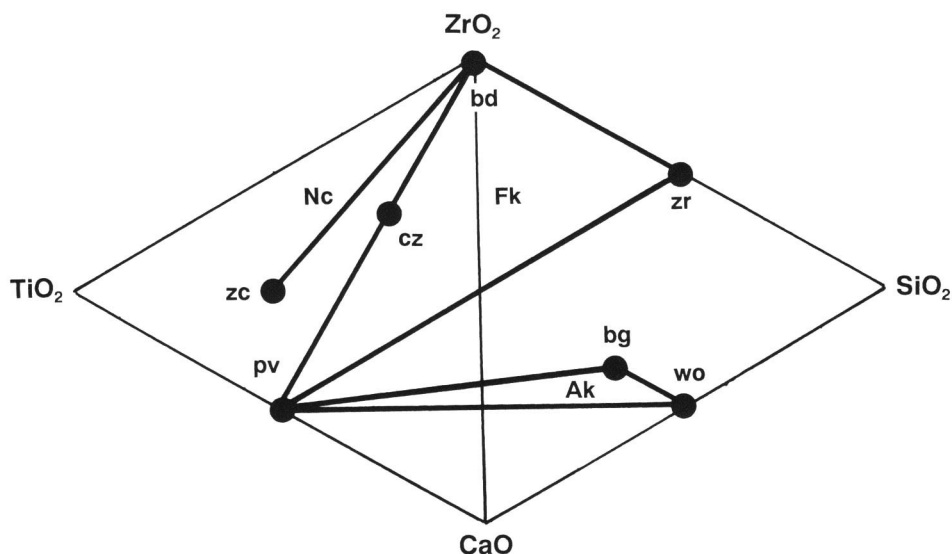


Fig. 4. Ca-Ti-Zr-Si diagram. Mineral symbols: bg (baghdadite); $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, pv (perovskite); CaTiO_3 , zr (zircon); ZrSiO_4 , bd (baddeleyite); ZrO_2 , cz (calzirtite); $\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}$, zc (zirconolite); $\text{CaZrTi}_2\text{O}_7$, wo (wollastonite); CaSiO_3 . Locality symbols: Nc (the Neichi mine), Fk (Fuka), Ak (the Akagane mine). Mineral assemblages are indicated by heavy solid lines.

silicates as zircon and zirconian titanian garnet have been reported in garnet-vesuvianite skarn from Fuka, Okayama Prefecture (Henmi *et al.*, 1996). The present baghdadite and perovskite assemblage is characterized by more Zr-poor and Ca-rich condition than the above two localities. The assemblage is considered to form by reaction between limestone and liquid from igneous rock under the following equation: $5\text{CaCO}_3 + 2\text{SiO}_2 + 2\text{TiO}_2 + \text{ZrO}_2 \rightarrow \text{Ca}_3\text{ZrSi}_2\text{O}_9 + 2\text{CaTiO}_3 + 5\text{CO}_2$.

Acknowledgements

We thank to Mr. O. Murakami, Izawa Town, Iwate Prefecture, and Mr. Y. Suzuki, Hitachi City, Ibaragi Prefecture, for their providing the studied materials, and also to Mrs. M. Shigeoka for her preparing the polished thin sections.

References

- Aisawa, K., 1966. Geology and mineralization of the Akagane mine. *Mining Geol.*, **16**: 124–131. (In Japanese.)
- Al-Hermezi, H. M., D. McKie & A. J. Hall, 1986. Baghdadite, a new calcium zirconium silicate mineral from Iraq. *Mineralogical Magazine*, **50**: 119–123.
- Bunno, M., H. Shimazaki, K. Sato & M. Aoki, 1975. The occurrence of bicchulite and its associated

- minerals from the Akagane mine, Iwate Prefecture. *Abst. Mineral. Soc. Japan, 1975 Annual Meeting*, 19. (In Japanese.)
- Henmi, C., I. Kusachi, & K. Henmi, 1996. Zirconium minerals and zirconian garnet from Fuka, Okayama Prefecture, Japan. *Mineralogical Journal*, **18**: 54–59.
- Kato, A. & S. Matsubara, 1991. Geikielite, baddeleyite and zirconolite in dolomite marble from the Neichi mine, Miyako City, Iwate Prefecture, Japan. *Bull. Natn. Sci. Mus., Tokyo*, Ser. C, **17**: 11–20.
- Nambu, M., K. Tanida, T. Kitamura & S. Oikawa, 1975. Vesuvianite-foshagite-bicchulite-garnet-wollastonite-calcite skarn from Sakae ore deposit of the Akagane mine. *Abst. Mineral. Soc. Japan, 1975 Annual Meeting*, 20. (In Japanese.)
- Yokoyama, K., S. Matsubara, Y. Saito, T. Tiba & A. Kato, 1993. Analyses of natural minerals by energy-dispersive spectrometer. *Bull. Natn. Sci. Mus. Tokyo*, Ser. C, **19**: 115–126.