

## Baghdadite, a new calcium zirconium silicate mineral from Iraq

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**ABSTRACT.** Baghdadite, a new calcium zirconium silicate mineral has been found in melilite skarn in contact with banded diorite, from the Qala-Dizeh region, NE Iraq. Electron microprobe analysis yielded: SiO<sub>2</sub> = 29.26, ZrO<sub>2</sub> = 27.00, TiO<sub>2</sub> = 2.11, Fe<sub>2</sub>O<sub>3</sub> = 0.11, Al<sub>2</sub>O<sub>3</sub> = 0.03, MgO = 0.05, CaO = 41.44, Na<sub>2</sub>O = 0.02, sum = 100.02 wt. %. The mineral contains about 0.16% HfO<sub>2</sub>. This analysis calculates to Ca<sub>3.00</sub>(Zr<sub>0.89</sub>Ti<sub>0.11</sub>)(Si<sub>1.98</sub>Fe<sub>0.01</sub>)O<sub>9</sub> which leads to the ideal formula Ca<sub>3</sub>Zr[O<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>]. X-ray single crystal study showed it to be monoclinic with space group *P2<sub>1</sub>/a*. The unit cell dimensions are: *a* = 10.42(2), *b* = 10.16(2), *c* = 7.36(1) Å, β = 91.1°, *Z* = 4 and cell volume = 779.04 Å<sup>3</sup>. The seven strongest lines in the powder diffraction pattern are (*d*, *l*, *hkl*): 7.30 (45)(110), 3.23 (80)(130), 3.04 (75)(202), 2.98 (85)(202), 2.88 (70)(320,212), 2.84 (100)(230), 1.702 (40)(522). It is colourless, lustre vitreous, no cleavage and VHN<sub>50</sub> = 725–783 kg mm<sup>-2</sup> with *H* ~ 6. Calculated density = 3.48 g cm<sup>-3</sup> which is very close to 3.46 measured density of a synthetic Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub>. It is optically biaxial, positive, 2*V* ~ 72°, dispersion indiscernible. The cathodoluminescence colour is dull grey with a greenish tint. Refractive indices: α = 1.652, β = 1.658, γ = 1.670. The crystal habit is stumpy prismatic and a contact twin with *b* as twinning axis is observed. Optic orientation: α = *c*, β//*b*, γ = *a*.

**KEYWORDS:** baghdadite, new mineral, Qala-Dizeh region, Iraq.

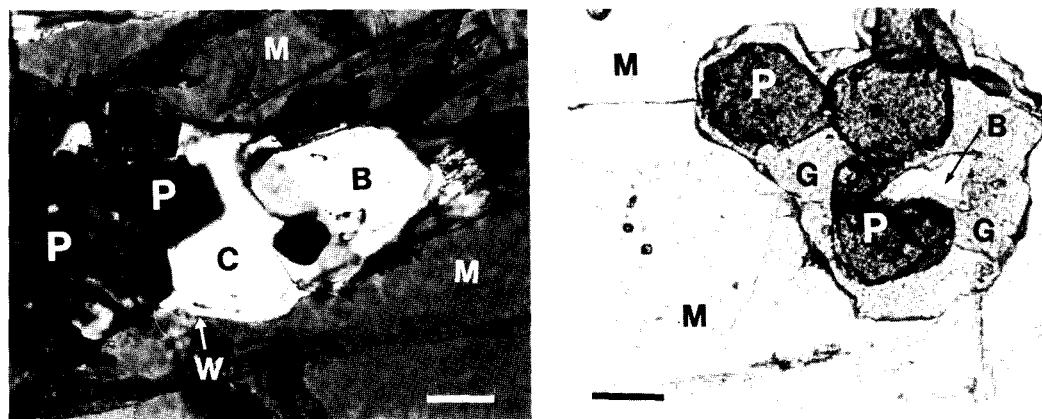
**BAGHDADITE** occurs in the Qandil Group of metamorphic rocks at Dupezeh mountain, near Hero Town, Qala-Dizeh region, NE Iraq. The occurrence is 420 m W. 44° S. of Dupezeh mountain summit (2314 m) and 1.4 km from the Iraq-Iran border. This occurrence is 1.0 km E. 13° S. of the iraqite type locality reported by Livingstone *et al.* (1976) and 230 m N. 22° E. of the qandilite type locality (Al-Hermezi, 1985). In this area the Qandil Group rocks are xenoliths of Cretaceous calcareous sediments engulfed by huge Eocene dioritic and gabbroic intrusions cut by a few small bodies of Oligocene syenite and granite. The xenoliths are preserved as long belts forming roof pendants which run parallel to the strike of the country rocks. The lithology of the xenoliths is dominated

by calc-silicate marbles and hornfelses with subordinate magnesian skarns, such as forsterite hornfels and marble, in addition to brucite marble, variety pentacite. None of the xenoliths shows relics of unmetamorphosed sediments and the grade of metamorphism lies within that of the pyroxene hornfels facies.

Baghdadite is named after Baghdad, the capital of Iraq. The mineral and the name were accepted, prior to the publication, by the Commission on New Minerals and Mineral Names, IMA (1982–75).

*Nature of occurrence.* Baghdadite is found in a melilite skarn in contact with banded diorite, composed chiefly of andesine and kaersutite with ubiquitous titanite, ilmenite and titaniferous magnetite. The melilite skarn is grey, very hard, massive, and coarsely crystalline and is cut by randomly distributed white-coloured veinlets (< 1 mm in width) of foshagite and a few small lenticular patches of monticellite and wollastonite surrounded by a xonotlite rim. The maximum grain size of melilite reaches 5 × 10 mm and it is impregnated with brownish-coloured, euhedral perovskite grains. The modal analysis showed the mineral assemblage of the melilite skarn to be composed of 90% melilite (G<sub>11</sub>Ak<sub>89</sub>), 5% perovskite, 1.5% garnets (grossular, schorlomite and Zr-schorlomite), and in addition monticellite, wollastonite, fassaite and foshagite with accessory phlogopite, green chlorospinel, cuspidine, baddeleyite, baghdadite, pyrrhotite, djerfisherite, and valleriite. The optical identification of all these minerals is supported by electron microprobe analyses and X-ray powder diffraction studies.

The baghdadite host rock seems to represent a complex metamorphic history in which titanium and to a lesser extent zirconium metasomatism have been superimposed on a high-temperature thermal metamorphism. In the late stages of thermal metamorphism, the rock was subjected to successive waves of hydrothermal alteration. As a result of this some of the melilite altered to



FIGS. 1 and 2. FIG. 1. (*left*). A twinned crystal of baghdadite (B) associated with calcite (C), perovskite (P), wollastonite (W), melilite (M) and containing minute bleb-like inclusions of baddeleyite and a large dark euhedral inclusion of perovskite. Crossed polars transmitted-light. FIG. 2 (*right*). Dorsal fin shaped baghdadite (B) sandwiched between perovskite (P) and garnet of Zr-schorlomite variety (G). Garnet occurs as a reaction rim around perovskite. A few drop-like perovskite inclusions are embedded in the melilite groundmass (M). Plane polarized transmitted light. Scale bars = 100  $\mu\text{m}$ .

monticellite and wollastonite giving a graphic texture. Furthermore some of the pyrrhotite and chlorospinel were altered to djerfisherite and valleriite respectively and in addition foshagite was precipitated in small veins.

Baghdadite is extremely scarce; only four grains were noted in a polished thin section with an area of about 9  $\text{cm}^2$ . One crystal was observed in thin section to be twinned so as to give a square cross section and it was closely associated with perovskite, calcite, wollastonite, melilite and contained minute inclusions of possible baddeleyite (fig. 1). One of the grains is triangular (dorsal fin) in shape and is enclosed partly by perovskite and zirconium schorlomite (fig. 2). The other two grains showed rectangular cross section and are contiguous either to calcite, wollastonite, baddeleyite and melilite or to perovskite and melilite. The few single crystals which we have managed to separate from the rock have a stumpy prismatic habit except for one which was obviously twinned. The occasional twins appear to be contact twins with common *b*-axis. The grain size of baghdadite in thin section and in separated grains does not exceed 250  $\mu\text{m}$  in length.

*Physical, chemical and optical properties:* Baghdadite is colourless, with vitreous lustre. It is devoid of cleavage and displays a tendency to conchoidal fracture. Measured  $\text{VHN}_{50}$  on four grains gave: 725–783,  $\text{mean}_8 = 750$  and in terms of the Mohs' hardness number approximately 6. The small number of small crystals separated gave too small a bulk for accurate density determination, but the density of the synthetic analogue  $\text{Ca}_3\text{ZrSi}_2\text{O}_9$  of

baghdadite has been determined by Kordyuk and Gul'ko (1962) by pycnometry as 3.46 which is in good agreement with the density of 3.48 calculated for baghdadite from the average chemical analysis shown in Table I and the unit-cell constants shown in Table II on the assumption that the unit-cell contains 36 oxygen atoms. The mineral is slowly soluble in concentrated HCl and insoluble in concentrated  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$ . In transmitted polarized light baghdadite is transparent, colourless, non-pleochroic and non-dispersive. The optic axial angle was determined on the universal stage as  $2V \sim 72^\circ$ . The refractive indices were determined as  $\alpha = 1.652$ ,  $\beta = 1.658$ ,  $\gamma = 1.670$ . It is biaxial positive with maximum birefringence

Table 1. Wavelength-dispersive electron microprobe analyses of baghdadite

	Crystal 1		Crystal 2		Crystal 3		Crystal 4		Average
	core	rim	core	rim	core	rim	core	rim	
$\text{SiO}_2$	29.42	29.09	29.32	29.20	29.30	29.21	29.26		29.26
$\text{ZrO}_2$	26.36	26.42	26.69	26.89	27.83	27.78	27.00		27.00
$\text{TiO}_2$	2.03	2.49	2.50	2.38	1.74	1.52	2.11		2.11
$\text{Fe}_2\text{O}_3$	0.08	0.14	0.10	0.16	0.12	0.07	0.11		0.11
$\text{Al}_2\text{O}_3$	0.04	0.03	0.03	0.03	0.03	0.03	0.03		0.03
MgO	0.07	0.04	0.04	0.04	0.04	0.04	0.05		0.05
CaO	41.45	41.15	41.51	41.51	41.53	41.46	41.44		41.44
$\text{Na}_2\text{O}$	0.02	0.01	0.02	0.02	0.02	0.02	0.02		0.02
Total	99.47	99.37	100.21	100.23	100.61	100.13	100.02		100.02

$\gamma - \alpha = 0.018$  and the fast vibration direction lies almost along the trace of the twin plane. The cathodoluminescence colour observed using a Technosyn cold cathode luminescence model 8200 Mk. II operated at 15 kV and 600  $\mu\text{A}$  is dull grey with greenish tint. Associated wollastonite gives a brighter blue colour whereas associated calcite gives a very weak dull red colour.

Table 11.

Unit-cell constants of minerals of the wöhlerite-cuspidine group

	1	2	3	4	5	6	7
a Å.	10.83	10.95	10.95	10.83	11.39	10.80	10.42
b Å.	10.41	10.31	10.01	10.42	10.12	10.26	10.16
c Å.	7.53	7.29	7.19	7.38	7.27	7.26	7.36
$\alpha$	90°	90.32°	90°	90°	80.36°	90°	90°
$\beta$	110.07°	109.03°	110.30°	109.67°	88.65°	109.05°	91.1°
$\gamma$	90°	90.08°	90°	90°	111.91°	90°	90°
$V \text{ Å}^3$	797.4	778.0	739.1	784.2	763.1	760.4	779.0

- Cuspidine. Mt. Vesuvius, Italy. Smirnova *et al.* (1955).
- Hiortdahlite. Kipawa River, Villedieu Township, Quebec. Aarden and Gittins (1974).
- Låvenite. Isle of Låven, Langesundsfjord, Norway. Gossner and Kraus (1934).
- Niocalite. Oka, Quebec. Nickel *et al.* (1958).
- Rosenbuschite. Langesundsfjord, Norway. Peacock (1937). Unit-cell re-oriented to make a,b,c consistent. It remains surprising that  $\gamma$  is so large.
- Wöhlerite. Langesundsfjord, Norway. Gossner and Kraus (1934).
- Baghdadite. Dupezeh mountain, Horo Town, Qala Dizah region, Ne Iraq. Present study.

**X-ray crystallography.** The unit-cell dimensions of baghdadite were determined initially by measurement of  $0kl$ ,  $1kl$ , and  $2kl$  Weissenberg photographs; and  $h0l$ ,  $h1l$ ,  $hk0$ , and  $hk1$  precession photographs of the same crystal without changing the setting of the crystal on its arcs by more than about  $1^\circ$  on transfer from the Weissenberg camera to the precession camera. Measurement of the precession photographs within a Supper Precession Measurer yielded the angle  $\beta^* = 88.92^\circ$  and  $\gamma^* = 90^\circ$ . The photographic determination yielded the unit-cell constants  $a = 10.40 \pm 0.02$ ,  $b = 10.16 \pm 0.02$ ,  $c = 7.35 \pm 0.01$  Å,  $\beta = 91.1^\circ$ ,  $\alpha = \gamma = 90^\circ$ . The same crystal of baghdadite was then transferred to a Philips PW1100 4-circle automatic single crystal diffractometer which yielded a consistent set of unit-

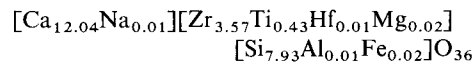
cell constants,  $a = 10.42$ ,  $b = 10.16$ ,  $c = 7.35$  Å,  $\beta = 91.1^\circ$ ,  $\alpha = \gamma = 90^\circ$ .

Systematic absence on the precession and Weissenberg photographs, confirmed by data collection on the PW1100, indicated that  $h0l$  reflections occur only for  $h = 2n$  and that  $0k0$  reflections occur only for  $k = 2n$ . The diffraction symbol of baghdadite is therefore  $2/mP2_1/a$  and the space group of baghdadite is uniquely determined as  $P2_1/a$ .

The X-ray powder diffraction pattern of baghdadite was recorded from single crystals mounted in a 114.6 mm diameter Gandolfi camera using Co-K $\alpha$  radiation ( $\lambda = 1.7902$  Å). Indexing of the pattern was achieved by comparison of the observed  $d$ -spacing with a list of sorted  $d$ -spacings calculated from unit-cell constants given above by a program of the Cambridge Crystallography Subroutine Library (Matthewman *et al.*, 1982) and comparison of the estimated intensities of powder lines with the single crystal intensity data collected on the 4-circle diffractometer taking multiplicity into account. The indexed powder pattern for  $d > 1.7$  Å is shown in Table III, and includes twenty-one additional lines of lower  $d$ -spacing, between 1.667 Å and 0.8998 Å which were recorded but not indexed.

**Chemical composition.** The composition of baghdadite was determined initially by twenty electron microprobe spot analysis (EDS), followed by six wavelength dispersive analyses on the microprobe from four available crystals and gave the result shown in Table I. In each of the wavelength dispersive analyses Nb, all the rare earths (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Cr, Y, Mn, K, F, and Cl were found to be below the limit of detection. One specimen was analysed for hafnium and the HfO<sub>2</sub> content was estimated as 0.16% by reference to a zircon of known hafnium content. It is clear from Table I that baghdadite crystals are quite homogeneous in composition.

It has not been possible, because of the scarcity of the mineral, to determine the density of baghdadite experimentally. But the density of the synthetic analogue Ca<sub>3</sub>ZrSi<sub>2</sub>O<sub>9</sub> has been determined by Kordyuk and Gul'ko (1962) as 3.46 g cm<sup>-3</sup>. Taking their density, the unit-cell volume calculated from the unit-cell constants given above as 779.04 Å<sup>3</sup> together with the average chemical composition shown in Table I, the unit-cell of baghdadite is found to contain 35.80 oxygen atoms, which may be regarded as a close approximation to a real content of 36 oxygen atoms. Normalized to 36 oxygen atoms the unit-cell contents of baghdadite are



which, neglecting minor elements, corresponds to a

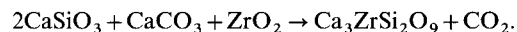
Table III. X-ray powder diffraction data for baghdadite

<i>hkl</i>	<i>d</i> <sub>calc.</sub>	<i>d</i> <sub>obs.</sub>	<i>I</i> <sub>est.</sub>	<i>hkl</i>	<i>d</i> <sub>calc.</sub>	<i>d</i> <sub>obs.</sub>	<i>I</i> <sub>est.</sub>
110	7.27	7.30	45	052, 530, 512	1.779–1.771	1.778	5
011	5.96	5.94	5	$\bar{5}22$	1.726	1.724	30
$\bar{1}11$	5.21	5.21	5	522	1.696	1.702	40
021	4.18	4.20	10			1.6765	8
121	3.87	3.88	10			1.6070	5
012	3.46	3.46	5			1.5945	5
$\bar{2}21$	3.28	3.29	5			1.5617	8
130	3.22	3.23	80			1.5502	8
$\bar{2}02$	3.03	3.04	75			1.5380	8
202	2.98	2.98	85			1.4946	5
$\bar{2}12$	2.91	2.90	5			1.4591	5
320, 212	2.87, 2.86	2.88	70			1.4430	5
230	2.84	2.84	100			1.3485	8
032	2.49	2.50	20			1.3367	8
$\bar{1}32, 312, 330, 132$	2.43, 2.42	2.43	35			1.3227	8
240, $\bar{3}22$	2.28	2.29	10			1.2373	8
322	2.24	2.25	10			1.1169	5
421, $\bar{2}41$	2.20, 2.19	2.20	5			1.0457	5
510, $\bar{3}32$	2.04	2.04	5			1.0096	5
332	2.01	2.02	15			0.9725	8
150, $\bar{3}13$	1.994, 1.983	1.987	10			0.9670	8
250	1.893	1.895	5			0.9096	10
004	1.840	1.842	30			0.9025	15
$\bar{4}32$	1.812	1.819	15			0.8998	15
432	1.789	1.795	25				

The measurements were made on photographs taken in a 114.16 mm Gandolfi camera with Co-K $\alpha$  radiation (1.7902Å).

composition close to  $\text{Ca}_{12}(\text{Zr}_{3.57}\text{Ti}_{0.43})\text{Si}_8\text{O}_{36}$ , that is to an idealized formula  $\text{Ca}_3\text{Zr}[\text{O}_2|\text{Si}_2\text{O}_7]$  with  $Z = 4$  and 11% substitution of  $\text{Ti}^{4+}$  for  $\text{Zr}^{4+}$ .

**Paragenesis.** The synthetic analogue of baghdadite  $\text{Ca}_3\text{ZrSi}_2\text{O}_9$  was prepared by Kordyuk and Gul'ko (1962) from the mixture of the following compounds: (a) larnite  $\text{Ca}_2\text{SiO}_4$ , wollastonite  $\text{CaSiO}_3$ , and baddeleyite  $\text{ZrO}_2$ ; and (b) rankinite  $\text{Ca}_3\text{Si}_2\text{O}_7$  and baddeleyite  $\text{ZrO}_2$ , at temperatures between 1400–1500 °C. Baghdadite is a product of high-temperature skarn formation and is considered to form by a reaction involving the pre-existing wollastonite and calcite in the country rock and zirconium evolved from the intrusive igneous liquid:



Larnite and rankinite have not been found in this paragenesis; they occur neither in the baghdadite host rock nor in any calc-silicate skarns in the study area. The absence of these minerals, which are characteristic of very high temperatures, is attributed to temperature deficiency rather than bulk composition of the country rocks. The evalu-

ated  $T$ - $P$  for the calc-silicate skarns in the Qandil Group metamorphic rock are  $T = 770$  °C and  $P = 512$  bars; this result is based on calcite-dolomite geothermometry in the brucite marble (pencatite variety). The presence of melilite (akermanite variety) in the innermost part of the skarns suggests that  $T = 790$  °C and  $P_f = 1$  kbar (Zharikov *et al.*, 1977).

**Discussion.** Baghdadite is evidently related crystallographically and chemically to the wöhlerite group of minerals, comprising cuspidine, lavenite, rosenbuschite, hiortdahlite, wöhlerite, and niocalite. Unit-cell dimensions of the monoclinic and triclinic members of the wöhlerite group are shown in Table II. It is immediately apparent that (1) except for rosenbuschite the departure from monoclinicity in unit-cell dimensions is slight, being less than 0.5° in  $\alpha$  and  $\gamma$ , (2) the unit-cell constants approximate to  $a \sim 10.9$ ,  $b \sim 10.3$ ,  $c \sim 7.3$  Å,  $\beta \sim 109^\circ$  and (3) the unit-cell volumes for 36 anions approximate to 775 Å<sup>3</sup>. The unit-cell volume at 779.04 Å<sup>3</sup> and the unit-cell edge dimensions of baghdadite are consistent with the extended wöhlerite group, but its  $\beta$  angle of 91.1° is exceptionally small.

Table IV.

Unit-cell contents of minerals of the wöhlerite-cuspidine group  
assuming 36 anions in the unit-cell

	1	2	3	4	5	6	7
Ca	14.84	8.11	2.04	13.11	6.83	7.86	12.04
Na	0.01	3.43	5.98	0.32	4.86	3.95	0.01
F	0.15	-	-	-	-	-	-
Y	-	0.48	-	-	-	-	-
TR	-	0.16	-	-	0.03	-	-
Zr	-	2.34	3.90	-	2.51	2.15	3.58
Nb	-	0.08	0.51	2.14	-	1.50	-
Ti	-	0.04	0.42	0.05	1.32	0.08	0.43
Fe	0.03	0.04	0.86	0.11	0.20	0.38	0.02
Mn	0.05	0.08	1.70	0.24	0.30	0.23	-
Mg	0.02	0.04	-	0.25	-	0.05	0.02
Al	-	0.04	-	-	-	-	-
Al	-	-	-	0.17	-	-	0.01
Si	8.32	8.26	8.02	7.79	8.03	8.21	7.93
O	27.18	29.87	32.11	34.44	31.28	32.81	36.00
OH	4.45	0.73	0.59	0.15	-	0.66	-
F	4.37	5.40	3.30	1.41	4.72	2.53	-

1. Cuspidine. Tyrnyauzskii, U.S.S.R. Skripchenko (1960).
2. Hjordahlite. Kipawa River, Villedieu Township, Quebec. Aarden and Gittins (1974).
3. Låvenite. Isle of Låven, Langesundsfjord, Norway. Gossner and Kraus (1934).
4. Niocalite. Oka, Quebec. Nickel *et al* (1958).
5. Rosenbuschite. Langesundsfjord, Norway. Peacock (1937).
6. Wöhlerite. Langesundsfjord, Norway. Gossner and Kraus (1934).
7. Baghdadite. Duppezeh Mountain, Hero Town, Qala Dizah region, NE Iraq. Present study.

The unit-cell contents of members of the wöhlerite group are given in Table IV. The general formula for the group is given by Aarden and Gittins (1974) as  $X_4[\text{Si}_2\text{O}_7](\text{O},\text{OH},\text{F})_2$  where  $X$  represents metallic cations and is exemplified by the simplest member, cuspidine  $\text{Ca}_4[\text{Si}_2\text{O}_7](\text{O},\text{OH},\text{F})_2$ . It can be seen in Table IV that the composition of the other members is not as simple as cuspidine, but they contain considerable amounts of other metallic cations replacing calcium. Therefore the general composition for the group can be written as  $(\text{Ca},\text{Na})_3(\text{Zr},\text{Nb},\text{Ti},\text{Fe},\text{Mn},\text{Mg})\text{Si}_2\text{O}_7(\text{O},\text{OH},\text{F})_2$ .

The ideal composition of baghdadite is  $\text{Ca}_3\text{Zr}[\text{O}_2|\text{Si}_2\text{O}_7]$  and is distinguished from the rest of the wöhlerite group by the absence of significant  $\text{F}^-$  and  $\text{OH}^-$  ions. Nevertheless two members of the Commission on New Minerals and Mineral Names suggested that the composition of baghdadite is closely related to the wöhlerite species.

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