Bazirite, BaZrSi₃O₉, a new mineral from Rockall Island, Inverness-shire, Scotland

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SUMMARY. Bazirite, BaZrSi₃O₉, is one of several late-stage interstitial minerals present in the aegirine-riebeckite granite of Rockall Island. Crystals are hexagonal, probably 6m2, colourless, chiefly as anhedral grains. Only forms noted {1010} and probably {1014}, cleavage {0001} and probably {1014}. 'Low' and 'high' titanium varieties with respective mean compositions: SiO₂ 39.71 %, ZrO₂ 26.38%, BaO 33.69%, TiO₂ 0.17%, SnO₂ 0.06% and SiO2 39.59%, ZrO2 26.12%, BaO 34.12%, TiO2 0.51%, SnO₂ 0.11%. Low and high refractive index types exist; uniaxial positive with $\omega = 1.6751 \pm 0.0003$. $\varepsilon =$ 1.6850 ± 0.0003 and $\omega = 1.6813 \pm 0.0003$, $\varepsilon = 1.691$ (deduced); probably due to differences in titanium content. Fluorescence (2537 Å), moderately strong, pale whitish blue. Space group almost certainly P6c2. Cell dimensions: low R.I. variety, $a = 6.7690 \pm 0.0005$ Å, $c = 10.020 \pm 0.001$ Å; high R.I. variety, $a = 6.7662 \pm 0.001$ 0.0005 Å, $c = 10.0158 \pm 0.0010$ Å. Strongest lines are 3.80 Å (100), 2.800 (100), 5.85 (35), 3.38 (35), Z = 2. $D_{calc} =$ 3.82. Related minerals, benitoite and pabstite.

Rockall Island (57° 36' N.; 13° 41' W.), an isolated pinnacle of Eocene aegirine-riebeckite granite, is situated in the North Atlantic approximately 294 km west of the St. Kilda Isles, Invernessshire. Despite problems of access, the island has been a focus of scientific interest since the first documented landing by Lieutenant Basil Hall, R.N., in 1810 (MacCulloch, 1814; Judd, 1897; Washington, 1914; Lacroix, 1921; Sabine, 1960; Hawkes et al., 1975). Lacroix's recognition of the hydrated sodium zirconium silicate, elpidite, in material obtained during the 1921 Pourquois Pas expedition is especially relevant in the context of this paper. Sabine (1960, p. 168) subsequently described a colourless accessory barium- and zirconium-bearing mineral in samples returned by the H.M.S. Vidal landing of 1955. The mineral was later isolated from granite specimens collected during the 1971 and 1972 R.F.A. Engadine expeditions and confirmed as a new species with composition BaZrSi₃O₉ (Hawkes et al., 1975). The partly mnemonic name bazirite originally proposed has been approved by the International Commission on New Minerals and Mineral Names.

Bazirite is associated with a variety of interstitial constituents, which on cut or freshly broken surfaces occur in irregular, buff-coloured patches up to 50 mm across. The patches commonly aggregate in the granite with up to seven occurring per cm², although a more usual density is one per cm². These field observations, along with modal data from thin sections, suggest that the interstitial minerals constitute between 1 and 5% of the rock by volume, with the bazirite accounting for perhaps 0.1% by volume. Preferential weathering generally reduces the patches to rusty voids.

Elpidite, the most abundant interstitial mineral, is accompanied in places by acmite, albite, bazirite, disordered α -cristobalite, leucophosphite, monazite, and quartz. Crushes of the whole rock have yielded additional accessory minerals: apatite, eucolite-eudialyte, magnetite, pyrochlore, xenotime (Sabine, 1960); also baryte and sphene.

Physical properties. Bazirite occurs as single or clustered, colourless anhedral grains and as subhedral or, more rarely, euhedral prismatic crystals with partially developed pyramidal terminations (fig. 1). Grains and crystals vary considerably in size up to about $0.25 \times 0.25 \times 0.65$ mm (S 57923, 57926, 57937*). The mineral contains numerous minute cavities and unidentified inclusions, the largest observed measuring, respectively, 0.001 × 0.008 mm and 0.001×0.002 mm. Fractures are common in all grains and crystals, most apparently relating to a strong basal parting and to a cleavage, which parallels the rarely developed pyramidal faces. Measurements of about 20° for the acute angle between these planes of fracture and between the basal parting and pyramidal faces indicate that if the axial ratio c/a 1.4803 obtained from the unit cell is used, the latter faces may be the form $\{10\overline{1}4\}$. A third plane of fracture may reflect a poorly developed prismatic cleavage. A mean interfacial angle of 60° for prismatic faces (which single crystal

* Numbers prefixed by S refer to specimens in the Petrographical Department's Collections, Institute of Geological Sciences.



FIG. I. A photomicrograph showing anhedral and subhedral crystals of bazirite (b) associated with quartz (q), acmite (a), and elpidite (e). A riebeckite crystal (r) forms one margin to this patch of interstitial minerals. (S 57926; plane polarized light; magnification × 110.)

X-ray studies show to be the form $\{10\overline{1}0\}$ was obtained from basal sections. Finally, since it has been shown that the X-ray patterns of bazirite and benitoite are similar, bazirite probably belongs to the same crystal class, $\overline{6m2}$.

The following optical properties were established (using microscopy, Abbé refractometer, and UV-source techniques) on thin sections and grains separated from crushes by means of methylene iodide (sp. gr. 3.4). Bazirite is uniaxial positive, length slow, with straight extinction and moderately low birefringence (0.010). Refractive index (Na_{D}) determinations indicate two sets of values: $\omega = 1.6751 \pm 0.0003$, $\varepsilon = 1.6850 \pm 0.0003$ and $\omega =$ 1.6813 ± 0.0003 , $\varepsilon = 1.691$ (deduced from the maximum birefringence colour). Sabine (1960) also recorded two similar sets of values, which seem now to reflect compositional differences. The mineral does not fluoresce under long-wave UV light (3650 Å), but shows moderately strong pale whitish blue fluorescence under short-wave UV (2537 Å). Strong bright-blue cathodoluminescence is observed under electron-beam bombardment.

Density and hardness determinations were not attempted because of the numerous cavities, inclusions, and fractures. The calculated density is 3.82 g/cm^3 .

Chemistry. Nine grains of bazirite in one polished thin section (S 57923) were analysed by means of a Cambridge Instruments 'Geoscan' electron microprobe. An accelerating voltage of 20 kV, a specimen current of 1×10^{-7} amps, and wollastonite (Si), baryte (Ba), and Ti, Zr, and Sn metals were used as standards throughout. Raw data were corrected using the methods described by Sweatman and Long (1969) and the computer program of Mason, Frost, and Reed (1969).

Each grain was analysed several times. Some may possess slight chemical inhomogeneity but this could not definitely be proved. Table I shows the mean of the determinations for each grain and the calculated molecular percentages of Ti, Zr, and Sn. The latter figures indicate limited substitution of Ti for Zr with an approximately bimodal distribution. Such a distribution could account for the two sets of refractive index and cell-size values. The means of the compositions of the 'high' and 'low' titanium types are given in Table II, from which ionic formulae and densities have been calculated.

The new analyses of bazirite all differ from the previously published analysis (Hawkes *et al.*, 1975, p. 28) in having a higher Zr content. This is thought to be due to an erroneously high background measurement in the earlier work, which produced a low Zr value, and hence a low total. The K reported in the previous analysis is spurious, probably having come from surrounding feldspar or leucophosphite grains. Hafnium could not be detected in any of the grains.

X-ray crystallography. An X-ray powder pattern (X 7610*) obtained from three bazirite crystals (R.I. ω 1.6751, ε 1.6850) using an 11.46 cm diameter Gandolfi camera, is similar to that of benitoite, BaTiSi₃O₉, from San Benito County, California (X 7612). The bazirite spacings, however, are slightly larger due to the larger ionic radius of Zr⁴⁺ (0.79 Å)

^{*} Numbers prefixed by X refer to X-ray films in the Petrographical Department's Collections, Institute of Geological Sciences.

		TABLE	E I. Ele	ctron mi	croprob	e analys	es of ba	zirite		com r	positio atios o	ns and ionic f bazirite
		2	3	4	5	6	7	8	9	'Low	' Ti type	'Hìgh' Ti type
SiO ₂	40.56	39.70	38.76	40.01	39.53	39.82	39.58	39.57	39.37	39.7	71±0·66	39 [.] 59±0·18
TiO ₂	0.19	0.13	0.15	0.24	0.16	0.68	0.43	0.47	0.42	0.	17±0.05	0·51±0·11
ZrO ₂	26.27	25.94	26.50	26.62	26.57	26.06	26.09	26 [.] 14	26.17	26.	38 ± 0.28	26·12±0·05
SnO ₂	0.06	0.06	0.02	0.04	0.02	0.08	0·11	0.15	0.11	0.0	06∓0.01	0·11±0·02
BaO	33.94	33.12	33.55	33.60	34.53	33.88	34.03	34.09	34.49	33.6	69±0.41	34 [.] 12±0.26
Sum	101.02	98.97	98.98	100.21	100.56	100.52	100.24	100.39	100.01	100.0	01	100.45
Molecu	lar % of te	travalent o	cations:							Num	ber of io	ns on a basis of
Ti	1.10	0.71	0.69	1.37	0.92	3.85	2.48	2·7 0	2.69	9 ox	ygen:	
Zr	<u>9</u> 8·70	99.11	99.17	98.50	98.85	95.92	97.20	96.94	96.99	Ti	0.010	0.029
Sn	0.50	0.19	0.14	0.14	0.53	0.53	0.35	0.32	0.35	Zr	0.976	0.964
Analyses 1 to 5, 'low' Ti grains)									Sn	0.001	0.003	
Analyses 6 to 9, 'high' Ti grains S 57923											0.987	0.992
NW. fa	ce of Rock	all Island.	13.7 m a	hove sea-l	evel and 5	·8 m from	E. face.			Si	3.013	2.997
			- , u		, ,					Ba	I.005	1.015

compared with that of Ti^{4+} (0.68 Å), and there are also differences in the intensities of many of the lines. Indexed powder data and cell dimensions for both minerals are presented in Table III and are in agreement with published data for synthetic BaZrSi₃O₉ (Masse and Durif, 1973) and for benitoite (Robbins and Levin, 1961, p. 130). The line intensities were estimated visually by comparison with an intensity scale, but values quoted for the bazirite from reflections from planes with low multiplicity factors (such as 002 and 004) are less reliable because the Gandolfi device did not completely eliminate spottiness. Cell dimensions for both bazirite and benitoite were calculated from selected high-angle spacings and refined by plotting the values obtained against the Nelson and Riley function $(\cos^2\theta/\sin\theta + \cos^2\theta/\theta)/2$ and extrapolating to $\theta = 90^{\circ}$. A slight difference between the observed and calculated *d*-spacings is presumably due to specimen absorption. Slightly smaller cell dimensions $(a 6.7662 \pm 0.0005 \text{ Å}, c 10.0158 \pm 0.0010)$ Å) were obtained from a Gandolfi film (X 7671) of a single bazirite crystal with the higher R.I. ω 1.6813, ε 1.691. This X-ray data reinforces the chemical evidence that observed differences in refractive index are probably due to limited replacement of Zr by Ti.

A Laue photograph confirmed the hexagonal symmetry of bazirite, while the space group was deduced from Weissenberg and precession photographs to be $P\overline{6}c2$, the same as that of benitoite.

Related minerals and genesis. Bazirite becomes the third natural member of a group of barium silicates with the Si₃O₉ ring structure (Zachariasen, 1930) in which Ti⁴⁺, Sn⁴⁺, and Zr⁴⁺ show varying degrees of substitution, and which probably all belong to the rare crystal class $\overline{6}m_2$. The titanium member, benitoite, BaTiSi₃O₉, was the first to be discovered (Louderback, 1907; 1909) and it has since been made synthetically with an upper stability limit reported as $965^{\circ} \pm 10^{\circ}$ C at 5000 lb. in.⁻² (345 bars) water-vapour pressure (Rase and Roy, 1955). Titanian pabstite, $Ba(Sn_{0.77}Ti_{0.23})Si_3O_9$, the second member, was described by Gross et al. (1965), who also synthesized BaSnSi₃O₉, in a hydrothermal apparatus at 330 °C and saturated water-vapour pressure, and at 500 °C and 15000 lb. in.⁻² (1035 bars) water-vapour pressure. The zirconium member of the group, BaZrSi₃O₉, had been synthesized dry at 1250-1300 °C by Galkin and Chukhlantsev (1965) prior to the recognition of bazirite in 1971. In another experiment, Masse and Durif (1973) produced BaZrSi₃O₉ also under dry conditions at temperatures between 1000° and 1350 °C.

The similarity of the ionic radii of Ti^{4+} (0.68 Å) and Sn⁴⁺ (0.71 Å) suggests that a wide range of solid solution may be expected between benitoite and pabstite. However, other discoveries of bazirite will probably show (as in the present case) only limited substitution of Ti and/or Sn for Zr, because of the appreciably larger ionic radius of Zr⁴⁺(0.79 Å).

A summary of some of the properties of bazirite, benitoite, titanian pabstite, and $BaSnSi_3O_9$ are shown in Table IV.

In contrast to the experimental preparations by Galkin and Chukhlantsev (1965) and by Masse and Durif (1973), the bazirite of Rockall Island seems to have formed at low temperatures. The mineral is

II. Mean

| TABLE

TABLE III. Observed and calculated X-ray powder diffraction data for bazirite (1) and benitoite (2) obtained from films taken in 11.46 cm diameter cameras at room temperature (around 23 °C) with Cu-Ka radiation (λ Ka₁ = 1.54051 Å)

	I				2			-	-			7	
<i>I/I</i> 1	$d_{\rm obs}$	$d_{ m calc}$	hkl*	<i>I/I</i> 1	d _{obs}	d_{calc}	<i>I/I</i> 1	$d_{\rm obs}$	d_{calc}	hkl*	<i>I/I</i> 1	$d_{\rm obs}$	d _{calc}
35	5.85 Å	5.862 Å	001	18	5-74 Å	5.750 Å			(1·1015 Å	406	m	1.0766 Å	I-0771 Å
8	5.00	5.010	002	5	4.87	4.879	IO	I.100 A	1·1006	332		1.0786	1-0793
100	3.80	3-809	102	100	3.72	3.720	4	060-1	1.0903	218	m	1.0631	1.0637
35	3:38	3.384	0110	16	3.32	3.320	4	1.081	1.0817	422	4	1-0600	1-0607
16	3.20	3-207	111	16	3.14	3.143	I	1-060	6190-1	504	7	1650.1	I -0403
30	2.93	160.2	200	25	2-873	2.875	r	1.050	§1.0545	308	ŝ	1.0284	1.0291
100	2-800	2-805	112	80	2.742	2.745		5CA 1	[1-0529	510	Ι	1.0320	1.0328
4	2.525	2.530	202	9	2-477	2:477	7	1-047	1.0474	326	7	1.0243	1.0245
12	2.498	2.505	004	12	2.438	2.439	r T	960.1	1.0304	512	m	6600-1	1-0104
7	2.376	2.377	113	I	2.319	2-323	n/	070.1	1.0287	334	4	1700·1	1-0078
5	2.301	2-303	104	12	2.245	2-246	7	1-014	1.0155	416)	-	90000	(o-9935
25	2.213	2-216	210	24	2-171	2.173	L	1.012	1.0132	424 }	4	0766.0	0-9927
9	2.160	2.163	211	12	2-119	2.121	4	1-005	1-0067	228	6	0.9824	0.9829
×	2.025	2.026	212	14	1-983	1-985	. I	166.0	0-9922	318	. I V	0.9686	0.9689
30	2.012	2.013	114	26	1-965	996.1	I	0.987	0-9877	01.0.10	Ι	0.9616	0-9620
18	1.952	1.954	300	16	1.915	L19-1	÷	9696.0	90/6-0	514	Ι	0-9507	0-9511
14	1.902	1.904	204	22	1-859	1.860			0.9637	430	I >	0.9450	0-9454
7	1·846	1·846	213	ę	1-805	1.807	ę	0-9604	0.9608	1.1.10	7	0.9360	0-9362
22	018·1	1·820	302	18	1-783	1.784	loh	0.0586	J0-9596	506	1	1	0-9390
8	069.1	1.692	220	4	1-660	1-660	201	00660	lo:9590	602	ŝ	0.9400	0.9404
14	1.657	1-660	214	12	1.621	1.623	7	0.9459	0-9464	432	I	0.9278	0.9281
7	1.623	1·626	310	2	1.593	1.595	б	0.9383	0-9387	520	7	0-9206	0-9208
24	1-603	∫1∙606	106	IO	1.563	1.565	5	0-9340	0-9348	336	ŝ	0-9143	0.9149
ſ	(l1-603	222	IO	1.571	1.572	6	0-9220	0-9226	522	2	0-9044	0-9048
18b	1.542	J1-546	312	14	1.515	1.516	I	0.9156	0.9160	328	I	0.8953	0-8956
	- - -	l1·541	304	7	1-506	I-So7							
12	1.496	1.4976	116	12	1.459	1.4605	I	0.9124	05190	2.1.10	Ι	0-8896	0-8902
m	1.460	1.4618	313	3	1.431	1.4320	6	0.9094	0.9102	604	I	0.8919	0-8920
		1.4510	206	I >	1.416	1-4156	ŝ	0-8989	0-8995	434	7	0-8811	0-8815
14b	1.402	∫1·4066	402	ŝ	1.378	1-3790	IO	o-8944	0-8949	418	10	o ^{.8743}	0-8746
+		l1·4023	224	8	1.372	1.3724	9	0-8915	0.8916	3.0.10	4	o-8692	0-8696
3	1.362	1.3638	314	7	1-334	1.3349			0.8801	612	I >	0-8629	0-8631
3	1.344	1.3449	320	6	615.1	1.3192	0I	o.8785	0628-0	524	IO	0-8612	0-8615

0-8412	0.8368	0.8324	0-8300	0-8257	0.8196	0.8215	0.8182	0.8114	0-8074	0-8052	0-8101	0-8013	0.7965	0-7898	0.7882	0.7825	0-7870	0.7752	0.7785			
0-8407	0-8365	0.8322	0.8300	0.8255	0.8193	0.8216	0.8180	o ⁻⁸¹¹⁴	0-8076	0-8052	6608.0	0-8012		0.7897	0.7881	0.7825	0.7871	0.7751	0.7786			
I	I	ŝ	3	9	I >	7	4	2	2b+	I	6	4		17	7	4	4	I	9			
2.2.10	508	3.1.10	440	606	338	530, 700	442	428	4.0.10	1.0.12	702, 532	526	533	1.1.12	518	2.0.12	622	3.1.11	704, 534	4.1.10	2.1.12	710
0-8622	0.8559	0-8530	0-8461	o ^{.8} 433	f 0-8383	l o ^{.8} 374	0-8343	0-8298	0-8271	0.8267	0.8260	0-8183	0-8123	0-8107	0-8059	0-8030	0-8024	o-7947	0.7942	0.7888	0-7814	0-7765
0.8615		0-8526	0-8461	0-8428	0-8-76	0/000	0-8341	0.8294	0.8269	ļ	0-8257	0-8181	0-8122	0-8105	0-8058	0.8030	0-8023	0-7947	0-7941	o-7888	0.7813	o-7765
4		3	3	9	ç	ŋ	9	ŝ	ŝ	1	7	9	I	4	4	7	4	I	4	IO	9	IO
1.3021	1.2853	1.2735	1.2548	1.2401	1·2446	1.2350		1.2198	I-2225	1.2153	1.1932	1·1734	l1•1617	l1∙1604	I.1449	1.1501	1.1387	1.1229	1.1159	1.1067	0500-1	1.0867
1.302	1.284	1.274	1.255	1.239	1-245	1.236		1-2195	1.2218	1.2156	1.1935	1.1730	1.161.4	4101 1	1.1446	1.1501	1.1386	I·1226	1.1162	1·1062	1.0935	1.0868
7	I	3	9	S	I V	ભ		I	I V	9	I V	1 ~	49	0 0	I	I	4	3	4	I V	I V	< I >
216	117	322	410	306	411	315		800	323	412	108	217	226	324	118	500	316	208	414	330	325	420
1-3336	1.3184	1·2989	1.2792	J1-2695)1·2689	1-2626		{I.2525	11.2475	1.2394	1.2248	1.2023	∫1·1887	(1·1849	1·1746	1.1724	1.1649	1.1517	1.1393	I-1282	1.1167	1.1078
1.332	1.316	1.298	1.278	1.768	1 200			0361	067 1	1.238			1.186	1 100	1.174		1·164	1.152	1.139	1.127	1·116	Loi
ŝ	I	4	IO	×	b			٩c	n C	10			٩r ب	2	4		5	ę	12	ę	ŝ	7

* Hexagonal indices *hkil* with third index omitted. The intensities were estimated visually by comparison with an intensity scale. b = broad, + = broadening due to 702, 532 α_2 line.

1. Bazirite, Rockall Island (Registered No. S 57926), Gandolfi camera, $a 6.769 \pm 0.0005$ Å, $c 10.020 \pm 0.001$ Å (cell volume 397.60 Å³), space group $P\overline{6}c_2$, Z = 2. (Data applies to bazirite with ω 1-6751, ε 1-6850.) 2. Benitoite, San Benito County, California, U.S.A. (Registered No. M.I. 31669), Debye-Scherrer camera, $a 6.640 \pm 0.001$ Å, $c 9.758 \pm 0.001$ Å (cell volume 372.59 Å³), space group $P\overline{6}c2$, Z = 2. (Data group $P\overline{6}c2$, Z = 2.

	Bazirite Rockall, Scotla	nd	Benitoite San Benito	Pabstite* Santa Cruz, California	Synthetic barium tin silicate*
	А	В	California	California	thi shicate
Composition	BaZrSi ₃ (D ₉	BaTiSi ₃ O ₉	$Ba(Sn_{0.77}Ti_{0.23})Si_{3}O_{9}$	BaSnSi ₃ O ₉
Refractive indices $\begin{cases} \alpha \\ \varepsilon \end{cases}$	1·6751 1·6850	1·6813 1·691‡	1·757† 1·804	1·685 1·674	
Optic sign Unit cell a (hexagonal) c Measured density Calculated density	Uniaxial + ve 6.769 Å 10.020 	Uniaxial + ve 6.766 Å 10.016 3.82 g/cm ³	Uniaxial + ve 6·640 Å 9·758 3·65 g/cm ³ 3·68(5) g/cm ³	Uniaxial – ve 6 706 Å 9 829 4 03 g/cm ³ 4 07 g/cm ³	6.724 Å 9.854
Space group	P6c2	P6c2	P6c2	P6c2	?P6c2

TABLE IV. Summary of data for bazirite, benitoite, pabstite, and synthetic $BaSnSi_3O_9$

A, 'low' Ti type; B, 'high' Ti type. * Gross et al., 1965. † Louderback, 1909. ‡ Deduced from birefringence.

associated with interstitial constituents that apparently developed after a partial conversion of albite to K-feldspar and of pyroxene to riebeckite had occurred in the main body of the granite (Hawkes et al., 1975). As the K-feldspar is maximum microcline, the interstitial minerals probably crystallized at temperatures within or below the maximum microcline stability range of 250-300 °C. Hydrous conditions are indicated both by the K-feldspar and riebeckite conversions and by the dominance of elpidite among the interstitial constituents. Even lower temperatures of formation can be contemplated if account is taken of the occurrence of albite, acmite, magnesio-riebeckite, and elpidite in the Eocene Green River Formation, U.S.A. These minerals have grown authigenically in unmetamorphosed calcareous shale where temperatures are thought not to have exceeded 200 °C (Milton et al., 1960).

The low-temperature hydrous conditions inferred for bazirite accord well with the hydrothermal environments in which benitoite and titanian pabstite are found (Louderback, 1909; Gross *et al.*, 1965).

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