

Ferrierite: an Australian occurrence

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SUMMARY. An occurrence of the magnesian zeolite ferrierite at Unanderra, New South Wales, represents the first reported locality for this mineral in Australia. The ferrierite occurs in vesicles in latite and is associated with heulandite, laumontite, and calcite. Its crystal morphology is essentially similar to that of specimens from the type locality at Kamloops Lake in British Columbia. EPMA results are given for the Unanderra ferrierite and its chemistry relative to other known occurrences is discussed. Unanderra ferrierite contains appreciably more SrO_2 than other ferrierites, but is significantly lower in K_2O and Na_2O .

THE rare magnesian zeolite ferrierite was first described by Grahame (1918) following the examination of specimens collected by Dr. W. F. Ferrier of the Canadian Geological Survey in a railway cutting on the north shore of Kamloops Lake in British Columbia. At this locality the ferrierite occurs as spheroidal groups of bladed crystals up to 9 mm in diameter within a pale translucent chalcedony, which fills veins and vesicles in an olivine basalt.

A calcium-rich ferrierite has been recorded from the Eastern Rhodopes (Kirov and Filizova, 1966) and an iron-rich variety from Alberto Bassi in the province of Vicenza, Italy (Alietti *et al.*, 1967). In recent years several ferrierite occurrences have been recorded in the United States of America. These include: Agoura and Sonora Pass in California (Wise *et al.*, 1969); central Nevada (Regis, 1970); Altoona in western Wahkaikum County, Washington; and Silver Mountain, California (Wise and Tschernich, 1976).

Additional localities have also recently been reported from British Columbia. Ferrierite is found near Monte Lake, 6 miles W. of Westwold in the south-east Kamloops District; on the shores of Pinaus Lake, 8 miles SE. of Westwold; and Francois Lake, 300 miles NW. of Kamloops Lake (Wise and Tschernich, 1976). Ferrierite has also been found in Japan (Yajima *et al.*, 1971) and from Weitendorf, Styria, Austria (Zirkl, 1973).

In August 1966, a Sydney mineral collector, Mr.

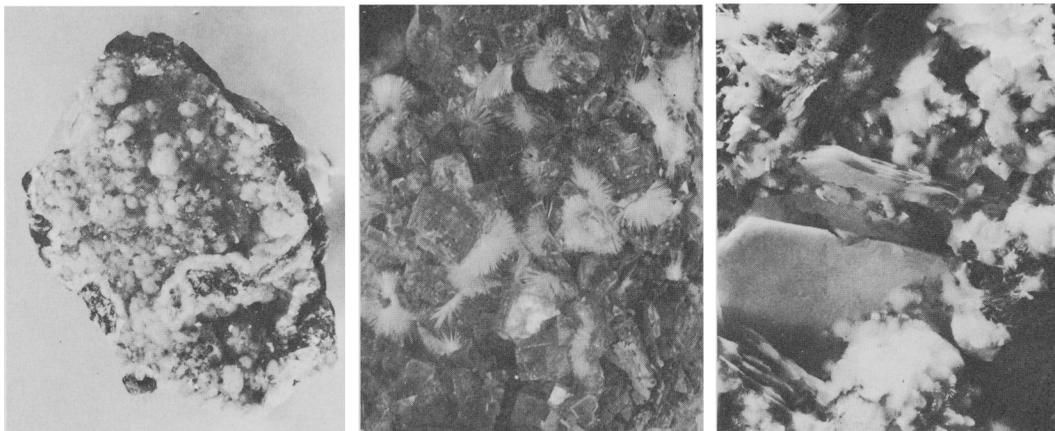
Barry Cole, discovered specimens of an unknown mineral in vesicles in latite while collecting in the then-working Wollongong City Council Quarry at Unanderra on the south coast of New South Wales. The crushed rock was being used for roadbase for the Southern Freeway being constructed at that time and the quarry ceased operations on the completion of that work.

Subsequent X-ray powder diffraction analysis of these samples carried out by the New South Wales Mines Department at their Geological and Mining Museum in Sydney proved the mineral to be ferrierite, the data agreeing with that published by Staples (1955). This locality at that time represented the first occurrence of ferrierite in the southern hemisphere and the fourth in the world.

Geological setting of the ferrierite. The ferrierite and associated minerals are found filling large vesicles in the Dapto Latite Member of the Permian Shoulhaven Group, which outcrops between Dapto and Unanderra, on the south coast of New South Wales. The section of latite exposed in the quarry is distinctly porphyritic in texture with well-formed plagioclase (labradorite) crystals up to 10 mm in length. It is partially overlain by sediments of the Pheasant's Nest Formation (Bowman, 1970).

The occurrence of ferrierite and associated minerals. The original specimens found showed spherulitic groups of closely packed bladed ferrierite crystals deposited on transparent heulandite crystals (fig. 1). Associated minerals were occasional prisms of aragonite up to 10 mm in length, and crystallized calcite as both obtuse rhombohedrons and thin sheet-like crystals tabular on {0001}. These minerals were occasionally found associated directly with the ferrierite but more commonly occurred separately in near-by vesicles.

During July 1970, after the closure of the quarry, the locality was again visited by Mr. Cole and one of the authors (B. M. E.). In the south face of the quarry a very large vesicle, almost completely filled with very coarsely crystalline fawn and brown calcite with cleavage faces up to 30 cm across, was



FIGS. 1-3: FIG. 1 (*left*). One of the original specimens of ferrierite collected from the Unanderra Quarry showing the compact spherical groups of bladed crystals on heulandite. Specimen is 5 cm diameter. FIG. 2 (*centre*). Spherical groups of bladed ferrierite crystals with well-formed transparent heulandite. Specimen is 3 cm in length. FIG. 3 (*right*). Tabular calcite associated with radiating groups of ferrierite crystals. Specimen is 3 cm diameter.

found. This calcite is strongly fluorescent in long-wave ultra-violet light, the fawn calcite showing strong yellow and the brown showing patches of orange fluorescence revealing growth zoning not otherwise visible in the specimens. Electron probe microanalysis of these calcites showed only traces of Fe and Mg in the brown calcite and Mg in the fawn calcite. No other elements were present at EPMA levels of detection.

The first mineral to be deposited in the vesicle was laumontite, as large well-formed prismatic crystals up to 5 cm in length penetrating into the coarse calcite. Patches of crystalline laumontite also occurred throughout the calcite body. This laumontite rapidly dehydrates to powdery leonhardite, leaving moulds of the crystals in the calcite.

Towards the centre of the calcite body a large vug was encountered which contained ferrierite, heulandite, and calcite. Here the ferrierite occurred as acicular bladed crystals arranged in spherical groups averaging 2.5 mm in diameter deposited on well-formed transparent heulandite crystals (fig. 2). These groups were occasionally partly enclosed by the heulandite crystals. Each spherical aggregate of ferrierite crystals is composed of several groups of divergent blades with sub-parallel orientation, like the leaves of an open fan. This fan-like arrangement of the blades was also noted by Grahame (1918) in the Kamloops Lake material. Very small perfectly formed heulandite crystals were occasionally seen to be supported by groups of divergent ferrierite blades, the ferrierite often completely penetrating the crystal.

Deposited after the ferrierite-heulandite are very thin plate-like crystals of calcite up to 3 cm² in area

arranged in sub-parallel groups (fig. 3). These plates are rarely more than 0.1 mm in thickness and are tabular on {0001}, as shown by trigonal growth markings. Near-by vugs in the calcite body were completely filled by this variety of calcite.

The minerals in the vug are deposited on a layer of fine-grained intermixed calcite and chalcedony 0.5 to 1.5 cm in thickness, which is separated from the coarse calcite by white and iron-stained crystallized laumontite (fig. 4).

The sequence of crystallization of the ferrierite and its associated minerals is summarized in Table I.

Crystal morphology of the ferrierite. Optical studies by Grahame (1918) proved the mineral to be orthorhombic. The Kamloops Lake crystals were

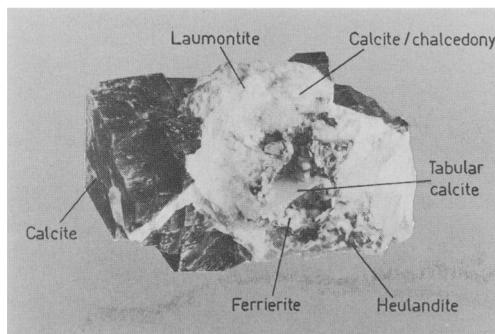


FIG. 4. Part of the large cavity exposed, showing ferrierite crystal groups with tabular calcite and heulandite crystals deposited on a fine-grained aggregate of calcite/chalcedony, which is separated from the coarse calcite by white crystalline laumontite. Specimen is 7 cm in length.

TABLE I. *Paragenetic sequence of minerals at Unanderra*

Laumontite	—	vug
Coarse calcite	—	
Fine calcite/chalcedony	—	
Heulandite	—	
Ferrierite	—	
Bladed calcite	—	
Aragonite	—	
	wall of vesicle	centre of vesicle

found to be tabular on $\{100\}$ with elongation along the c -axis. Forms present were the pinacoids $\{100\}$ and $\{010\}$ with the macrodome $\{101\}$ terminating the crystals. A perfect cleavage parallel to $\{100\}$ was also reported.

Accurate measurements of refractive indices and 2V were not possible due to the small size of the individual crystals (less than 0.01 mm in diameter) but the optical properties of the Unanderra ferrierite conform well with the data published by Grahame (1918) and Staples (1955).

The crystal morphology of the Unanderra ferrierite was further examined by transmission electron microscopy. Some difficulty was experienced in preparing samples for electron microscopy because of the tendency of the ferrierite crystals to distort and intumescence under the heating effect of the electron beam in samples prepared by normal dispersion techniques. This was overcome by modifying the technique as follows: several crystal groups were selected under a binocular microscope and these were gently mixed with ethyl alcohol to form a slurry, which was dispersed on a glass microscope slide and allowed to dry. The surface of the slide supporting the crystals was then replicated using a two-stage plastic/carbon replica technique (Kay, 1965). Samples prepared by this method showed greatly increased stability, the crystals being firmly locked in the carbon support film, enabling more accurate representation of crystal morphology in the photographs.

Electron microscopy showed the major crystal forms of Unanderra ferrierite to be the two pinacoids $a \{100\}$ and $b \{010\}$. A perfect cleavage parallel to $\{100\}$ is present, conforming with the observations made by Grahame (1918) (fig. 5). The present study also suggests the presence of a less perfect $\{001\}$ cleavage. The dome form $d \{101\}$ of Grahame's investigations was not seen on the

Unanderra ferrierite and at first it was thought that this may have been due to the ferrierite crystals lying with the $a \{100\}$ face parallel to the carbon support film, in which case the dome $d \{101\}$ faces would not be observed. However, examination of the crystals under an optical microscope showed them to be terminated by the $\{001\}$ face only.

The *chemical composition* of a number of individual crystals of the ferrierite was obtained by electron probe microanalysis. Crystals broken from the groups were mounted on an epoxy resin surface. All crystals were checked by optical microscopy for the presence of extraneous minerals, and only monomineralic crystals were analysed. Analyses were carried out on an ARL-EMX unit at 15 keV accelerating voltage, 0.07 μ A specimen current and a focused beam of about 2 μ m diameter. Counting times were 20 seconds and the counting data were corrected by a programme devised by Wright (1973), based on the methods of Duncumb and Reed (1968), Duncumb and Shields (1966), and Reed (1965). All crystals examined were of approximately similar thicknesses and all were analysed under similar conditions.

As is well known, the analysis of zeolites presents difficulties to the electron-probe microanalyst, especially in relation to bound-water volatilization and in sodium and potassium analyses. The heating effect of the electron beam causes the water to boil off, causing the counting rates of the major elements to increase, as their effective concentration within the excitation microvolume increases. The case with sodium is more complex. In tectosilicates, sodium count rates have often been found to decrease with analysis time (Siivola, 1969; Baird and Zenger, 1966), but in alkali glasses an initial decrease in sodium count rate is often followed by a

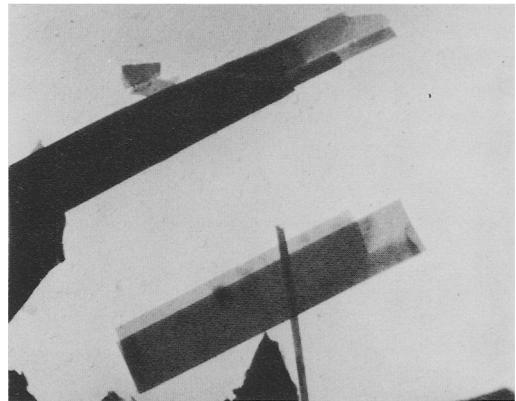


FIG. 5. Transmission electron micrograph of the ferrierite crystals showing $\{100\}$ cleavage planes and the pinacoid $\{010\}$ faces. Magnification $\times 7000$.

large increase (Borom and Hanneman, 1967). Recently Butt and Vigers (1977) noted a rapid increase in count rate for sodium during an EPMA analysis of sepiolite and they attributed this to a build-up of negative charge on the crystal surface. As a result, sodium ions that are associated with the zeolitic water in internal lattice channels migrate through this natural electrolyte to the electron beam position, thus causing a rapid anomalous increase in count rate. A similar effect has been observed by the authors in the EPMA analysis of levyne-offretite intergrowths. Here sodium counts increased twentyfold after an analysis time of only 10 min (Ostwald and England, in preparation).

The analyses (listed in Table II) must be considered in the light of these difficulties. Though measurements were made under similar instrumental conditions and on similar size grains, the analytical totals vary considerably. This may well be due to variation in thickness of the material analysed, i.e. variation in case of dehydration. Some of the analyses (notably 1, 4, 5, and 7) are within the range of chemical variability of the mineral as described by Wise and Tschernich (1976). The variation in sodium and potassium is of interest, with some crystals apparently being entirely free of alkali metals while others contain low to appreciable levels. The virtual absence of potassium in this material is in contrast with the consistent presence

of the element (range 0.63–3.78 %) in the specimens recorded by Wise and Tschernich (1976). To what extent alkali metal variations in zeolites are real or instrument-induced is an open question.

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TABLE II. *Chemical composition of Unanderra ferrierite*

	1	2	3	4	5	6	7	8	9	Average
SiO ₂	73.3	68.9	58.1	65.9	69.3	61.2	71.5	60.6	69.1	66.4
Al ₂ O ₃	13.6	11.4	11.7	15.5	12.7	14.3	13.1	11.8	12.8	12.9
Fe ₂ O ₃	nd*	nd	nd	0.1	1.2	nd	0.1	nd	nd	0.1
MgO	3.4	3.4	2.3	3.6	3.4	3.6	4.0	3.1	3.1	3.3
CaO	1.3	1.2	1.2	1.2	1.3	1.7	1.3	1.1	1.2	1.3
SrO	1.1	1.0	0.5	1.0	0.8	0.5	1.1	1.0	0.8	0.9
Na ₂ O	nd	0.7	nd	2.7	0.1	1.8	0.7	0.1	0.1	0.6
K ₂ O	nd	0.1	nd	0.2	nd	0.3	nd	0.3	0.1	0.1
H ₂ O†	7.3	12.4	26.2	9.8	11.3	16.6	8.3	22.0	13.0	—
Number of ions on the basis of 72 oxygens										
Si	30.02	29.22	29.79	28.24	29.74	26.31	29.73	29.76	30.19	
Al	6.49	5.63	6.98	7.74	6.34	7.75	6.32	6.81	6.55	
Fe	—	—	—	0.02	0.36	—	—	—	—	
Mg	1.59	2.09	1.77	2.22	2.12	2.39	2.47	2.31	2.05	
Ca	0.41	0.51	0.61	0.51	0.56	0.83	0.54	0.58	0.58	
Sr	0.22	0.28	0.12	0.23	0.17	0.11	0.22	0.26	0.17	
Na	—	0.53	—	2.27	—	1.54	0.86	0.12	—	
K	—	—	—	0.05	—	0.14	0.34	0.15	—	
Si + Al + Fe	36.51	34.85	36.77	36.00	36.44	34.06	36.05	36.57	36.74	

* Not detected by EPMA.

† By difference.

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