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Ferrierite from Tapu, Coromandel Peninsula, New Zealand, and a crystal chemical study of known occurrences

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ABSTRACT. Ferrierite has been found at Tapu, Coromandel Peninsula, New Zealand, as a mineral vein with calcite in altered hornblende andesite lava of the Miocene Beeson's Island Volcanics. The ferrierite is low in SiO_2 (63.67%) and high in Al_2O_3 (13.75%), MgO (3.48%), and BaO (2.35%). The large *a* axis and cell volume (*a* 19.236(4), *b* 14.162(6), *c* 7.527(3) Å, *V* 2050 $Å^3$) are consistent with the low SiO_2, high Al_2O_3, high MgO chemistry. Optical orientation and optical sign ($a = Z$, $b = X$, $c = Y$, 2V(−)55°) of the mineral are different from those of the Lake Kamloops ferrierite reported by Graham (1918). Refractive indices α 1.487, γ 1.489, and density 2.136 were measured. Cleavage observed on (100) is perfect and on (001) is imperfect. Using data from eighteen occurrences so far reported including the Tapu mineral, the crystal chemistry of ferrierite has been studied.

KEYWORDS: ferrierite, crystal chemistry, Tapu, New Zealand.

Tapu, Coromandel Peninsula, ferrierite. An Auckland mineral collector, Mr N. Savage, supplied an unknown mineral from a locality 6 km east of Tapu, north of Thames, on the Coromandel Peninsula of the North Island. At this locality, a brecciated hornblende andesite of Miocene Beeson's Island Volcanics contains a calcite vein showing strong swell and pinch with a maximum thickness of 30 mm. A selvedge of ferrierite 1 mm thick forms the margins of the vein.

Optical thin sections were cut from the vein and mounted with unheated media. Under the microscope, the ferrierite appears as radiating fibrous prisms which projected originally into a cavity that was later filled by calcite crystals. The prismatic crystal is platy on (100), with cleavage perfect on (100) but imperfect on (001). The elongation axis is *c* which is the optical elastic axis Y, so that the elongation sign cannot be defined. The optical constants were measured on the unheated thin sections and grains, and the results are shown in Table I.

Table I. Chemical composition, cell dimension and optical properties of Tapu, Coromandel ferrierite

			O = 72	Orthorhombic cell
SiO_2	63.67	Si	28.58	a 19.236(4) A
TiO_2	0.01	Ti	0.00	b 14.162(6) A
Al_2O_3	13.75	Al	7.27	c 7.527(3) A
Fe_2O_3	0.15	Fe	0.05	V 2050.5 A^3
MnO	0.02	Mn	0.01	Dx 2.138
MgO	3.48	Mg	2.33	Dm 2.136
CaO	1.12	Ca	0.54	α 1.487
SrO	0.43	Sr	0.11	β 1.489
BaO	2.35	Ba	0.41	2V(-) 55°
Na_2O	0.36	Na	0.31	a = Z, b = X, c = Y
K_2O	0.99	K	0.57	Cleavage (100) perfect
$H_2O(+)$	12.96			(001) imperfect
Total	99.29			

Tapu ferrierite has different optical orientation and optical sign from the Lake Kamloops mineral reported by Graham (1918). The orientation of the latter is $a = X$, $b = Y$, $c = Z$ with optical axial angle 2V(+)50.5°. Alietti *et al.* (1967) described Albero Bassi, Italy, ferrierite with the same orientation as the mineral from Lake Kamloops.

Despite the difference in optics, the X-ray diffraction pattern of the Tapu ferrierite is similar to that of the Lake Kamloops mineral, though there are slight differences with much weaker 110, and absence of 121, 130 diffractions in the former mineral. The cell edge *a* and the cell volume of the Tapu mineral are quite large and that is consistent with its low SiO_2, high Al_2O_3, high MgO composition.

Chemical analysis (Table I) shows that the Tapu ferrierite is a low SiO_2, high Al_2O_3 variety and contains considerable amounts of MgO and BaO. The chemical composition of this mineral is similar to the Ba-rich ferrierite of Silver Mountain, California (Wise and Tschernich, 1976) though the latter is somewhat less aluminous and magnesian.

Mineral chemistry of ferrierites. Ferrierite was found by Dr W. F. Ferrier in altered basalt of early Miocene age from north shore of Kamloops Lake, British Columbia, Canada, which was studied by Graham (1918) who named the mineral. It was the sole locality of the mineral for nearly fifty years. Staples (1955) studied the original material, suggested a three-dimensional framework structure, and concluded the mineral was a zeolite.

The crystal structure of ferrierite was analysed by Kerr (1966) and by Vaughan (1966). Both authors showed virtually the same structural framework with a ten-membered ring channel along the *c*-axis and an eight-membered ring channel along the *b*-axis. However, the former author did not show water and cation sites, yet had a structure refinement result $R = 16.5\%$; the latter author showed 2 Mg as an essential constituent in the unit cell, occupying two fixed sites in cavities and surrounded by six H_2O molecules, with a structure refined to $R = 10.7\%$.

About the same time, new occurrences of ferrierite were reported successively from Yugoslavia (Baric, 1965), Bulgaria (Kirov and Filizova, 1966) and two separate localities in Central Nevada, USA (Sand and Regis, 1966; Regis, 1970). The Nevada occurrences are zeolitized sedimentary rocks, with ferrierite as the major constituent mineral in altered Tertiary bedded pyroclastics. This mode of occurrence stimulated the studies in agricultural and industrial applications of this mineral (Chi *et al.*, 1978; Hayhurst, 1978; Townsend and Loizidou, 1984). From 1967 onward, ferrierite has been reported from a number of localities throughout the world. The 20 known localities are summarized in Table II. Of the 20 localities 14 were reported from Tertiary or Miocene altered volcanics, 5 were from altered volcanics without reference to the geological age, and 1 was from Permian latite.

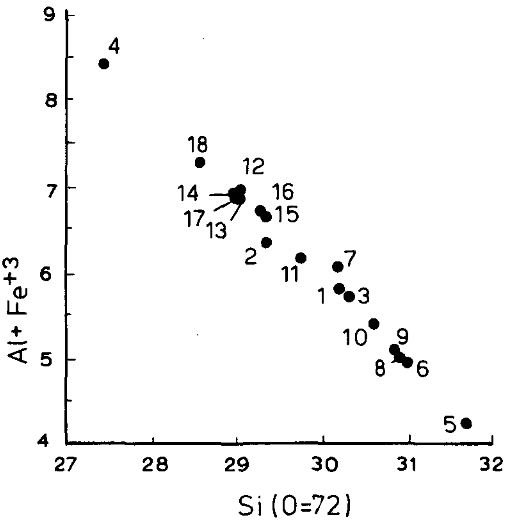


FIG. 1. Si:Al+Fe^{3+} diagram for eighteen ferrierite samples. 1. Kamloops Lake. No. 4 of Wise and Tschernich (1976). 2. Bulgaria. Kirov and Filizova (1966). 3. Bulgaria. No. 9 of Wise and Tschernich (1976). 4. Italy. Alietti *et al.* (1967). 5. Agoura. No. 4 of Wise *et al.* (1969). 6. Santa Monica Mountains. No. 3 of Wise and Tschernich (1976). 7. Sonora Pass. No. 6 of Wise *et al.* (1969). 8. Itomuka. Yajima and Nakamura (1971). 9. Altona. No. 1 of Wise and Tschernich (1976). 10. Altona. No. 2 of Wise and Tschernich (1976). 11. Pinaus Lake. No. 5 of Wise and Tschernich (1976). 12. Francois Lake. No. 6 of Wise and Tschernich (1976). 13. Monte Lake. No. 7 of Wise and Tschernich (1976). 14. Silver Mountains. No. 8 of Wise and Tschernich (1976). 15. Phillip Island. Birch and Morvell (1978). 16. Unanderra. England and Ostwald (1978). 17. Sardinia. Orlandi and Sabelli (1983). 18. Tapu. This paper.

The frequently reported minerals associated with ferrierite are calcite, chalcedony, clinoptilolite, heulandite, quartz, montmorillonite, and mordenite, while associated minerals reported, each from one locality, are aragonite, apatite, analcite, chabazite, collinsite, dachiardite, marcasite, mesolite, opal, and pyrite.

Data from seventeen ferrierite localities have been selected from the literature, and together with data of the Tapu mineral, eighteen analyses have been recalculated into the cationic number based on the unit cell oxygen number O = 72. The unit

TABLE II. Twenty reported ferrierite occurrences

Locality	Geology	Occurrence	References
Kamloops Lake, Canada	Miocene basalt	in calcite chalcedony vein	Graham (1918), Staples (1955), Wise & Tschernich (1976)
Gotalovec, Yugoslavia	spilite	wall of calcite-pyrite vein	Baric (1965)
Chernichino, Bulgaria	Tertiary volcanics	associated with chalcedony	Kirov & Filizova (1966), Wise & Tschernich (1976)
Lovelock, Nevada Fallon, Nevada	Tertiary pyroclastics	major constituent mineral of the pyroclastics with mordenite and clinoptilolite	Sand & Regis (1966), Regis (1970)
Tadami, Fukushima, Japan	Miocene pyroclastics	major constituent mineral of the pyroclastics often with mordenite	Hayakawa & Suzuki (1970)
Albero Bassi, Italy	green porphyrite	fillings with calcite	Alietti et al (1967)
Agoura, California	Miocene andesite	associated with clinoptilolite, calcite, chalcedony	Wise et al (1969), Wise & Tschernich (1976)
Sonora Pass, California			Wise et al (1969)
Itomuka Mine, Japan	Miocene andesite	in cinnabar quartz vein	Yajima & Nakamura (1971)
Weitendorf, Austria	shoshonitic basalt	cavity filling	Zirkl (1973)
Altona, Washington	Miocene basalt	as fillings with clinoptilolite, mordenite, siderite	Wise & Tschernich (1976)
Pinaus Lake, Canada	Tertiary basalt	in calcite filled nodules	Wise & Tschernich (1976)
Francois Lake, Canada	Tertiary andesite	in cavities with collinsite, carbonate, fluorapatite	Wise & Tschernich (1976)
Monte Lake, Canada	Miocene basalt	in calcite filled nodules	Wise & Tschernich (1976)
Silver Mountains, California	altered andesite	associated with heulandite, baryte	Wise & Tschernich (1976)
Phillip Island, Australia	Tertiary basalt	in cavities with calcite, heulandite	Birch & Morvell (1978)
Unanderra, Australia	Permian latite	associated with aragonite, calcite	England & Ostwald (1978)
Monastir, Sardinia, Italy	Tertiary andesite	with quartz, calcite, zeolites	Orlandi & Sabelli (1983)
Tapu, New Zealand	Miocene andesite	vein with calcite	This paper

cell cationic number of the eighteen ferrierites have been plotted on the five diagrams: $\mathrm{Si:Al+Fe^{3+}}$ (fig. 1), $\mathrm{Si+Na+K:Al+Fe+Mg+Ca+Sr+Ba}$ (fig. 2), $\mathrm{Mg:Na+Ca+Sr:K+Ba}$ (fig. 3), frequency diagram of Mg (fig. 4), and $\mathrm{Si:Mg}$ (fig. 5).

The variation in Si unit cell content (27.5–32.0) for ferrierite (fig. 1) is considerably greater than in the related zeolites mordenite (28.5–31.0) and heulandite–clinoptilolite (26.5–30.0) as calculated on the basis of 72 oxygens (Sameshima, 1978). The wider variation for ferrierite seems inconsistent with the rarity of the mineral, however, the Mg requirement along with Si variation may be the reason for its limited occurrence. The plotted points are closely gathered on a line $\mathrm{Si+Al+Fe} = 36$, indicating that the chemical analysis data are reasonably reliable.

The diagram for $\mathrm{Si+Na+K:Al+Fe+Mg+Ca+Sr+Ba}$ (fig. 2) shows a narrow linear cluster of plotted points along the line $\mathrm{Si+Na+K+Al+Fe+Mg+Ca+Sr+Ba} = 40$. This suggests that the ferrierite crystallized with $\mathrm{Si(Na,K)} \rightleftharpoons \mathrm{Al(Ca,Mg)}$ type substitution equilibrium, and that no significant later cation exchange process has occurred.

The cationic distribution for ferrierite is given in fig. 3, where three similar ionic size cation groups are shown. Mg varies 7 to 70% among the cations, similar to the range for the Na, Ca, Sr group, but the K, Ba group extends from only 2 to 50%.

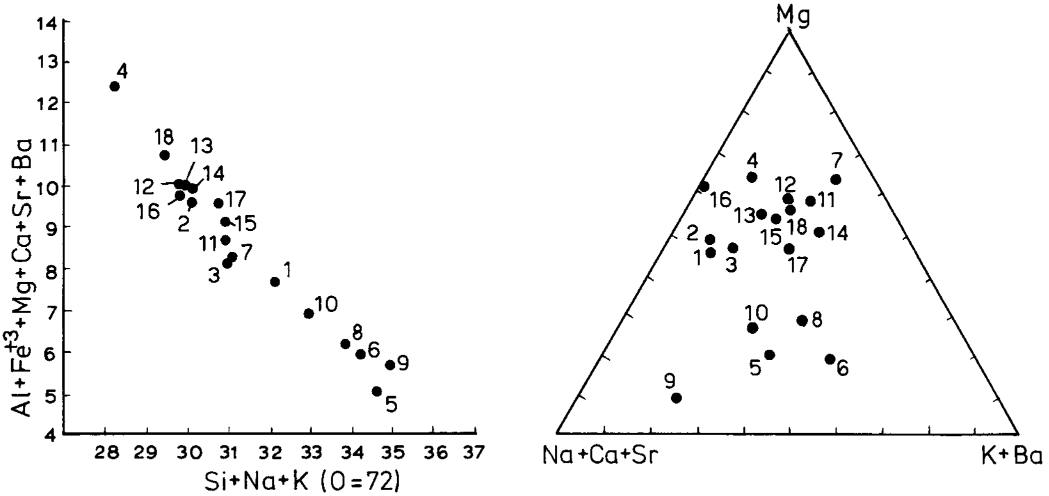
The high Mg content of ferrierite has been considered to be the important characteristic of this zeolite. However, Wise and Tschernich (1976) described low Mg varieties from the western states of USA and concluded that Mg is not an essential component of ferrierite.

The frequency distribution of Mg content for the eighteen ferrierites (fig. 4) indicates there is a maximum at 1.75–2.25 Mg, which includes nine of the samples, but the remaining nine are rather evenly spread between 0.38 and 2.97.

The Mg content of ferrierite varies with Si in the unit cell (fig. 5). The plotted points of the Si:Mg diagram are somewhat dispersed, but the diagram probably shows the inclination $\mathrm{Mg} = 0.5\mathrm{Si}$ expected for the $2\mathrm{Si} \rightleftharpoons \mathrm{Mg}$ substitution relation.

Wise and Tschernich (1976) found the cell edge *a* of ferrierite varies with Si:Al ratio. Fig. 6 shows *a* versus Si content using data from sixteen occurrences. The diagram indicates a negative correlation between Si content and *a*; however, the plotted points are rather dispersed.

Fig. 7 shows the Mg unit cell content versus *a* and this diagram indicates an obvious positive linear correlation between Mg content and *a*. Increase of 1 atom Mg in the unit cell corresponds to 0.22 Å



FIGS. 2 and 3. FIG. 2 (*left*). Si + Na + K : Al + Fe + Mg + Ca + Sr + Ba diagram for eighteen ferrierites. FIG. 3 (*right*). Mg : Na + Ca + Sr : K + Ba diagram for eighteen ferrierites. For data numbers see fig. 1.

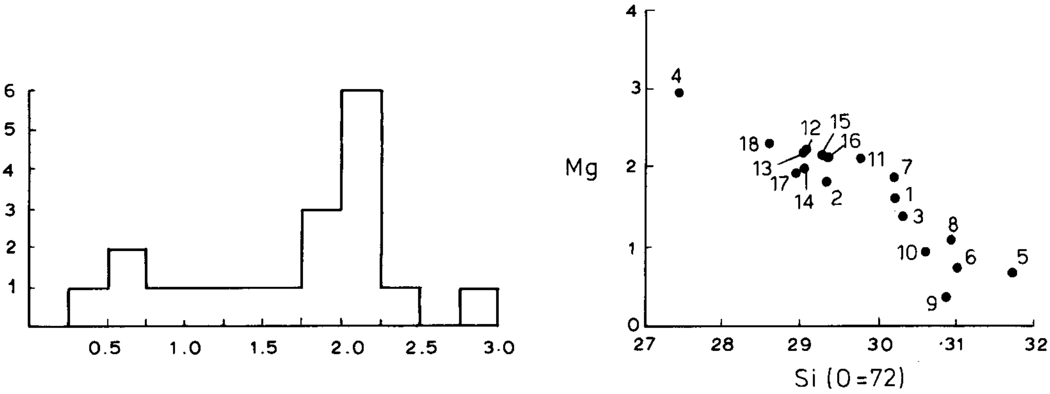
increase of *a*. Probably, *a* of ferrierite is actually controlled by Mg content and the apparent Si : Al ratio correlating to the constant is likely to be of indirect relation.

Boles (1972) reported that added Mg causes a notable increase of the *b* value for heulandite-clinoptilolite. Although this zeolite contains only up to 1 atom Mg in the unit cell (O = 72), the effect on *b* is 0.2 Å per 1 atom of Mg in the unit cell.

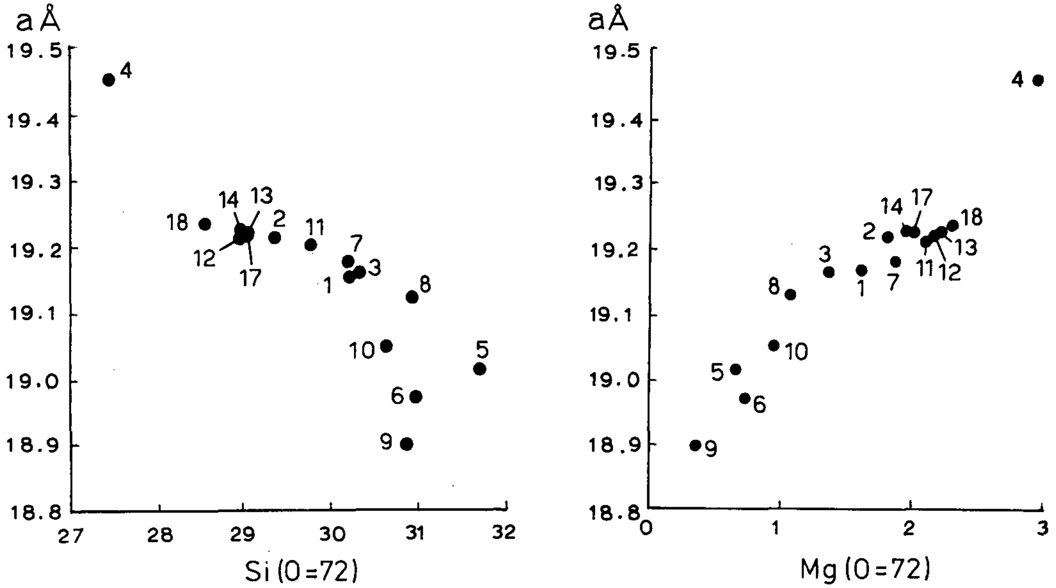
Coombs *et al.* (1959) hydrothermally synthesized a zeolite phase 'Z' in a non-magnesian, lime-soda-alumina-silicate system, in association with mordenite. Their X-ray pattern for the 'Z' phase coincides with that of ferrierite. Axis constants calculated on their X-ray data (*a* 18.90(1), *b* 14.14(1), *c* 7.48(1) Å, *V* 1999 Å^3) indicate it is an extremely silica-rich variety in terms of fig. 6.

Also Senderov (1963) obtained sodic ferrierite in association with mordenite in a non-magnesian system and Barrer and Marshall (1965) hydrothermally synthesized a strontian ferrierite. These experiments indicate that no particular alkali or alkali-earth is essential for the formation of ferrierite, though non-magnesian ferrierite are likely to be extremely silica-rich (Si 32–33, Al 4–3).

Vaughan (1966) postulated exactly 2 Mg in the unit cell for the Kamloops Lake ferrierite and assigned two fixed sites for Mg in cavities, where Mg is surrounded by 6 H_2O. As seen in fig. 4, half of the eighteen ferrierites contain 1.75–2.25 Mg in the



FIGS. 4 and 5. FIG. 4 (*left*). Unit cell Mg content frequency distribution diagram for eighteen ferrierites. FIG. 5 (*right*). Si : Mg diagram for eighteen ferrierites. For data numbers see fig. 1.



FIGS. 6 and 7. FIG. 6 (*left*). Unit cell Si content versus *a* for sixteen ferrierites. FIG. 7 (*right*). Unit cell Mg content versus *a* for sixteen ferrierites. For data numbers see fig. 1.

unit cell and this supports Vaughan's deduction, but fig. 5 shows that the same nine samples have Si cell contents dispersed over a range of 29.0–30.2.

Vaughan reported an acid leaching experiment for the Kamloops Lake mineral which resulted in no Mg extraction and thus inferred that Mg in the fixed sites is protected from leaching. A Tapu ferrierite powder was treated with 1N ammonium acetate solution for 24 hours, and another split of the powder was treated with boiling 1N HCl solution for 1 hour. In both cases only a trace amount of Mg was detected in the leachate solution.

The Tapu ferrierite contains 2.33 Mg in the unit cell but no Mg is leachable, indicating that in 'protected sites' as well as in channels this element is anchored to the framework structure by some mechanism. As Mg seems unleachable, the cation exchange capacity of ferrierite must be diminished with increase in Mg content.

Feldspar group and zeolite group tectosilicates do not normally contain Mg and this may be explained by Pauling's crystal chemical law. The co-ordination number of Mg is 6, which requires an average of $\frac{1}{3}$ negative charge from each of the six anions. Ca, Na, and K require an 8, 10, or 12 co-ordination number, so that only $\frac{1}{4}$–$\frac{1}{12}$ average negative charge is needed for neutralization. In the tectosilicates, a 6 co-ordination site with total of −2 charge, and thus suitable for Mg, is not possible.

For ferrierite, the interpretation of Vaughan (1966) is that the Mg is surrounded by 6 H_2O to make an $Mg(H_2O)_6^{2+}$ group, and that this group is situated in a cavity surrounded by 24 oxygens of the framework. This seems to be a most likely structure solution, but an explanation is required for the role of excess Mg in the channels, and also for the role of Mg in heulandite–clinoptilolite system, which has no suitable cavity site for Mg. The evidence shows that Mg increase causes a distinct increase of axis length and cell volume in both zeolites, and the same tendency linearly extends to the 3 Mg range in ferrierite.

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