

A calcian ralstonite-like mineral from the Cleveland Mine, Tasmania, Australia

W. D. BIRCH

Department of Mineralogy and Petrology, Museum of Victoria, 285 Russell Street, Melbourne, Victoria, 3000

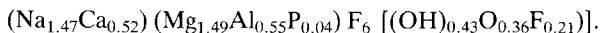
AND

A. PRING

Department of Mineralogy, South Australian Museum, North Terrace, Adelaide, South Australia, 5000

Abstract

A calcium-rich ralstonite, forming colourless octahedral crystals up to 2 mm across, occurs in a F-rich assemblage at the Cleveland Mine, northwestern Tasmania. Other minerals present include well-crystallized morinite, gearsutite, vivianite, siderite, K-rich feldspar (adularia), fluorite and quartz. The F-rich assemblage probably formed during greisenization when Na and F-rich magmatic brines reacted with enclosing carbonate host rocks to produce hydrothermal Na-Ca-Mg-bearing solutions. Chemical analysis of the ralstonite-like mineral gave a formula



This differs from the 'pyrochlore' formula, due to the substitution of Ca + (OH,O,F) for H₂O, in addition to the coupled substitution of Na + Mg for Al in 'normal' ralstonites. The Cleveland Mine ralstonite has the highest recorded Ca, Na and Mg contents. While the mineral is likely to be a new species on chemical grounds, single crystal X-ray photographs indicate the structure is disordered, possibly composed of small compositional domains.

KEYWORDS: ralstonite, Cleveland Mine, Tasmania, Australia.

Introduction

NORTHWESTERN Tasmania is a major tin-bearing province, with important deposits associated with granites, greisens and skarns, such as Renison Bell, Mt Bischoff, St Dizier and Cleveland. The potential of these mines for providing fine mineral specimens and rare species has never been fully realized and only sporadic reports have been made on the mineralogy (e.g. Kwak and Nicholson, 1988). Few specimens exist in museum collections.

The Cleveland Mine is situated 14 km southwest of Waratah, close to the mining township of Luina in western Tasmania. The mine has been an important hard-rock tin mine since opening in 1968, producing nearly 25 000 tonnes, but closed in 1986 due to ore depletion. The main lode-bearing unit consists of lenses of pyrrhotite, pyrite, marcasite and cassiterite, with accessory sulphides, silicates and fluorite in a gangue comprised mainly of quartz and carbonates (Cox and

Glasson, 1971; Ransom and Hunt, 1975). The host rocks for these lenses are shales and cherts of the Hall Formation, of either Upper Precambrian or Lower Cambrian age. As well as replacement-type lenses, veins and greisen-type mineralization is also present (Jackson, 1985).

Several small specimens of well-crystallised colourless and white minerals from the Cleveland Mine were submitted to the Museum of Victoria early in 1986 by Mr Peter Hall. Investigation showed the assemblage consisted mainly of fluorine-rich species such as morinite, gearsutite and a calcium-bearing ralstonite-like mineral together with K-rich feldspar, siderite and vivianite. The rare minerals encrusted quartz crystals and colourless to pale green fluorite on a chert-like matrix. These specimens are exceptional for the excellent degree of crystal development of the fluoride species, which in most other localities worldwide are fine-grained and massive.

Although their precise location within the mine was not recorded, it seems likely the specimens

came from quartz and fluorite-bearing vugs in an upper series of five stratigraphically controlled replacement lenses (Ransom and Hunt, 1975). The fluoride minerals represent late-stage, low-temperature hydrothermal crystallization in the Cleveland deposit. Their formation may have been associated with greisenisation of the host rocks (Wright, 1985). The sequence calcian 'ralstonite'-morinite-gearsutite suggests crystallization from Na-Ca-Mg-bearing solutions derived by reaction between Na and F-rich magmatic brines and the enclosing calcic and dolomitic host rocks. These solutions became more calcic and less sodic with time.

This note concentrates on a description of the ralstonite-like mineral. Although ralstonite is known from a number of localities [Ivigtut, Greenland (Pauly, 1965), Gjerdingen, Norway (Raade and Haug, 1980), several localities in the USSR (Stepanov and Moleva, 1962; Ryabenko *et al.*, 1988), St Peters Dome, Colorado (Cross and Hillebrand, 1883) and Mt Bischoff, Tasmania (Wright, 1985)], it is considered rare and its full chemical range is undefined.

On two of the Cleveland Mine specimens, well-formed, colourless to white octahedral crystals, up to 2 mm across, of the ralstonite-like mineral occur as individuals or clusters showing the octahedral form {111} only; the cubic {100} and dodecahedral {110} forms have not been observed (Fig. 1).

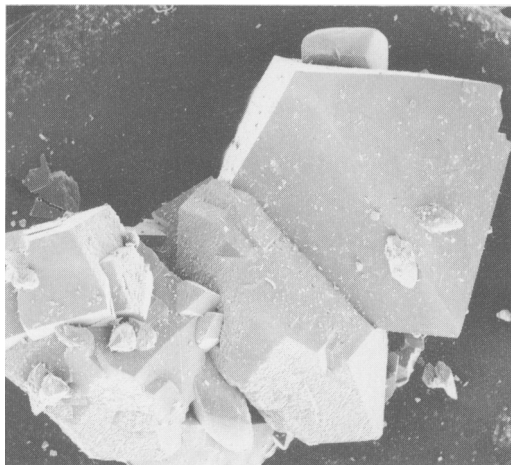


Fig. 1. Scanning electron micrograph showing octahedral calcian ralstonite crystals 2.4 mm on edge with morinite crystals.

Microprobe analyses (Table 1) show that Ca

Table 1. Microprobe analyses of calcian ralstonite from Cleveland, Tasmania.

	1.	2.
Al	6.21	6.13
Mg	15.09	15.28
Ca	8.71	8.83
Na	14.12	14.15
P	0.53	0.36
F	49.16	49.27
O	5.25	4.76
Heat	0.18	0.14
Total	99.25	98.92

Formulae: (based on 7 anions)

1. $(\text{Na}_{1.47}\text{Ca}_{0.52})(\text{Mg}_{1.49}\text{Al}_{0.55}\text{P}_{0.04})\text{F}_6[(\text{OH})_{0.43}, \text{O}_{0.36}, \text{F}_{0.21}]$

2. $(\text{Na}_{1.49}\text{Ca}_{0.52})(\text{Mg}_{1.52}\text{Al}_{0.55}\text{P}_{0.03})\text{F}_6[\text{O}_{0.39}, (\text{OH})_{0.33}, \text{F}_{0.28}]$

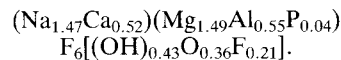
Notes:

1. Colourless octahedra, Museum of Victoria specimen M38127, average of 7 analyses.

2. Milky octahedra, Museum of Victoria specimen M38124, average of 2 analyses.

Analyses obtained on a Cameca microprobe at 15 kV with standards corundum (Al), periclase (Mg and O), wollastonite (Ca), villiaumite (Na and F) and apatite (P). Analyst: W. Birch.

is a significant component in addition to Na, Mg, Al and minor P, and that some oxygen is present as O^{2-} and OH in addition to fluorine. The analysis when calculated on the basis of seven anions and expressed in terms of the pyrochlore general formula, $\text{A}_2\text{B}_2\text{X}_7$ (Pabst, 1939), gives



The substitution of Ca means that the formula does not fully agree with the general formula proposed for ralstonite by Pabst (1939), $\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{F}, \text{OH})_6 \cdot \text{H}_2\text{O}$, which is based on a coupled substitution of Na+Mg for Al. The small amount of P present in all analyses is essential for charge balance, and it is presumed to be substituting for Al.

The ralstonite 'series' can be defined as the substitution of Na+Mg into $\text{Al}_2\text{F}_6 \cdot \text{H}_2\text{O}$, i.e. $x = 0$ (Cowley and Scott, 1948). The highest Na, Mg substitution reported previously is for $x = 0.88$. Ignoring Ca, the Cleveland 'ralstonite' has $x = 1.5$, close to an as-yet-undescribed analogue, $\text{Na}_2\text{Mg}_2(\text{F}, \text{OH})_6 \cdot \text{H}_2\text{O}$ (Fig. 2). The presence of Ca seems to be due to the coupled substitution of $\text{Ca} + (\text{OH}, \text{O}, \text{F}) = \text{H}_2\text{O}$, with the additional anions entering the water site and the Ca going into the pyrochlore A site. For the Cleveland ralstonite, the Ca content is 0.52, over halfway in this particular substitution series, which competes with the Na+Mg = Al substitution for occupancy of the A site. The content of the A site is limited

by $\text{Na} + \text{Ca} = 2$. On several chemical grounds it therefore appears that the Cleveland ralstonite-like mineral is a new species (Fig. 2).

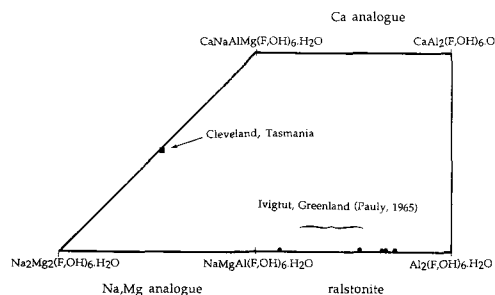


FIG. 2. Diagram showing relationships between substitutional series and theoretical end-members in ralstonite-like minerals.

X-ray powder diffraction data were obtained on a colourless octahedral crystal of the calcian ralstonite-like mineral (from specimen M38127) using a 5.73 cm diameter Gandolfi camera with Co-K radiation. The diffraction pattern (Table 2) is similar to those of ralstonite from Greenland and elsewhere, published by Pauly (1965), although the relative intensities of corresponding lines may differ considerably (this factor is most likely associated with the geometry of the Gandolfi camera). The X-ray data for the Cleveland mineral were indexed with reference to Pauly (1965) and gave a cubic unit cell with $a = 10.081(3) \text{ \AA}$. The cell edge and the Mg and Na contents of the Cleveland ralstonite are higher than for any of the Greenland ralstonites, in agreement with Pauly's observation that a increases with increasing Mg+Na.

Table 2. Powder X-ray diffraction data for calcian ralstonite from Cleveland Mine, Tasmania.

hkl	$d_{\text{obs}} \text{ \AA}$	$d_{\text{cal}} \text{ \AA}$	I/I_0
111	5.838	5.820	10
200	5.144	5.045	5
220	3.541	3.564	10
222	2.906	2.911	100
331	2.314	2.313	50
442	2.054	2.058	10
511	1.940	1.940	20
440	1.783	1.782	60
531	1.704	1.704	5
620	1.597	1.594	10
622	1.524	1.520	50
444	1.455	1.455	10
711	1.417	1.412	10
731	1.319	1.313	5
800	1.264	1.260	10

Pauly noted a number of significant correlations between composition and physical properties. Associated with a change from a predominantly cubic habit to one showing mainly octahedral faces were a decrease in density, an increase in RI, decreases in the Na and Mg contents and a lowering of F/OH. The Cleveland ralstonite has the highest reported Na+Mg contents and its density ($2.99(1) \text{ g cm}^{-3}$ measured; 3.06 g cm^{-3} calculated), refractive index (1.40) and cell volume (1024.5 \AA^3) are all relatively high. On the basis of Pauly's observations, the crystals from Cleveland would be expected to be simple cubes rather than the simple octahedra observed. This suggests that the Ca-substitution has a significant effect on the crystal morphology.

A full crystal structure study of the calcian ralstonite-like mineral from Cleveland is highly desirable, particularly as there is some question as to whether the space group of ralstonite has been correctly assigned (Pauly, 1965, and Pabst, 1939) and the role of Ca requires clarification. However, preliminary single crystal X-ray photographs of the Cleveland mineral were heavily streaked, indicating that the material is disordered, possibly being composed of small compositional domains. Such a domain structure must be fine-scale, as crystals are compositionally homogeneous at the scale of the electron microprobe beam ($40 \mu\text{m}$). Until the crystal structure is determined and the crystal chemistry clarified, the status of the Cleveland mineral as a possible new species (however strong the chemical evidence) must remain in doubt.

Acknowledgements

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