

Hentschelite is isostructural with lazulite and the lazulite-group minerals which include scorzalite and barbosalite (Sieber *et al.*, 1984). It may be regarded as the Cu-Fe³⁺ analogue of lazulite (scorzalite). As such, Cu occupies the 2(a) site and Fe³⁺ a 4(e) site (of space group No. 14, P2₁n/n) instead of, respectively, (Fe²⁺, Mg) and Al in lazulite (scorzalite). Alternatively, hentschelite may be regarded as the Cu analogue of barbosalite, in which case Cu occupies the 2(a) site instead of Fe²⁺.

The deficiency in Cu in the formula presented above for Spring Creek hentschelite (relative to the lazulite-type formula) is best explained not by invoking vacancies in the 2(a) sites but by redistribution of some of the total Fe to the divalent state. The formula for Spring Creek hentschelite which best fits the ideal structural formula for the lazulite-group minerals, $M^{2+}M_2^{3+}(PO_4)_2(OH)_2$, is one for which approximately 7% of the total Fe is present as Fe²⁺. The formula, based on 10 oxygen atoms, is $(Cu_{0.84}Fe_{0.15}^{2+})_{0.99}(Fe_{1.93}^{3+}Al_{0.02})_{\Sigma 1.95}(PO_4)_{2.05}(AsO_4)_{0.03}(OH)_{1.79}$ (Table 1, 3a). The preferred simplified formula for the South Australian hentschelite is therefore $(Cu, Fe^{2+})Fe_2^{3+}(PO_4)_2(OH)_2$, representing a ferroan hentschelite. This suggests a degree of solid solution from the end-member hentschelite composition towards the end-member barbosalite composition.

Five analyses were obtained on perloffite, three on crystals and two on the massive material. All analyses are richer in Ba than the type material from the Big Chief Mine, South Dakota, USA (Kampf, 1977), to the extent that it was necessary to group all Ca with Mn and Mg for formula calcula-

tion. In both the crystals and the massive variety, variation in Mn, Ca and Fe was noted, with an apparent substitution relationship between Mn and Ca. In the massive form, some of the total iron was assigned to Fe to fill the divalent cation (i.e. 'Mn') site.

The amorphous dark brown glassy material occurring on the perloffite specimens was found to be silica-rich (94 wt. % SiO₂), with small amounts of manganese (4 wt. % MnO) and barium (2 wt. % BaO) and trace amounts of sodium and phosphorus. This composition suggests that the dissolution of this glassy material may have provided the necessary elements for crystallisation of the perloffite.

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New mineral records from Funafuti, Tuvalu: gypsum, brucite, ettringite

AMATUKU is one of the northern islets of Funafuti atoll (lat: 179° E., long: 8° 30' S.) lying north and west of the main inhabited islets of Fongafale-

Tengako. On the eastward-facing ocean coast, ruins of an old wall occur at the top of the intertidal zone, built on an eroding low rampart of dead

reef—part of the 'old breccia sheet undergoing corrosion' of David and Sweet (1904). A large, semi-detached slab of the wall which lies astride the main structure, is encrusted on its landward face by a dense, tubercular growth consisting of aragonite, gypsum and brucite.

The wall is built from algal and coral boulders cemented by gypsum, presumably applied as plaster of Paris. No information could be elicited as to when (or why) it was built. It could date from World War II but may be younger. At its highest point the wall is no more than two metres above the shore platform with about a metre exposed at high tide. Algae and other biogenic deposits encrust the surface and occur within the structure.

The matrix consists of typical bioclastic beach sand cemented by gypsum. Under the microscope this mineral can be seen dusting all the bioclasts as well as occurring in distinct patches between them. Fragments of green bottle glass and coconut fibre were occasionally present in the matrix. No secondary carbonates were found playing an active cementing role. Those that were seen were passive, syntaxial rim cements and, presumably, an original portion of the clast concerned.

Table 1. Partial analyses of ettringite crystals from Tuvalu and elsewhere recalculated anhydrous to 100%

	1	2	3	4	5	6
SiO ₂	—	2.9	2.8	0.4	6.0	—
Al ₂ O ₃	14.4	13.9	13.7	14.0	9.9	15.0
CaO	50.5	52.8	52.8	52.3	53.0	52.8
FeO	1.9	1.6	1.7	1.1	—	—
SO ₃	32.7	26.2	26.3	32.0	24.9	32.2
Cl	0.5	2.6	2.7	0.2	—	—

1,4 Tuvalu

2,3 Two spot analyses of the same crystal, Tuvalu

5 Franklin, New Jersey. After Hurlbut and Baum (1960).

6 Ettringen, Germany. After Lehmann (1874).

Small (<0.5 mm) vugs occur throughout the matrix. Many are lined with fine (50 × 3 μm) acicular crystals, energy dispersive analyses of which are comparable to published analyses of ettringite, recalculated anhydrous to 100% (Table 1 and Fig. 1). No further analytical data could be obtained for these crystals but weak reflections at 9.61, 5.57, 2.77 and 2.56 Å were noted in the X-ray powder diffraction pattern of a crude concentrate prepared by dry mechanical means, and correspond to prominent reflections of ettringite. The crystals proved particularly susceptible to alteration by various liquids and heat.

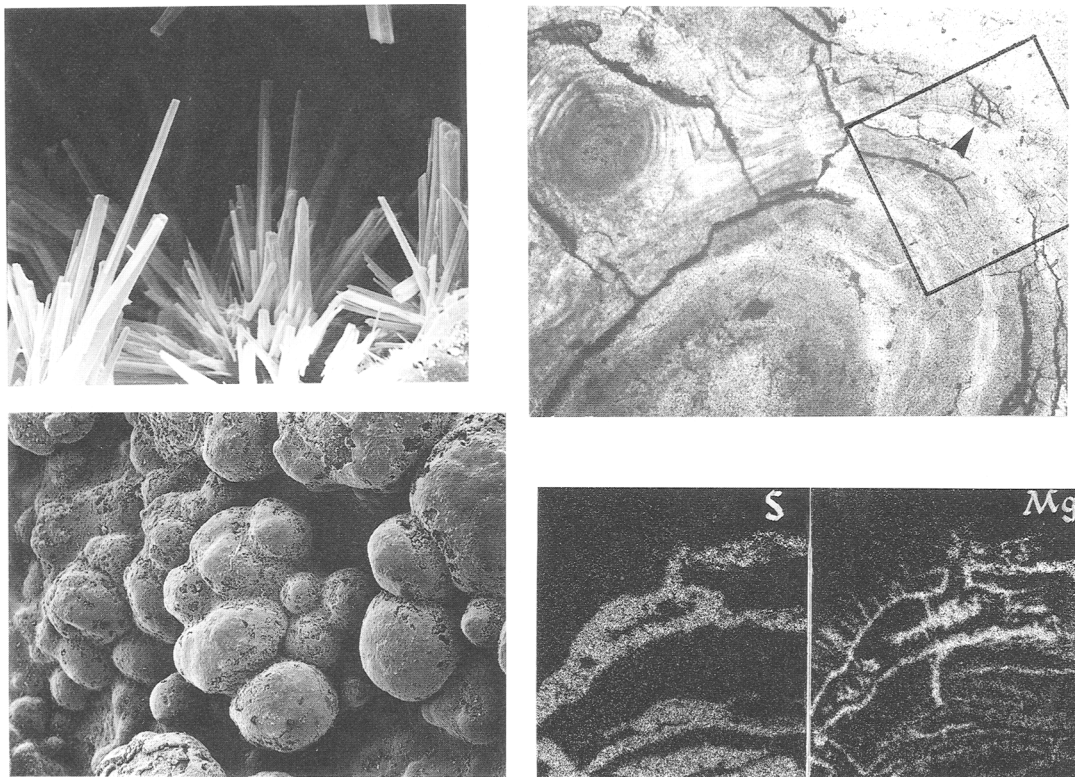
The tubercles of the surface crust are white and commonly 0.25–3 mm in diameter (Fig. 2). They smother the outer face of the slab and are also developed to a minor extent in the interior. Patches on the surface, contrast in having the tubercles mottled grey. Microscopic examination of these areas show the tubercles to be degrading and having a karst topography closely resembling the microphytokarst of Bull and Laverty (1982).

The individual tubercles consist of up to 50 concentric layers, 3–5 μm thick, of microcrystalline aragonite fibres (Fig. 3). Typically, two to three dozen layers are present and the general appearance in thin section is both mottled and faintly pleochroic in pale browns, although these effects may be a consequence of both the slide thickness and its somewhat irregular relief. Fibres are length-fast and arranged with *c* perpendicular to the tubercle surface. No black cross was observed between crossed polars. The smallest crystallite seen was about 0.8 μm long. Most tubercles have from one to six layers of cusp-shaped masses of crystalline gypsum up to 0.04 mm thick, inter-laminated with the aragonite fibre (fig. 3, arrowed). Small veins, <0.01 mm thick, interlink some gypsum layers, several of which are continuous across adjacent tubercles.

X-ray powder diffraction patterns of the tubercles showed strong signatures for both aragonite and gypsum and somewhat diffuse reflections at 4.8, 2.36 and 1.79 Å, corresponding to major reflections of brucite. No brucite could be found in thin sections using conventional optical methods, nor could it be located by staining (Haines, 1968). Back scattered electron imaging of polished sections showed magnesium to be concentrated between gypsum cusps and layers of aragonite as well as being diffused upwards into overlying layers of aragonite fibres. An infra-red absorption spectrum of the tubercles showed a weak absorption at 3700 ± 10 cm⁻¹ which corresponds to a vibrational mode of basic hydroxides with a small to intermediate cation (e.g. Ryskin, in Farmer, 1974). Schmalz (1965) claimed that similar infra-red evidence supported his identification of Mg(OH)₂ in skeletons of *Goniolithon*.

The encrusting tubercles are an efflorescence formed on the highest, sun-facing surface of the wall. While gypsum is documented as an evaporite mineral in an atoll situation (e.g. Schlanger, 1965), brucite is not, although the mineral has been recorded as a sedimentary precipitate at ambient temperatures from high pH waters (Luce, 1971).

The solutions from which the efflorescence formed were presumably sweated-out from and evaporated on the upper surface during dry weather with the solid content crystallizing from



FIGS. 1-4. FIG. 1 (*top left*). Vug lining of acicular ettringite. Base of SEM photograph corresponds to 0.1 mm. FIG. 2. (*lower left*). Tubercles encrusting intertidal surface, Amatuku. Those at centre and right are supported on small pedestals. Cracks and flaking occurred during sample preparation. Base of SEM photograph corresponds to 3 mm. FIG. 3 (*top right*). Micro photograph of thin section of tubercles showing multiple, concentric layer of radially arranged, microcrystalline aragonite fibres and interlaminated, cusp-shaped masses of more coarsely crystalline gypsum (arrowed). Plane polarised light. Base of photograph is 1.5 mm. FIG. 4 (*lower right*). X-ray scanning images of area outlined in Fig. 3 for sulphur and magnesium showing concentration of magnesium about, but not within the sulphur-rich areas, as well as occurring within immediately overlying layers of fibrous aragonite.

successive liquid films. Sea water was a likely component of the parent solution but rainwater would probably have been the primary solvent, saturating the upper levels of the wall during the frequent tropical downpours and promoting solution of the various biominerals (magnesian calcite, aragonite and brucite) along with the artificial gypsum cement.

The precise sequence of crystallization is unclear. Thin section examination suggests that in part aragonite \rightarrow gypsum \rightarrow brucite \rightarrow brucite + aragonite \rightarrow aragonite. However, other phases may have crystallized only to be dissolved during the next shower, and the substrate on which the next brine film evaporated may simply have been the least soluble layer remaining following any dissolution; invariably a layer of aragonite fibres.

Crystallization of aragonite would have been

promoted by the presence of Mg^{2+} in solution (Lippmann, 1973) while gypsum is known to accompany the precipitation of $CaCO_3$ during the artificial evaporation of sea water (Usiglio, in Clarke, 1924). Brucite is not known to crystallize naturally from sea water but has been obtained experimentally by Gulbrandson and Cremer (1970) as a co-precipitate with aragonite when the pH had been artificially brought to 9.9. Further, aragonite and brucite are known to enjoy a metastable relationship over a range of calcium and magnesium concentrations where p_{CO_2} is less than 10^{-7} atmospheres (Carpenter, in Schmitt, 1962). Reduced carbonate concentrations consequential upon rapid non-equilibrium crystallization of aragonite from a diminishing brine film, may have provided conditions comparable to those resulting from reduced partial pressures of CO_2 . A heightened

pH coupled with an increase in the activity of Mg^{2+} following precipitation of aragonite and gypsum, may have provided the necessary conditions to initiate crystallization of brucite.

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