

BAYERITE, NORDSTRANDITE, GIBBSITE, BRUCITE, AND PSEUDOBOEHMITE IN DISCHARGED CAUSTIC WASTE FROM CAMPBELL ISLAND, SOUTHWEST PACIFIC

Key Words—Aluminum hydroxide, Bayerite, Brucite, Campbell Island, Gibbsite, Nordstrandite, Pseudoboehmite.

Rodgers *et al.*, (1989) described a deposit of bayerite [β -Al(OH)₃] on subtropical Raoul Island (lat. 29°14'S, long. 177°55'E), which resulted from discharge of spent caustic solutions used to produce hydrogen at a meteorological station. In the few samples available for study, no other aluminum hydroxide phases were recognized. Subsequently, two small collections of specimens from a similar discharge on subantarctic Campbell Island (lat. 52°33'S, long. 169°08'E) were obtained from the New Zealand Department of Conservation. A preliminary X-ray powder diffraction examination indicated that although bayerite was the principal constituent here also, gibbsite and nordstrandite were probably present. Additional study of the samples was undertaken to confirm the presence of all three polymorphs and to ascertain if these mineralogical differences were significant. The two deposits have developed under distinctly different climatic regimes.

FIELD OCCURRENCE

Campbell Island lies about 600 km south of the main islands of New Zealand. On Beeman Point, in Perseverance Harbour, the New Zealand Meteorological Service maintains a low-pressure hydrogen generator for servicing high-altitude balloons. Hydrogen has been produced at this station since the early 1960s by reacting aluminum filings with caustic soda solution, using the same recipe as at Raoul Island (Rodgers *et al.*, 1989). The spent liquor is flushed from the chamber and discharged through a sluice channel made of steel drums into Perseverance Harbour; the waters in the vicinity of a spill becoming markedly cloudy.

Brown-stained, solid aluminum hydroxide lines the sluice and coats rocks in the upper intertidal zone for about 20 m along the shore. Much of the exposure is coated with blue-green filamentous algae. Reaction between these algae and the caustic solution seemingly gives rise to the all-pervading brown stain (see Stach *et al.*, 1975, 36–37).

EXPERIMENTAL

Two small bags of loose-packed samples were examined: one consisted of pieces broken from the deposit lining the steel sluice (Auckland University Geology Department, Mineralogy Collection: #3065), the other of fragments from the intertidal deposit (AU #3066, #3067). These samples may not be fully rep-

resentative of the deposit, but access difficulties precluded a visit by the authors and systematic sampling. As most pieces were coated with degraded organic matter, few were found to be suitable for scanning electron microscope (SEM) examination of crystal morphologies.

X-ray powder diffraction (XRD) of ten pieces from each bag was made using a Philips diffractometer fitted with a graphite monochromator. Raman and infrared (IR) spectroscopic examinations of the samples were also made using the instrumental conditions detailed by Cooney *et al.* (1989) and Rodgers *et al.* (1989) to confirm the mineral identity of the various aluminum hydroxide polymorphs. Both macroscopic and microscopic sampling procedures were used with the Raman instruments, but, whereas XRD permitted sampling of a relatively large portion of each piece, constraints of time and technique allowed the Raman spectra to be measured of only a few small areas and of crystal fragments of each sample.

RESULTS

Petrography

In hand specimen and thin section the aluminum hydroxide encrustations from Campbell Island are less coarsely crystalline and lack the botryoidal habit of those from the Raoul Island deposit (Rodgers *et al.*, 1989). All Campbell Island specimens are strongly laminate (Figure 1A). Algal threads abound, and large plant fragments, such as twigs and leaves, are common. Thin sections of the deposit have a pale, yellow-brown color in plain polarized light, presumably arising from the pervasive organic contamination. An irregular and indistinct, clotted texture, reminiscent of bacterial clumps, is similar to, although less pronounced than that noted at Raoul Island (Rodgers *et al.*, 1989). Locally restricted and patchy mosaics of vesicle-like structures are suggestive of original bubbles or 'frozen foam' (Figure 1B).

X-ray powder diffraction

XRD powder patterns of three typical fragments from Campbell Island are compared in Figure 2 with that obtained from one Raoul Island specimen reported by Rodgers *et al.* (1989) and with published patterns of Al(OH)₃ polymorphs. Both the Campbell Island and

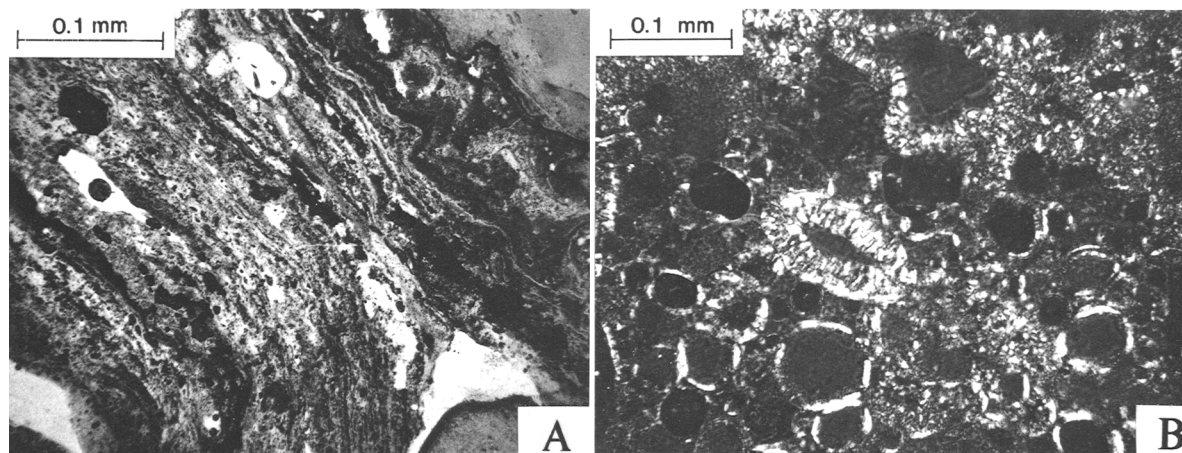


Figure 1. Photomicrographs showing: (A) typical layered aluminum hydroxide encrustation with cryptocrystalline texture and finely multilaminar fabric; and (B) possible 'frozen bubbles,' some displaying passive crystal growths around periphery. Sample AU #3066.

Raoul Island samples show a strong, high-angle reflection at 4.77–4.79 Å. This d-value is close to the ~4.8-Å spacing reported for both gibbsite and nordstrandite, and, although it is in the range reported for bayerite, it is larger than is typical for this mineral (4.71–4.72 Å) (see Rodgers *et al.*, 1989). Nevertheless, this 4.77–4.79-Å reflection, shown by all Campbell Island samples, is always accompanied by strong reflections at 4.4 and 2.2 Å, which are characteristic of bayerite. A distinct nordstrandite pattern accompanying strong reflections of bayerite was noted in the XRD trace of only one sample: a brown-stained surface layer (AU #3065) taken from within the sluice. This sample appears to be a very recent precipitate.

In most Campbell Island samples, the shape of the 4.77–4.79-Å peak is markedly more asymmetric than those observed in patterns of Raoul Island samples, and the peak is skewed towards low 2θ angles (Figure 2, trace 1). In some patterns, this peak appears as a doublet having submaxima at about 4.85 and 4.78 Å (Figure 2, traces 2 and 3). The 4.85-Å submaximum is accompanied by weak, diffuse gibbsite reflections at 3.31, 2.37, 2.04, and 1.998 Å, with weak shoulders at about 3.18 and 2.24 Å on the side of strong 3.2- and 2.22-Å bayerite reflections. This dual pattern is common for samples examined from the intertidal zone and for several fragments from the sluice.

Some bayerite exhibits strong 4.4- and medium 2.2-Å reflections, with the 4.7-Å reflection being weak or missing as a result of poor development of the basal planes (e.g., Yamaguchi and Sakamoto, 1960; Schoen and Roberson, 1970). The intensity of nordstrandite and gibbsite lines in the Campbell Island XRD patterns suggests that the overall patterns did not arise from a mixture of bayerite having poorly developed basal planes and significant nordstrandite and/or gibbsite;

these last two minerals give rise to the very strong 4.77–4.79-Å reflection.

The sluice sample (AU #3065) that showed the XRD trace of nordstrandite also contained broad reflections at about 8 and 3.8 Å, suggestive of pseudoboehmite, sometimes reported as a precursor of bayerite (Herbillion and Gastuche, 1962; Schoen and Roberson, 1970; Violante and Huang, 1984).

The XRD pattern of one fragment (AU #3067) showed weak, broad reflections at 2.36 and 1.78 Å, indicative of brucite; the major brucite reflection at 4.77 Å is coincident with the prominent 001 reflection of bayerite. The presence of poorly crystalline brucite in this environment is not inconsistent with the chemistry of the system, Gulbrandson and Cramer (1970) having obtained brucite + aragonite on titrating seawater with an excess of NaOH. Furthermore, spot electron microprobe analyses of polished thin sections of both intertidal and sluice samples indicated appreciable amounts of MgO (0.5–11.2 wt. %) in some samples, along with CaO (0.1–2.1 wt. %). The highest levels of Mg (and Ca) were found in patches of the sample most intensely stained by brown organic mucilage.

Raman spectra

A laser Raman spectra of the surface of samples taken from within the steel sluice and of all but one area of one specimen examined from the intertidal deposit showed the distinctive ν -(OH) stretching modes of bayerite at about 3425, 3545, and 3655 cm^{-1} , as did the Raman spectra of all microsampled crystal fragments (cf. Huneke *et al.*, 1980; Cooney *et al.*, 1989; Rodgers *et al.*, 1989). A diffuse spectrum obtained from a surface area of one fragment of the intertidal deposit (AU #3066) contained two major Raman lines of gibbsite and none of bayerite. SEM examination of an area

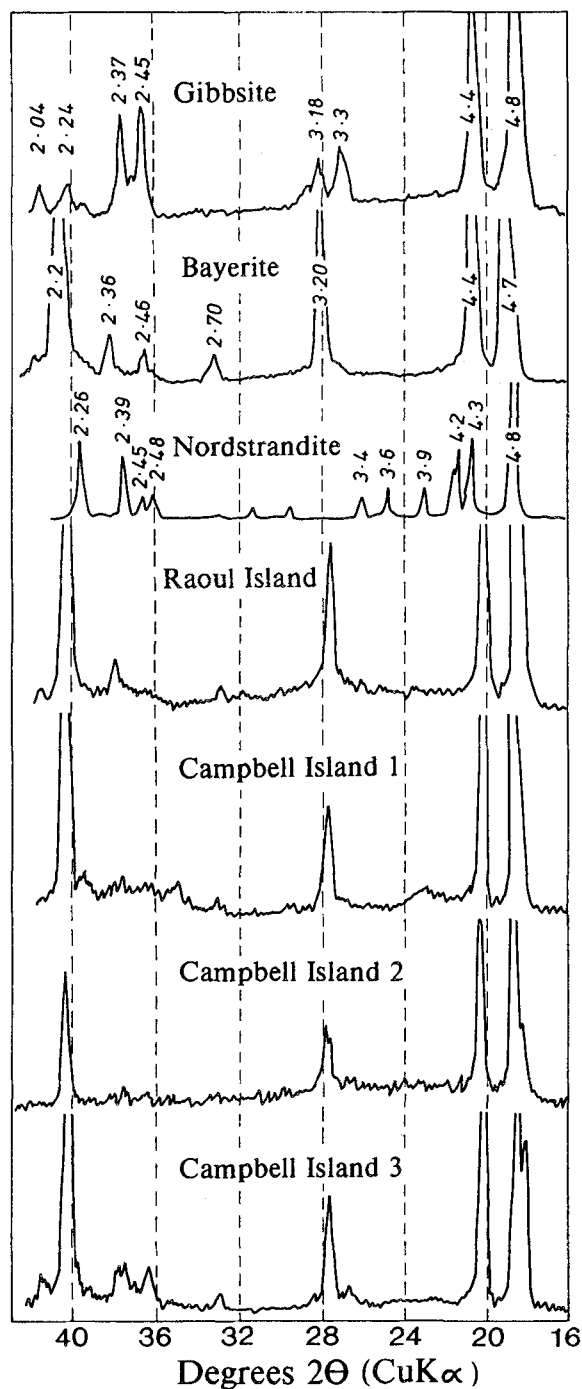


Figure 2. X-ray powder diffraction patterns of alumina polymorphs (after Schoen and Roberson, 1976) and hydrogen generator precipitates from Raoul Island and Campbell Island. Campbell Island 1: typical bayerite trace of sample from sluice, sample AU #3065. Campbell Island 2 and 3: examples of patterns of samples from shore deposit consisting of bayerite and minor gibbsite, sample AU #3067.

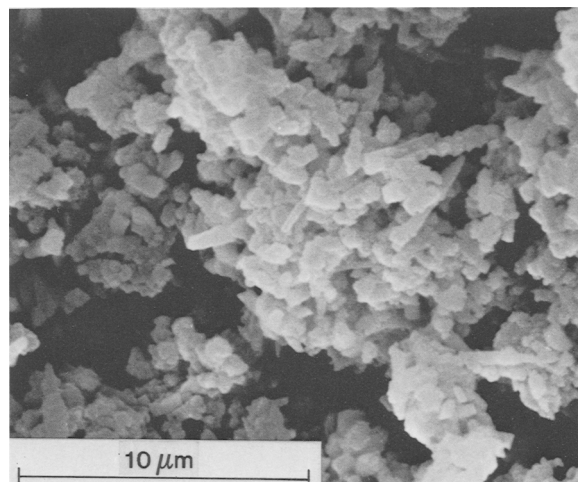


Figure 3. Scanning electron micrograph of ultra fine grained aluminum hydroxide microlites. Photographed area of specimen is adjacent to that examined by laser Raman analysis, which yielded gibbsite scattering bands.

of this same specimen, adjacent to that examined by Raman spectroscopy showed a felted mat of ultrafine crystallites (Figure 3), which included both hexagonal tablets, 1–2 μm across, and prismatic laths as long as 3 μm , which are similar to crystallites identified as gibbsite by McHardy and Thomson (1971, p. 363, Figures 2b and 2d). Elsewhere in sample AU #3066 clusters of larger crystals, as wide as 13 μm , showed boss-like protuberances atop the uppermost layer of crystal sediment (Figure 4). Energy-dispersive X-ray examination indicated Al to be the only abundant cation: the protuberances are therefore probably parallel growths of prismatic bayerite.

Infrared spectra

The IR spectra of all Campbell Island samples showed absorption bands at about 3550, 3470, 3420, and 760 cm^{-1} which are typical of bayerite. No distinct bands of gibbsite were recognized, but in a fragment from the sluice (AU #3065), a series of shoulders on prominent bayerite bands were noted at 3555, 3360, 1030, 965, 820, 770, and 700 cm^{-1} , coincident with nordstrandite absorptions (see van der Marel and Beutelspacher, 1976). Spectra of heavily brown-stained samples contained bands at about 2950, 2925, 2850, 2005, 1650, 1560, 1405, 860, and 515 cm^{-1} . Some of these absorptions are in the region of the IR spectrum in which contamination of samples by finger(print) grease has typically been recognized, but others might be due to carboxylates and aromatics, derived from degradation of algae.

DISCUSSION

Numerous factors influence the polymorphic nature of an initial aluminum hydroxide precipitate, including

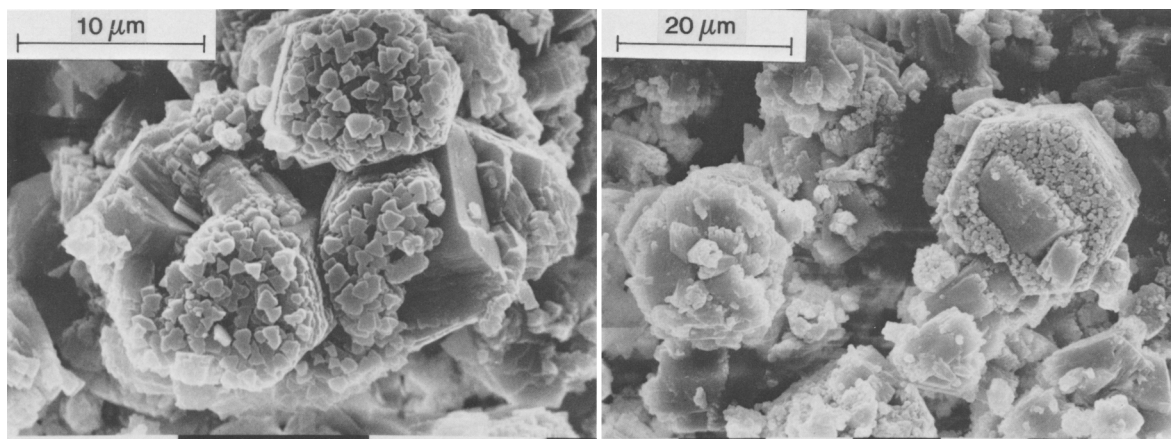


Figure 4. Scanning electron micrographs of boss-like, hexagonal, aluminum hydroxide crystal growths at top of uppermost crystal sediment layer, Campbell Island intertidal deposit. Sample AU #3066.

pH, NaOH/Al ratio, temperature, kinetics, the presence and absence of ligands and foreign ions, particularly anions (see Schoen and Roberson, 1970; McHardy and Thomson, 1971; Elderfield and Hem, 1973; Hsu, 1988; Singer and Huang, 1990). Subsequent crystal chemical changes that the precipitate may undergo through aging are dictated by similar chemical and physical influences (e.g., Herbillon and Gastuche, 1962; Hsu and Bates, 1964; Sato *et al.*, 1969; Schoen and Roberson, 1970; McHardy and Thomson, 1971; Elderfield and Hem, 1973). Consequently, the conditions of formation and any subsequent physicochemical history of a given deposit cannot readily be defined from the crystal chemical nature of the resultant products.

Manifest differences exist between Raoul and Campbell Islands in both climate and the substrates on which the aluminum hydroxide encrustations have developed, and these may have exercised some influence on the mineral phases precipitated. Raoul Island is subtropical: sunny, warm, moderately humid and given to periods of drought (Bates, 1922; Wright and Metson, 1959). In contrast, Campbell Island is subantarctic: cool and humid with persistent rain and drizzle. It has very few sunshine hours (Oliver *et al.*, 1950; De Lisle, 1964).

At subantarctic Campbell Island the aluminum hydroxide precipitates both directly in the sea and amongst semi-permanently wet rocks of the intertidal zone. The moist conditions might assist aging of the initial precipitate and consequential changes in the crystal chemistry in a manner similar to that described by Schoen and Roberson (1970) or Elderfield and Hem (1973). Whether bayerite forms directly in seawater and accumulates as a crystalline sediment between intertidal boulders, or crystallizes between tides directly on boulders, any alkali residue would be readily diluted. The periodic immersion at the pH of seawater could aid a

subsequent inversion to gibbsite, as reported by Fricke (1928), Sato (1961), Schoen and Roberson (1970), Elderfield and Hem (1973). Moreover, in the discharge sluice the crystallizing alkaline solution is probably relatively undiluted. At high pH bayerite can invert to nordstrandite (Schoen and Roberson, 1970).

At subtropical Raoul Island, the alkaline aluminate solution is discharged over and through well-drained cliffs of thick, highly porous tuffs that are exposed to the drying effects of wind and sun. A substantial portion of the liquor crystallizes well beyond the reach of the waves. The relatively dry conditions give only limited opportunity for solution aging of an initial precipitate and consequential changes in its crystal chemistry.

Brucite is not known to crystallize naturally from seawater. In Gulbrandson and Cramer's (1970) experiment, brucite formed at pH 9.9 and coprecipitated with aragonite. At Campbell Island, no calcium carbonate (or hydroxide) phase was identified in any of the samples examined. Whereas the formation of brucite may be a simple function of pH, it may also be related to local changes in the activity of Mg^{2+} , albeit temporary, immediately following admixing of the spent solution with seawater either directly into the sea, or, more likely, of that saturating the algal mats covering the foreshore boulders (cf. Marboe and Bentur, 1961).

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