

## SHORT COMMUNICATIONS

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### An occurrence of akaganéite ( $\beta$ -FeOOH · Cl) in Recent oxidized carbonate concretions, Norfolk, England

THE natural occurrence of  $\beta$ -FeOOH was first reported by M. Nambu (cited by Mackay, 1962), and named akaganéite after the locality, Akagané mine, Iwate Prefecture, Japan. Subsequent reports of natural occurrences of this mineral have been few. Logan *et al.* (1976) suggested on the basis of Mössbauer data that akaganéite is present in some New Zealand soils. Johnston (1977) identified akaganéite coating andesite boulders at White Island volcano, New Zealand. Johnston and Glasby (1978) reported akaganéite as a secondary oxyhydroxide mineral in marine and fossil manganese nodules. Rozenson *et al.* (1980) found the mineral in Jurassic evaporite deposits at Makhtesh Ramon, Israel. Akaganéite also occurs in Red Sea hot brines (Holm *et al.*, 1983; Holm, 1984).

The author recently identified akaganéite as a significant component in oxidized siderite-calcite-iron-sulphide concretions at Warham, north Norfolk, England. The concretions are actively forming in reduced intertidal marsh and sandflat sediments (Pye, 1981, 1984). Fresh, *in situ* concretions are black, but where they have been exposed by wave action or creek bank collapse they are partially oxidized and show brown, yellow and orange mottling. When sectioned many oxidized concretions were found to contain zones of relatively

pure iron oxyhydroxide, up to several  $\text{cm}^3$  in volume, close to the centre. This material appeared to be replacing wood and/or metal nuclei around which the concretions grew.

X-ray powder diffraction analysis indicated the oxyhydroxide is akaganéite. The diffraction patterns obtained showed a close similarity to that for synthetic  $\beta$ -FeOOH reported by Mackay, 1960 (Table 1).

Energy-dispersive X-ray microanalysis performed in the scanning electron microscope showed the akaganéite contains a significant amount of  $\text{Cl}^-$ , with traces of Cr, Mn, Si and S (Fig. 1). Reliable quantitative chemical data could not be obtained by this method due to the very small size of individual akaganéite crystals ( $< 0.5 \mu\text{m}$ ) and the difficulty of preparing satisfactory polished sections.  $\text{Cl}^-$  is known to favour the formation of  $\beta$ -FeOOH (Weiser and Milligan, 1935), and may be essential to stabilize its structure which is of the hollandite type, comprising square-sided tunnels (each side  $5 \text{ \AA}$  in dimension) parallel to the *c*-axis. The tunnels can accommodate large anions, especially  $\text{Cl}^-$  but also  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ .

Table 1. XRD data for Norfolk akaganéite compared with synthetic  $\beta$ -FeOOH (Mackay, 1960) and natural akaganéite from the Red Sea hot brines (Holm *et al.*, 1983)

ASTM 13-157 (Mackay, 1960)		Norfolk (this paper)		Red Sea hot brine (Holm <i>et al.</i> , 1983)	
$d_{\text{obs}} \text{ \AA}$	$I/I_1$	$d_{\text{obs}} \text{ \AA}$	$I_{\text{rel}}$	$d_{\text{obs}} \text{ \AA}$	$I_{\text{rel}}$
7.40	100	7.48	medium	7.32	medium
5.25	40	5.23	weak	5.21	v. diffuse
3.70	10	3.72	v. weak		
3.31	100	3.32	v. strong	3.31	strong
2.61	40	2.63	weak	2.59	v. weak
2.54	80	2.54	strong	2.54	medium
2.34	20	2.33	v. weak		
2.28	40	2.29	medium		

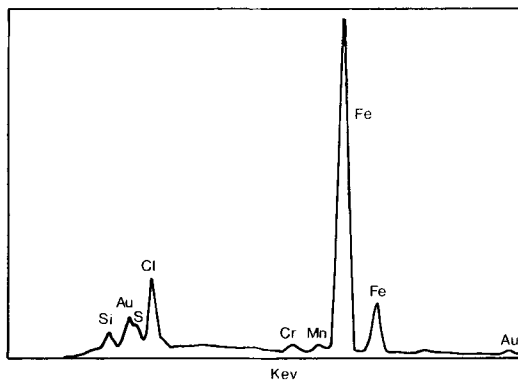


FIG. 1. Energy-dispersive X-ray spectrum obtained from a flat surface of aggregated akaganéite (specimen is gold coated).

(Gallagher, 1970; Murray, 1979). It is uncertain whether some  $\text{Cl}^-$  also substitutes for structural  $\text{OH}^-$ .

The  $\text{Cl}^-$ -rich nature of the Norfolk akaganéite is consistent with its formation in waters of near-marine composition. Surface waters in the lower marsh-sandflat system, which is covered by about 65% of tides, typically contain 18000–19000 ppm  $\text{Cl}^-$ ; porewaters from 10–40 cm below the surface of the lower marsh contain 20000–24000 ppm  $\text{Cl}^-$  (average seawater = 18986 ppm  $\text{Cl}^-$ ).

### References

- Gallagher, K. J. (1970) The atomic structure of tubular subcrystals of  $\beta$ -iron (III) oxide hydroxide. *Nature* **226**, 1225–8.
- Holm, N. G. (1984) The structure of  $\beta\text{-FeOOH}\cdot\text{Cl}$  (akaganéite) and its uptake of amino acids (from Red Sea hot brines). *Origins of Life* **14**, 343–50.
- Dowler, M. J., Wadsten, T., and Aarhenius, G. (1983)  $\beta\text{-FeOOH}\cdot\text{Cl}_n$  (akaganéite) and  $\text{Fe}_{1-x}\text{O}$  (wustite) in hot brine from the Atlantis II Deep (Red Sea) and the uptake of amino acids by synthetic  $\beta\text{-FeOOH}\cdot\text{Cl}_n$ . *Geochim. Cosmochim. Acta* **47**, 1465–70.
- Johnston, J. H. (1977) Jarosite and akaganéite from White Island volcano, New Zealand: an X-ray and Mossbauer study. *Ibid.* **41**, 539–44.
- and Glasby, G. P. (1978) The secondary iron oxide hydroxide mineralogy of some deep sea and fossil manganese nodules: a Mossbauer and X-ray study. *Geochem. J.* **12**, 153–64.
- Logan, N. E., Johnston, J. H., and Childs, C. W. (1976) Mossbauer spectroscopic evidence for the occurrence of akaganéite in New Zealand soils. *Austral. J. Soil Res.* **14**, 217–24.
- Mackay, A. L. (1960)  $\beta$ -ferric oxyhydroxide. *Mineral. Mag.* **32**, 545–57.
- (1962)  $\beta$ -ferric oxyhydroxide—akaganéite. *Ibid.* **34**, 270–9.
- Murray, J. W. (1979) Iron oxides. In *Marine Minerals* (Burns, R., ed.) Mineral. Soc. Am. Short Course Notes **6**, 47–98.
- Pye, K. (1981) Marshrock formed by iron sulphide and siderite cementation in saltmarsh sediments. *Nature* **294**, 650–2.
- (1984) SEM analysis of siderite cements in intertidal marsh sediments, Norfolk, England. *Marine Geol.* **56**, 1–12.
- Rozenson, I., Zak, I., and Spiro, B. (1980) The distribution and behaviour of iron in sequences of dolomites, clays and oxides. *Chemical Geol.* **31**, 83–96.
- Weiser, H. B., and Milligan, W. D. (1935) X-ray studies on hydrous oxides. V. Beta ferric oxide monohydrate. *J. Am. Ceram. Soc.* **57**, 238–41.
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## Spencerite from Kabwe, Zambia, and the infrared spectroscopy of the Kabwe zinc phosphates

AMONG a suite of specimens from Kabwe, Zambia (previously known as Broken Hill, Northern Rhodesia) sent to Mr L. Clark and the author for investigation was a small piece consisting mainly of a portion of a very pale greenish hemimorphite nodule with 2–3 mm thick solid walls. The matrix within this hemimorphite nodule had been dissolved away and partly replaced by tiny colourless spiky smithsonite crystals, while colourless thick blades of hopeite to about 5 mm sit on the hemimorphite. Spanning spaces between hemimorphite and hopeite crystals, and growing around the hopeite are

colourless pearly thin lath-shaped crystals to about 7 mm in length, representing the latest generation of mineralization present. The infrared spectrum of these laths indicates that they are the rare zinc phosphate spencerite,  $\text{Zn}_4(\text{PO}_4)_2(\text{OH})_2\cdot 3\text{H}_2\text{O}$ . Spencerite has only been reported before from two localities, Hudson's Bay mine, Salmo, British Columbia, the type locality (Walker, 1916, 1918), and Turf Pits mine, Grassington, Yorkshire (British Museum (Natural History) specimen, collected by A. W. G. Kingsbury in 1963; see Embrey, 1978). The rarity of spencerite is due to the fact that it is