

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

The 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 Cl^- ; porewaters from 10–40 cm below the surface of the lower marsh contain 20000–24000 ppm Cl^- (average seawater = 18986 ppm Cl^-).

References

- Gallagher, K. J. (1970) The atomic structure of tubular subcrystals of β -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 Fe_{1-x}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) β -ferric oxyhydroxide. *Mineral. Mag.* **32**, 545–57.
- (1962) β -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

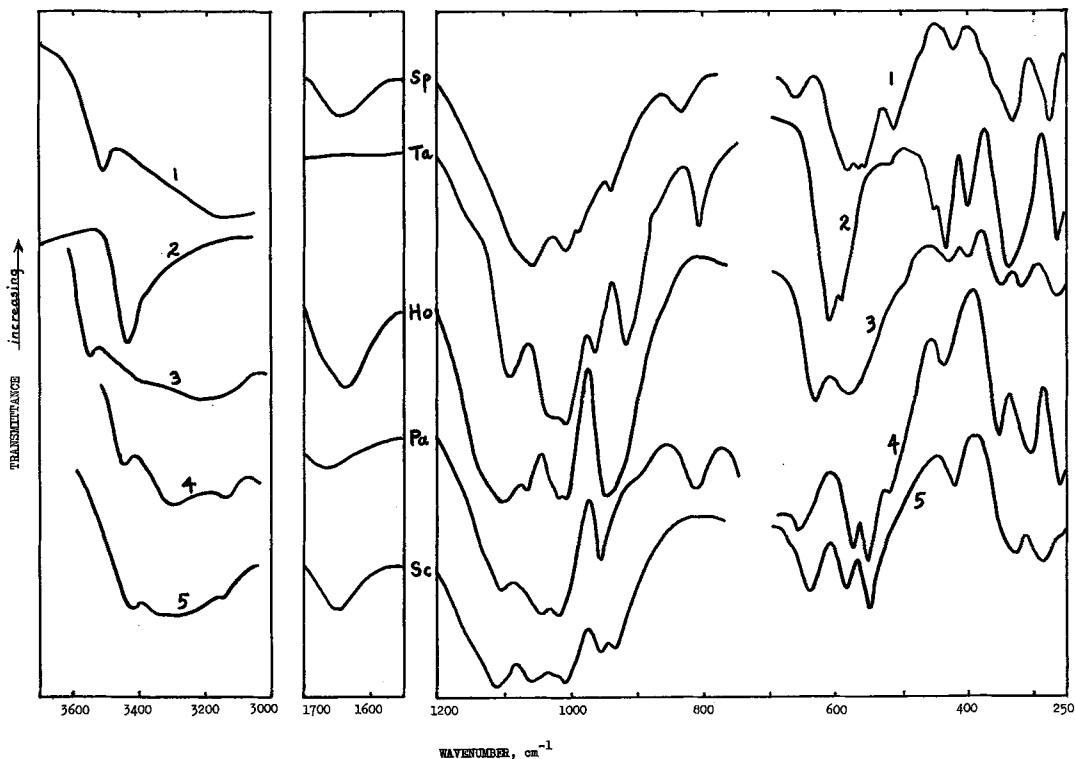


FIG. 1. Infrared spectra of the Kabwe zinc phosphate minerals, measured in Nujol mulls between CsI plates, using a Perkin-Elmer PE 783 precision grating spectrophotometer: 1, Spencerite, British Columbia, off RSWB 68-329; 2, Tarbuttite, Kabwe, off RSWB 82-20; 3, Hopeite, Kabwe, off RSWB 83-3; 4, Parahopeite, Kabwe, off RSWB 83-4; 5, Scholzite, Reaphook Hill, S. Australia, off RSWB 77-35. Spectra of spencerite and scholzite from Kabwe, off RSWB 83-9 and 83-6 respectively were measured under similar conditions (but using KBr plates) over the 4000–400 cm^{-1} range using a Perkin Elmer 397 spectrophotometer, and gave similar spectra over that range to those shown.

thermodynamically unstable with respect to tarbuttite in aqueous solutions at ambient temperature (Magalhães *et al.*, 1986). Tarbuttite is common at Kabwe, and the spencerite under study must have been formed as a metastable product within the protective confines of the hemimorphite nodule. The type material from British Columbia was also found in cores of protective hemimorphite (Walker, 1916, 1918).

For a fairly recent general account of the mineralisation at Kabwe see Notebaart and Korowski (1980).

The infrared spectrum of the Kabwe spencerite is similar to that of a spencerite from the type locality. The spectrum is quite characteristic, and easily distinguished from those of the related zinc phosphates hopeite, parahopeite, tarbuttite and scholzite, all of which are found at Kabwe, and of course also from the associated silicate hemimorphite, sometimes misidentified visually as a zinc phos-

phate. These spectra are shown in Fig. 1. Wavenumbers of absorption maxima and assignments are tabulated in Table 1. These assignments are based mainly on the known positions of absorption bands for isolated ions (Hertzberg, 1945; Nakamoto, 1978) and on comparison with published assignments for related compounds (see notes to Table 1).

From published X-ray structural data (Chao, 1969; Cocco *et al.*, 1966; Fanfani *et al.*, 1972; Hill and Jones, 1976; Taxer, 1975) it can be seen that in each of these minerals the phosphate ions occupy only one site, and that the PO_4 symmetries are C_1 in each case, although in the case of spencerite (Fanfani *et al.*, 1972) the coordination about the phosphate ions suggests a higher site symmetry, C_2 , and the uncertainties in the published P–O distances and O–P–O bond angles overlap, so that C_2 symmetry can indeed be accommodated. Examination of the site splittings of the infrared absorption

Table 1. Positions of infrared absorption maxima, and their assignments, for the Kabwe, Zambia zinc phosphate minerals

| Absorption maxima, cm^{-1} , Intensities | | | | | Assignments |
|---|---------------------|-----------------|--------------------------|-----------------------------|---|
| Spencerite | Tarbuttite | Hopelite | Parahopeite | Scholzite | |
| 3510 ms, sp | 3430 s, sp | 3530 s | 3440 ms | ~3510 mw, sh 3420 m | O-H stretch, increasingly hydrogen bonded as wavenumber decreases. |
| ~3140 s, br | | ~3160 vs, br | 3280 s, br 3120 s, br | ~3300 sm, br ~3150 m, sh | |
| 1650 mw | | 1640 s | 1680 m, br | 1653 m | H-O-H "scissor" in-plane deformation. |
| 1066 vs | 1090 s | 1066 s | 1060 sh | 1058 vs | PO ₄ ν_3 unsymmetrical stretch. Metal O-H in-plane bend. Note 1. |
| 1010 vs | 1030 vs | 1020 s, sh | 1046 vs | | |
| 992 s, sh | 1000 vs | 1006 vs | 1013 vs | 1003 vs | PO ₄ ν_1 symmetrical stretch. Metal O-H bend. Note 2. |
| 943 m | 955 s | 945 s | 952 s, sp | 955 s | |
| 843 wm | 802 ms | | 805 m | | Zn-O-H bend? Note 3. |
| 667 wm | | 633 ms | 650 ms | 638 ms | Zn-OH ₂ twist. Note 4. |
| 595 sm | 605 s | | | | PO ₄ ν_4 unsymmetrical bend. Note 5. |
| 580 sm | 583 s | 580 ms | 568 ms | 582 ms | |
| 560 sm | 525 m | | 545 s, sp | 545 s | Zn-OH ₂ wag. PO ₄ ν_4 unsymmetrical bend. Note 6. |
| 515 m | | 500 w, sh | 510 m, sh | | |
| 417 wm | 450 sh, m 435 ms | 433 mw | 425 m | 420 m | Zn-OH ₂ stretch (?), PO ₄ ν_2 symmetrical bend. Note 7. |
| 340 ms | 398 m, sp | 350 ms | 352 ms | ~350 sh | Metal-OH ₂ stretch. Note 8. |
| 270 ms | 321 ms 260 ms | 318 ms 272 m | 300 ms 260 ms | 322 ms 265 ms | Metal-O? |

s = strong, m = medium, w = weak, sh = shoulder, sp = sharp, br = broad, v = very

1. Spencerite, $\text{Zn}_4(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}$.
2. Tarbuttite, $\text{Zn}_2\text{PO}_4\text{OH}$.
3. Hopelite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (orthorhombic).
4. Parahopeite, $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ (triclinic).
5. Scholzite, $\text{CaZn}_2(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Notes to Table 1.

1. PO₄ ν_3 is at 1031, 999, 967 cm^{-1} in pyromorphite, for example (Levitt and Condrate, 1970). Three maxima expected for C₁ or C₂ symmetry. Metal O-H in-plane bending vibrations are near 1000-1100 cm^{-1} , at lower wavenumbers for bridging O-H (Nakamoto, 1978). Spencerite and tarbuttite both have bridging OH groups.
2. PO₄ ν_1 is at 980 cm^{-1} for isolated ion (Hertzberg, 1945), 927 cm^{-1} in pyromorphite (Levitt and Condrate, 1970). Should be one absorption, forbidden and therefore weak, and may be hidden under edge of ν_3 absorption. ZnO-H deformation in adamite is at 885 cm^{-1} (Braithwaite, 1983).
3. A ZnO-H out-of-plane bend in $\epsilon\text{-Zn}(\text{OH})_2$ is at 830 cm^{-1} and in ZnOHCl and ZnOHF at 855 and 790 cm^{-1} (Srivastava and Secco, 1967), but parahopeite has no non-water OH. The coordinated water rock in hydrated zinc sulphate is at 758 cm^{-1} according to Camo (1961).
4. The coordinated water twist in hydrated zinc sulphate is at 621 cm^{-1} (Kerमारrec, 1964). Absent in the spectrum of tarbuttite, which has no H₂O.
5. PO₄ ν_4 is at 575, 543 cm^{-1} in pyromorphite (Levitt and Condrate, 1970). Three maxima expected for C₁ or C₂ symmetry.
6. Coordinated water wag in hydrated zinc sulphate is at 541 cm^{-1} (Nakagawa and Shimanouchi, 1964), 555 cm^{-1} (Kerमारrec, 1964).
7. PO₄ ν_2 is at 436 cm^{-1} in pyromorphite (Levitt and Condrate, 1970). Forbidden, and therefore very weak. Doubly degenerate, with two maxima expected for C₁ and C₂, and one maximum for C_{2v} symmetry. See text. Stretching vibrations of coordinated water to metals such as Zn are also in this region.
8. The Zn-O stretching vibration of coordinated water in hydrated zinc sulphate is at 364 cm^{-1} (Nakagawa and Shimanouchi, 1964). Tarbuttite lacks water.

maxima by degeneracy removal cannot resolve this problem, unfortunately, as both C_1 and C_2 symmetry would involve loss of all degeneracy, giving nine infrared active modes ($1 \times \nu_1$, $2 \times \nu_2$, $3 \times \nu_3$, $3 \times \nu_4$). The spectra of spencerite, parahopeite and scholzite appear to show only one absorption maximum each in the $\text{PO}_4\nu_2$ region (at 417, 425 and 420 cm^{-1} respectively) as though their site symmetries were C_{2v} or higher. These absorptions, however, are appreciably stronger than would be expected for this symmetrical and therefore infrared forbidden vibration, and must be derived from some other vibration, possibly a Zn-OH_2 stretch, concealing the phosphate ν_2 band multiplicity by burial. Tarbutite has two rather strong bands in this region, of unknown assignment; it lacks co-ordinated water and the absorption bands are far too strong for phosphate ν_2 vibrations.

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References

Braithwaite, R. S. W. (1983) *Mineral. Mag.* **47**, 51–7.
Chao, G. Y. (1969) *Z. Kristallogr.* **130**, 261–6.

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Cocco, G., Fanfani, L., and Zanazzi, P. F. (1966) *Ibid.* **123**, 321–9.
Embrey, P. G. (1978) *Mineral. Mag.* **42**, 169–77.
Fanfani, L., Nunzi, A., and Zanazzi, P. F. (1972) *Ibid.* **38**, 687–92.
Gamo, I. (1961) *Bull. Chem. Soc. Japan*, **34**, 760–4.
Hertzberg, G. (1945) *Molecular Spectra and Molecular Structure*, Vol. 2. *Infrared and Raman Spectra of Polyatomic Molecules*. Van Nostrand, New York.
Hill, R. J., and Jones, J. B. (1976) *Am. Mineral.* **61**, 987–95.
Kermarrec, Y. (1964) *Compt. Rend.* **258**, 5836–8.
Levitt, S. R., and Condrate, R. A. Sr. (1970) *Am. Mineral.* **55**, 1562–75.
Magalhães, M. C. F., de Jesus, J. P., and Williams, P. A. (1986) *Mineral. Mag.* **50**, 33–9.
Nakagawa, I., and Shimanouchi, T. (1964) *Spectrochim. Acta*, **20**, 429–39.
Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. 3rd ed. John Wiley and Sons, New York.
Notebaart, C. W., and Korowski, S. P. (1980) *Mineral. Rec.* **11**, 339–48.
Srivastava, O. K., and Secco, E. A. (1967) *Can. J. Chem.* **45**, 585–9.
Taxer, K. (1975) *Am. Mineral.* **60**, 1019–22.
Walker, T. L. (1916) *Mineral. Mag.* **18**, 76–81.
— (1918) *Univ. Toronto Stud. Geol. Ser.* **10**, 1–25.

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Formal definitions of type mineral specimens

TYPE mineral specimens are reference samples for the definition of mineral species. The biological sciences have a long-established system of type specimens, but the formal designation of such samples is a relatively recent matter in mineralogy. Indeed, for a vast number of minerals, some first discovered in antiquity, and many others as recently as this century, there exist no type specimens at all. In many such cases, the best available information comes from designations such as

'original material' on museum catalogues, and on some old labels. Interpretations of labels, however, even if they are in the handwriting of the original describer, should always be treated with utmost caution.

Embrey and Hey (1970) provided a thoughtful discussion of the problems associated with type specimens, and the practices of our colleagues in the biological sciences, and proposed an argument for distinguishing seven kinds of type specimens. We