

Similar compositional changes involving K and Rb-enrichment and Ca, Sr and Ba-depletion have been reported to occur locally within major Laxfordian shear zones (Beach, 1976) and to characterise some areas of near pervasive amphibolitization of Scourian gneisses (Drury, 1974). It has been suggested that the major phase of fluid introduction was associated with Scourie dyke magmatism and the earliest phases of Laxfordian deformation (Beach and Tarney, 1978). The metasomatic phenomena at Garry-a-siar overprint a Laxfordian deformation fabric and indicate that some of these distinctive chemical changes may have occurred during later stages of the Laxfordian cycle.

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Ceruleite: infrared spectroscopy and a new locality in Cornwall

CERULEITE, $\text{Cu}_2\text{Al}_7(\text{AsO}_4)_4(\text{OH})_{13} \cdot 12\text{H}_2\text{O}$, is a rare supergene mineral, discovered by Dufet (1900) on material from the Emma Luisa gold mine near Huanaco, Taltal province, Chile, the only locality known until reported from Wheal Gorland, Gwennap, Cornwall, by Russell and Claringbull (1955), and from an unknown locality in southern Bolivia (Schmetzer *et al.*, 1976a, b, 1978).

In October, 1984, Mr V. T. Rae of Thornbury, Bristol, sent the author a specimen of suspected ceruleite he had collected, for confirmation or identification. This specimen was found in the material being excavated from 'the new shaft into Wheal Jane at St Day United'. Shortly afterwards Mr 'Sam' Weller notified the author of similar material sent to him and said to have been collected in 'Wheal Maid incline, part of Whiteworks mine', and accompanied by scorodite. Bryan V. Cooper, of Torquay Natural History Museum, carefully investigated the occurrence, and found the material only on a temporary dump at SW 745418 (since removed) derived from Western Decline, at SW

745421, a new incline shaft to Whiteworks lode in the Wheal Maid section of United Downs mine, a western extension of Wheal Jane. This shaft, in Gwennap parish, is 1.25 km SE of Wheal Gorland, the previous locality, and is about 0.6 km N of the site of Whiteworks shaft given in Dines (1956).

The ceruleite forms sky-blue radiating spherules of fine needles, mostly about 0.5 mm in diameter, closely invested or scattered on joint planes in grey tourmalinised killas, on sugary quartz or on felted crusts of sub-parallel aggregates of brown needles of tourmaline on killas. This tourmaline gives an infrared spectrum corresponding to that of the high-Al schorlite of Plyusnina *et al.* (1969). Other associated minerals include well-crystallised posnjakite in rippled crusts, thin crusts of pale greenish microcrystalline scorodite, cassiterite, very sparse tiny green square plates probably of zeunerite or metazeunerite, and small amounts of green to brown microcrystalline coatings giving ill-defined infrared spectra suggesting hydrated and probably basic sulphates and sulphate-arsenates. Native

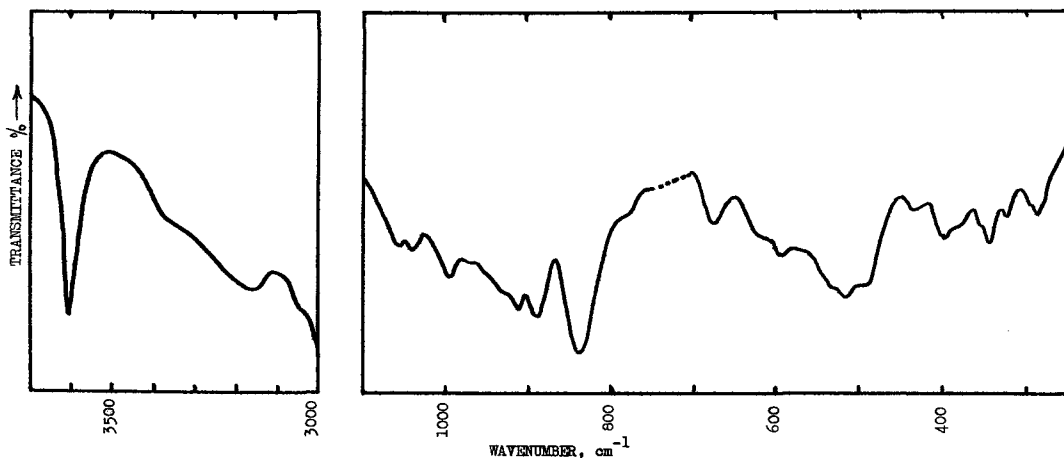


FIG. 1. Infrared spectrum of ceruleite from Western Decline, Wheal Maid, Gwennap, Cornwall, in Nujol mull (off RSWB 84-307).

silver is said to have been found also (B. V. Cooper, Private communication).

Infrared spectroscopy. The infrared spectrum of ceruleite from the new find was measured in Nujol mull over the range 250–4000 cm^{-1} between CsI plates using a Perkin-Elmer 783 precision grating spectrophotometer (Fig. 1 and Table 1), and those of ceruleites from Wheal Gorland and the new locality in Nujol mulls from 400–4000 cm^{-1} between KBr plates, using a Perkin-Elmer 397 spectrophotometer. The spectra of the Wheal Gorland ceruleites and those from the new find were similar over the ranges measured. Schmetzer *et al.* (1976a) published figures of the infrared spectra of the ceruleite from Bolivia, and of a partly dehydrated phase, over the range 200–4000 cm^{-1} , but did not quote wavenumber values or assignments of the absorption maxima, except for those in the O–H stretching region (3000–4000 cm^{-1}). The scale of these published spectra does not permit accurate measurement of wavenumbers, but the profile of their ceruleite spectrum is similar to that of ours.

Schmetzer *et al.* (1976a) report that ceruleite is partly dehydrated on heating to 250 °C to a crystalline phase giving a distinctive X-ray powder diffraction pattern. From the weight loss (14.76 wt. %) this phase was assumed to have the same formula as ceruleite, but with only 0.1 H_2O , the number of non-water hydroxyls being unchanged. The reported infrared spectrum of this phase, compared with that of ceruleite, shows that certain absorptions have been lost. These lost absorptions cannot reliably be ascribed to vibrations involving H_2O , as distinct from hydroxyl, as the dehydrated phase displays an H–O–H deformation vibration near

1600 cm^{-1} about as strong as that in ceruleite, and the sharp non-hydrogen-bonded O–H stretch of hydroxide (at 3610 cm^{-1} in ceruleite), though still present, is considerably reduced in relative intensity in the dehydrated phase. Ceruleite contains two rather different metal cations, in which, for example, the charge to radius ratio for Al^{3+} is more than twice that of Cu^{2+} . On this basis alone, hydroxyl ions would be expected to be bound much more firmly to Al^{3+} than to Cu^{2+} . This is borne out by thermal analyses, in which hydroxide bound to copper tends to come off at around 300 °C, whereas at least some of that bound to aluminium may be retained at well over 500 °C (Todor, 1976). Hydroxide bound to copper in some basic salts may even be removed well below 250 °C (Ramamurthy and Secco, 1970), a lower temperature than that of the removal of the last water from hydrated aluminium sulphate (about 400 °C; Todor, 1976). It is therefore possible that water loss from hydroxide bound to copper might take place at a lower temperature than that of some water coordinated to aluminium, and that this might explain the apparent retention of H_2O and loss of OH^- by 250 °C indicated by infrared spectroscopy. The formulation of the dehydrated phase requires modification, an unknown proportion of H_2O being retained, with a corresponding amount of hydroxide being converted to oxide: $\text{Cu}_2\text{Al}_7(\text{AsO}_4)_4\text{O}_n(\text{OH})_{13-2n} \cdot (0-1) + n\text{H}_2\text{O}$.

Assignments for the absorptions in the spectrum of ceruleite are given, and their bases discussed, in Table 1. The presence of hydrogen-bonded coordinated water is supported. The site symmetry of the arsenate is not readily determined, as the

TABLE 1. Absorption maxima in the infrared spectrum of ceruleite (off RSWB 84-308, Western Decline shaft, Wheal Maid, Gwennap, Cornwall).

Absorption maxima, cm^{-1} , intensities	Assignments
3610 s, sp**	O-H stretch, increasingly H-bonded as wavenumber decreases
~3370 sh	
3176 s, br	
~3060 sh*	Shoulder on "Nujol" absorption
~1650 w, br	H-O-H "Scissor" deformation, H-bonded
1058 s*	Metal-O-H in-plane bend. Note 1
1038 s*	
996 s*	
~930 w, sh	
913 s, sp	Cu-O-H bend, possibly $\text{AsO}_4 \nu_3$. Note 2
888 s	$\text{AsO}_4 \nu_3$ unsymmetrical stretch, possibly burying ν_1 , and coordinated water rock. Note 3
835 vs	
674 m*	
620 sh*	Cu-O-H bend. Note 4
595 s	Coordinated water wag. Note 5
~540 sh	
518 s, br	Al-OH ? Note 6
490 sh	Metal-OH ₂ or metal-OH stretch, possibly $\text{AsO}_4 \nu_4$ unsymmetrical bend. Note 7
440 w	
400 sm	
380 w, sh*	$\text{AsO}_4 \nu_4$. Note 8
353 w, sh*	Metal-OH, metal-OH ₂ , possibly $\text{AsO}_4 \nu_2$ symmetrical bend. Note 9
344 sm*	
326 w, m*	
290 m*	

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

* Lost on partial dehydration at 250°C (Schmetzer *et al.*, 1976a)

** Not appreciably hydrogen-bonded. Substantially reduced in intensity on partial dehydration at 250°C

NOTES TO TABLE 1

1. Metal-O-H bending vibrations are found near 1000-1100 cm^{-1} , at lower wavenumbers for bridging O-H (Nakamoto, 1978). Al-O-H in tunisite is at 985 cm^{-1} (Johan *et al.*, 1969). The various polymorphs of Al(OH)₃ and Al(OH) all have strong absorptions in the 960-1075 cm^{-1} region (Lyon, 1962, White and Roy, 1964; R S W Braithwaite, unpublished). Cu-O-H deformations in azurite are at 952 and 1035 cm^{-1} , and in malachite at 875 and 1045 cm^{-1} (Goldsmith and Ross, 1968), in olivenite at 943 cm^{-1} , and near 975 cm^{-1} in libethenite (Braithwaite, 1983).
 2. Rather high for arsenate ν_3 (see note 3). Possibly the Cu-O-H deformation found at 943 cm^{-1} in the spectrum of olivenite (Braithwaite, 1983). A Cu-O-H in-plane bend in Cu(OH)₂ is at 935 cm^{-1} (Jaggi *et al.*, 1961; Cabannes-Ott, 1957).
 3. The triply degenerate ν_3 unsymmetrical stretch of the free arsenate ion is near 878 cm^{-1} (Nakamoto, 1978) and is between 800-900 cm^{-1} in most arsenates (Moenke, 1962, 1966), and may be split by degeneracy loss on distortion. The non-degenerate ν_1 symmetrical stretch of arsenate is near 850 cm^{-1} (Nakamoto, 1978) but is forbidden and therefore absent, or weak when revealed by distortion of the anion, and is usually buried under the much stronger ν_3 absorption. The Al-OH₂ coordinated water rocking vibration in $[\text{Al}(\text{H}_2\text{O})_6]^{3+}\text{Cl}_3$ is at 844 (Camo, 1961a), 835 (Kemarrec, 1964) or 790 cm^{-1} (Prask and Boutin, 1966). The rocking vibration of coordinated water in $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}\cdot 5\text{H}_2\text{O}$ is at 867, 885 (Nakagawa and Shimanouchi, 1964) or 875 cm^{-1} (Camo, 1961b). A Cu-O-H deformation is found at 810 cm^{-1} in the spectrum of libethenite and near 820 cm^{-1} in that of olivenite (Braithwaite, 1983).
 4. A Cu-O-H in-plane bend in the spectrum of Cu(OH)₂ is at 685 cm^{-1} (Jaggi *et al.*, 1961; Cabannes-Ott, 1957). Al-O bond vibrations are also found in this region (Johan *et al.*, 1969; Frueh and Golightly, 1967).
 5. The wagging vibrations of coordinated water in $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ salts are at 570, 585 and 595 cm^{-1} for the chloride, sulphate and nitrate respectively (Prask and Boutin, 1966) and at 535 cm^{-1} in $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}\cdot 5\text{H}_2\text{O}$ (Nakagawa and Shimanouchi, 1964).
 6. The Al(OH)₃ polymorphs gibbsite, bayerite (Lyon, 1962) and nordstrandite (R S W Braithwaite, unpublished) all have strong, broad absorptions in the 515-530 cm^{-1} region.
 7. The metal-oxygen stretch of Cu-OH₂ in $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}\cdot 5\text{H}_2\text{O}$ is at 440 cm^{-1} (Nakagawa and Shimanouchi, 1964), and of Cu-OH in malachite is at 485 cm^{-1} and in azurite at 455 cm^{-1} (Goldsmith and Ross, 1968). The Al-O stretching vibrations of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ in the sulphate, chloride and nitrate are at 440, 465 and 475 cm^{-1} respectively (Prask and Boutin, 1966).
 8. The triply degenerate ν_4 unsymmetrical bending vibration of the arsenate ion is near 420 cm^{-1} (Nakamoto, 1978), for example at 419, 385 cm^{-1} in mimetite (Levitt and Condrate, 1970). Cu-O stretching vibrations are found in the spectra of malachite and azurite between 400-425 cm^{-1} (Goldsmith and Ross, 1968).
 9. The forbidden ν_2 symmetrical bending vibration of the arsenate ion is at 319 cm^{-1} in mimetite, for example (Levitt and Condrate, 1970), but would be weak, and should not be lost on dehydration. The twisting vibrations of coordinated water in $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ salts are at 300, 310 and 320 cm^{-1} for the chloride, nitrate and sulphate respectively (Prask and Boutin, 1966).
- Note that all bands below about 440 cm^{-1} disappear or become weak shoulders in the spectrum of the partially dehydrated phase reported by Schmetzer *et al.*, (1976a).

presence of $M\text{-OH}$ and $M\text{-OH}_2$ absorptions in the relevant regions of the spectrum confuse the identification of forbidden bands and of any splittings of degeneracy.

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$\text{Ag}_{1.2}\text{Sn}_{0.9}\text{Sb}_3\text{S}_6$, a tin-bearing andorite phase

ANDORITE is considered to be a relatively common Ag-sulphosalt mineral, and in some deposits it forms the chief silver ore (Chace, 1948). By substitution between 2Pb and Ag+Sb or 3Pb and 2Sb + □, andorite shows compositional variations from its formula $\text{PbAgSb}_3\text{S}_6$ (Nuffield, 1945; Mozgova *et al.*, 1983). In the system $\text{Ag}_2\text{S-PbS-Sb}_2\text{S}_3$, andorite displays an extensive range of solid solution at temperatures between 300 and 500 °C (Hoda

and Chang, 1975). An andorite-like phase was synthesized in the study of reactions of silver sulphantimonides and tin sulphides (Chang, 1983). The purpose of this investigation is to examine its stability in the system $\text{Ag}_2\text{S-SnS-Sb}_2\text{S}_3$, and its relations to andorite.

Experimental procedures. Experiments were performed by means of the conventional evacuated glass capsule technique using specpure elements