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Infrared spectroscopic analysis of the olivenite–adamite series, and of phosphate substitution in olivenite

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ABSTRACT. Infrared spectroscopy affords a rapid and easy method of estimating the position of a mineral in the olivenite–adamite solid solution series, and of estimating the amount of phosphate substitution in olivenites. Toman's discovery of the monoclinic symmetry of olivenites with up to approximately 20 atom % Zn/(Cu+Zn) has raised a problem in nomenclature. It is suggested that the definition of 'cuproadamite' be extended to cover all orthorhombic members of the series containing appreciable Cu. Studies of deuterated materials have helped to solve some of the absorption band assignments for olivenite–adamite, libethenite and related minerals.

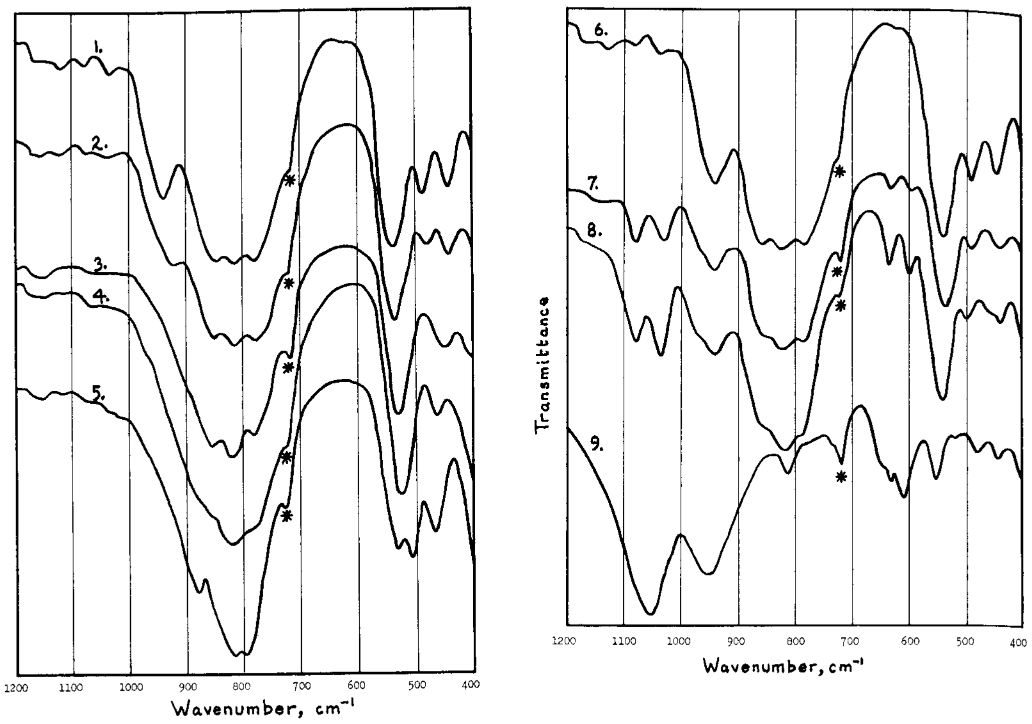
MEMBERS of the olivenite Cu_2AsO_4OH to adamite Zn_2AsO_4OH solid solution series are well-known minerals from the oxidation zone of Cu–Zn–As-containing ore deposits. The series is complicated by possibilities of further substitution by other cations, e.g. Fe(II), Co(II), Mn(II), and at the Cu end by anion substitution of phosphate towards libethenite Cu_2PO_4OH. Thus olivenite is sometimes phosphatian, in particular the classical specimens from Wheal Gorland and other mines in the St. Day area of Cornwall (see old analyses cited by Collins (1871) and Palache *et al.* (1951); also Table I).

Careful X-ray diffraction measurements by Toman (1977, 1978) have shown that whereas adamite is orthorhombic *Pnnm*, olivenite is monoclinic $P2_1/n$, the changeover in symmetry taking place near 20 atom % Zn/(Cu+Zn). In these structures, and in libethenite, the metals occupy 5-coordinate and 6-coordinate sites, the former preferred by Zn(II) and the latter by Cu(II) with its preference for square planar coordination. Long-range ordering was detected in a solid solution, replacement of Cu by Zn and vice versa taking place according to these site preferences, Zn initially replacing Cu in the 5-coordinate sites. These uncommon 5-coordinate Cu–O sites are primarily responsible for the lowering of symmetry in the olivenite structure (Toman, 1978).

Inspection of the infrared spectra of a number of natural samples suggested that infrared spectroscopy might afford a rapid and easy method for placing the approximate position of a small sample in the olivenite–adamite series and for estimating the amount of anion substitution by phosphate. Accordingly, numerous members of the olivenite–adamite series were synthesized by the method used by Guillemin (1956), Minceva-Stefanova *et al.* (1965), and Toman (1978). In addition, the method was extended to the preparation of phosphatian olivenites, libethenite, and some deuterated materials, required in order to distinguish vibrations involving O–H from other vibrations (see Experimental section).

The infrared absorption spectra of these samples, and of a number of natural specimens, were measured over the 400–4000 cm^{-1} range, in Nujol mulls between KBr plates, using a Perkin-Elmer 397 grating infrared spectrophotometer, each spectrum being calibrated against polystyrene. Examples are reproduced in figs. 1, 2, and 3. The Nujol mull technique uses less material than the pressed disc method, gives better resolution, and avoids the traces of water which are almost inevitable in pressed discs.

The spectra of all the non-deuterated materials show a sharp O–H stretching absorption of medium intensity near 3500 cm^{-1}, shifted on deuteration to near 2600 cm^{-1} with isotopic shifts ν_{OH}/ν_{OD} near 1.35. The position of this band alone can be used to estimate the approximate Cu:Zn ratio of a member of the series. For the Cu-rich members a single fairly sharp absorption, weakly H-bonded, is observed, at 3420 cm^{-1} in olivenite, shifting to 3490 cm^{-1} for the $(Cu_{0.27}Zn_{0.73})$ member. For material richer in Zn the intensity of this absorption drops sharply, nearly disappearing by $(Cu_{0.10}Zn_{0.90})$, where it is just discernible at 3490 cm^{-1}. The shift of this absorption to higher wavenumbers as Zn replaces Cu is accompanied by



FIGS. 1 and 2. FIG. 1 (*left*). Partial infrared spectra of selected synthetic members of the olivenite–adamite solid-solution series. 1. Cu_2AsO_4OH (olivenite), 2. $(Cu_{0.88}Zn_{0.12})_2AsO_4OH$, 3. $(Cu_{0.62}Zn_{0.38})_2AsO_4OH$, 4. $(Cu_{0.27}Zn_{0.73})_2AsO_4OH$. 5. Zn_2AsO_4OH (adamite). FIG. 2 (*right*). Partial infrared spectra of synthetic olivenite, phosphatian olivenites, and libethenite. 6. Cu_2AsO_4OH (olivenite), 7. $Cu_2(AsO_4)_{0.91}(PO_4)_{0.09}OH$, 8. $Cu_2(AsO_4)_{0.81}(PO_4)_{0.19}OH$, 9. Cu_2PO_4OH (libethenite). * Absorptions due to Nujol.

a slight sharpening of its profile, and is probably a consequence of decreasing hydrogen bonding. Pure adamite displays a single, very sharp absorption at 3540 cm^{-1}, not hydrogen bonded, which weakens without changing position on replacing some of the Zn(II) by Cu(II) in the 6-coordinate sites, nearly vanishing by $(Cu_{0.55}Zn_{0.45})$. An additional weak absorption at 3510 cm^{-1} is observed in the spectra of the $(Cu_{0.27}Zn_{0.73})$ to $(Cu_{0.05}Zn_{0.95})$ members. These absorption changes are summarized in fig. 4. The 3400 cm^{-1} band in the spectrum of adamite ascribed by Hill (1976) to Zn–O–H stretching is very weak and broad in our spectra and is probably due to traces of moisture. Our spectra show negligible absorption near 1620 cm^{-1}, where Hill's spectrum shows a fairly strong broad band, which must represent the H–O–H 'scissor' vibration of water.

Substitution of phosphate for arsenate in olivenite also affects the position of the O–H stretching absorption. The 3420 cm^{-1} absorption of pure olivenite shifts steadily to 3430 cm^{-1} for material containing 19 mole % phosphate, and to 3470 cm^{-1} for pure libethenite. When phosphate absorptions are present in a sample's spectrum (see below) care should therefore be taken to consider this when attempting to estimate its Cu : Zn ratio.

The OH group in these minerals is attached to three metal atoms in a distorted tetrahedral arrangement, the bond to hydrogen forming the fourth arm of the tetrahedron (Hill, 1976). With this arrangement the hydrogen atom has two nearest neighbour oxygen atoms with which it might form a hydrogen bond, one each from two separate arsenate anions, but both rather distant.

A strong absorption is observed in the spectrum of pure olivenite at 943 cm^{-1} (see fig. 1), shifting on deuteration to 700 cm^{-1}, and therefore due to an O–H deformation. On substituting Zn into the 5-coordinate sites the position of this band shifts to near 920 cm^{-1} for $(Cu_{0.88}Zn_{0.12})$, and on further substitution it becomes a shoulder on the strong arsenate ν_3 absorption centred near 850 cm^{-1}, and has almost disappeared into the arsenate absorption by $(Cu_{0.80}Zn_{0.20})$, but without changing its relative transmittance. The ratio of the % transmittance difference between the minima near 1000 cm^{-1} and 910 cm^{-1}, and the absorption maximum near 940 cm^{-1} and the minimum near 910 cm^{-1}, can be used as a fairly accurate measure of composition, given reasonable transmittance values, as can be seen from fig. 5. The presence of a distinct absorption maximum near 940 cm^{-1} in this series is thus a coincidental indication that the sample concerned is an olivenite, of monoclinic symmetry. Another indication of the symmetry change is the disappearance of the 480–500 cm^{-1} band (see below) as Zn/(Cu + Zn) exceeds about 20 atom %.

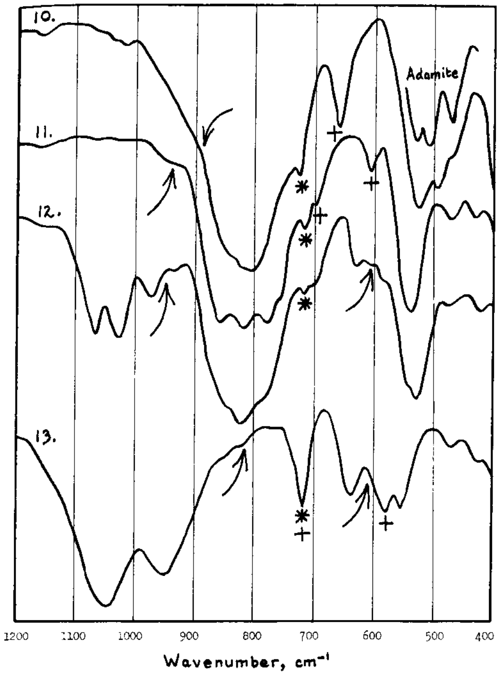


FIG. 3. Partial infrared spectra of deuterated materials. 10. Zn_2AsO_4OD (adamite). cf. fig. 1, spectrum 5. 11. Cu_2AsO_4OD (olivenite). cf. fig. 1, spectrum 1; fig. 2, spectrum 6. 12. $Cu_2(AsO_4)_{0.8}(PO_4)_{0.2}OD$ (phosphatian olivenite). cf. fig. 2, spectrum 8. 13. Cu_2PO_4OD (libethenite). cf. fig. 2, spectrum 9. * Absorptions due to Nujol. + O–D absorption, not present in parent mineral. → Position of O–H absorption present in parent mineral.

The '940 cm^{-1}' absorption band emerges again from the arsenate ν_3 band as a shoulder in the spectrum of $(Cu_{0.27}Zn_{0.73})$, and as a distinct maximum, now at 885 cm^{-1}, in those of more Zn-rich material up to pure adamite, but not in deuterated adamite.

In the spectrum of libethenite this absorption is concealed under a strong broad absorption at 950 cm^{-1}, unaffected by deuteration. Deuteration, however, reveals it at 720 cm^{-1}. Using the isotopic shift of 1.34 for D-libethenite, determined from $\nu_{OH\ stretch}/\nu_{OD\ stretch}$, the 720 cm^{-1} O–D band must be derived from an O–H band near 975 cm^{-1}.

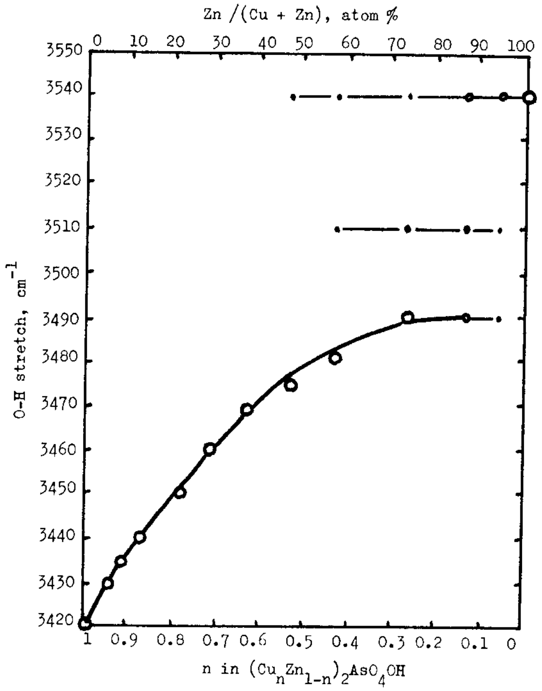


FIG. 4. Position of O–H stretch in the infrared spectra of members of the olivenite–adamite solid-solution series.

This absorption band is also present in the infrared spectra of many other basic copper arsenates and phosphates (e.g. Moenke, 1962, 1966; Sumin de Portilla, 1974; references cited by Ross, 1974).

Another O–H deformation is hidden under the arsenate ν_3 band in olivenite and is revealed by deuteration as an O–D band at 608 cm^{-1}. Using the isotopic shift of 1.35 calculated from $\nu_{OH\ stretch}/\nu_{OD\ stretch}$, the corresponding O–H band should be near 820 cm^{-1}. This might correspond with the O–H deformation observed in the spectrum of libethenite, with no arsenate absorption to conceal it, at 810 cm^{-1}, shifted to 580 cm^{-1} on deuteration.

The spectra of adamite and its deuterated derivative are less easy to analyse in this context, the absorption pattern in the 440–550 cm^{-1} region changing on deuteration in a confusing manner (fig. 3). The disappearance on deuteration of the strong band at 510 cm^{-1} in the spectrum of adamite indicates that it is an O–H deformation mode and not a degeneracy splitting of the 520 cm^{-1} Zn–O band as assumed by Sumin de Portilla (1974).

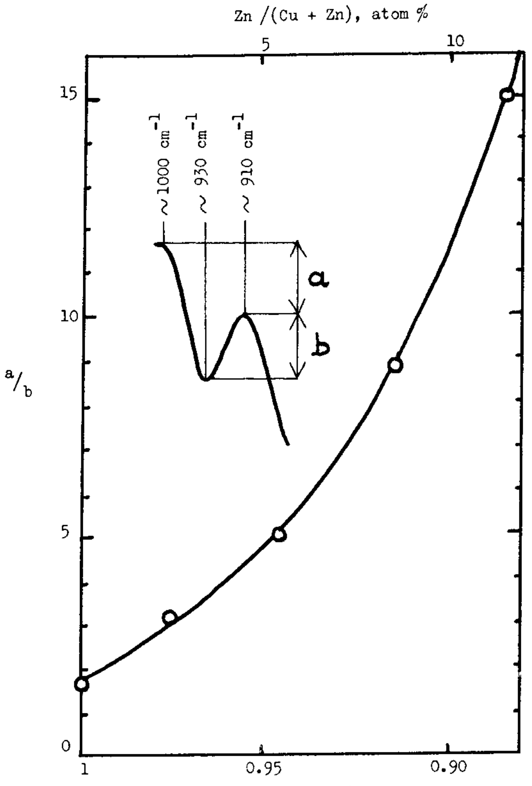


FIG. 5. Relative prominence of the ~ 930 cm^{-1} band in the infrared spectra of zincian olivenites.

From the isotopic shift of 1.35, the absorptions at 495 cm^{-1} and 530 cm^{-1} in the spectrum of deuterated adamite should be derived from O-H bands near 670 cm^{-1} (where nothing is observed) and near 720 cm^{-1} respectively. An absorption at 730 cm^{-1} for adamite was ascribed by Hill (1976) to the AsO_4^{3-} ν_1 absorption (which should indeed be near here) but might be this O-H deformation.

Yet another O-H deformation band lies at 610 cm^{-1} in the spectrum of libethenite.

These multiple O-H deformation modes are probably controlled more by the influence of the two arsenate oxygen atoms which are the nearest neighbours of the hydrogen atom (apart from its own oxygen) than by the metal-OH tetrahedra, but their presence indicates a degree of covalency in the metal-OH bonds (cf. Sumin de Portilla, 1974).

The ν_3 asymmetrical stretching mode of the AsO_4^{3-} anion appears in our spectra as a strong broad absorption in the 800 cm^{-1} region. X-ray diffraction measurements (Hill, 1976; Toman, 1977, 1978; also earlier workers) show that the arsenate ion is distorted in the crystal lattice of these minerals to C_s symmetry. The consequent removal of its spectroscopic triple degeneracy results in a triple profile for the ν_3 absorption, and should cause the forbidden ν_1 symmetrical stretch to appear near 750 cm^{-1}. Nujol has an absorption band at 720 cm^{-1} near here, and the ν_1 band in arsenates is often hidden under the ν_3 absorption or this Nujol band (which has sometimes been taken for the ν_1 band). The profile of the ν_3 absorption varies with composition, the band splitting increasing from adamite to olivenite (fig. 1). This is due to the increasing distortion of the arsenate ion in this direction, evidenced by bond angle and bond length measurements; for example the widest difference between As-O bond lengths in adamite is 0.006 Å (Hill, 1976) and in olivenite is 0.11 Å (Toman, 1977).

The corresponding ν_3 and ν_1 modes of the PO_4^{3-} ion have maximum absorption in the 1000 cm^{-1} and 930 cm^{-1} regions respectively. For the phosphatian olivenites studied, the latter is buried beneath the strong 950 cm^{-1} absorption and the ν_3 mode appears as two distinct absorptions near 1030 and 1080 cm^{-1}. In the spectrum of libethenite these merge into a strong absorption at 1050 cm^{-1}, accompanied by another strong absorption at 950 cm^{-1}. This latter absorption forms a weak shoulder near 970 cm^{-1} on the 950 cm^{-1} O-H band in the phosphatian olivenites, which again conceals the ν_1 band. This absorption profile in the spectrum of libethenite is very different from those in the spectra of the phosphatian olivenites studied (with up to 19 mole % phosphate) (fig. 2). Preliminary experiments suggest that phosphate substitution in olivenite may be limited, not being continuous to libethenite.

The ratio of the % transmittance difference between the ν_3 absorption maxima of phosphate and that of arsenate, at 1030 and 820 cm^{-1} respectively, measured against the common minimum at 1000 cm^{-1} is a fairly accurate measure of the phosphate content of phosphatian olivenites (fig. 6).

In the 400-700 cm^{-1} region lie the doubly degenerate ν_2 symmetrical deformation vibrations of PO_4^{3-} and the ν_4 triply degenerate asymmetrical deformation modes of AsO_4^{3-} and PO_4^{3-}. Metal-oxygen absorptions are also found here, at not easily predictable positions.

A strong absorption at 540 cm^{-1} in the spectrum of olivenite persists throughout the series, shifting slightly, to 525 cm^{-1} for compositions near $(Cu_{0.10}Zn_{0.90})$ and to 530 cm^{-1} for adamite, accompanied by the 510 cm^{-1} O-H deformation referred to previously (fig. 7); this band persists on substitution with phosphate and appears at 550 cm^{-1} in the spectrum of libethenite. Although the band appears whether copper or zinc, arsenate or phosphate, are present, it is not due to an O-H vibration as it is unaffected by deuteration (fig. 3), and must be a metal-oxygen band with Cu-O and Zn-O frequencies very close together. Sumin de Portilla (1974) and Sumin de Portilla *et al.* (1981, and unpublished results) assign bands at 562 and 585 cm^{-1} of bayldonite, and analogous bands of olivenite, conichalcite, euchroite, and liroconite to Cu-O vibrations, and authors cited by Ferraro (1971) point out that hydroxy-bridged complexes of Cu(II) absorb in this region.

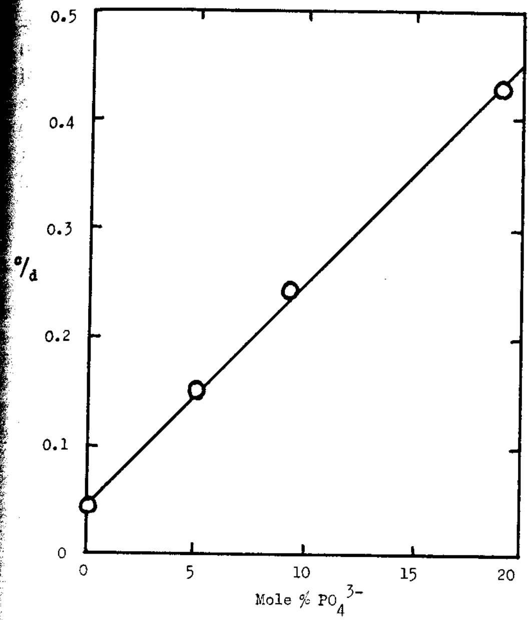


FIG. 6. Ratio of transmittance differences, c/d, in the infrared spectra of phosphatian olivenites. c = % transmittance difference between 1000 and 1030 cm^{-1}. d = % transmittance difference between 1000 and 820 cm^{-1}.

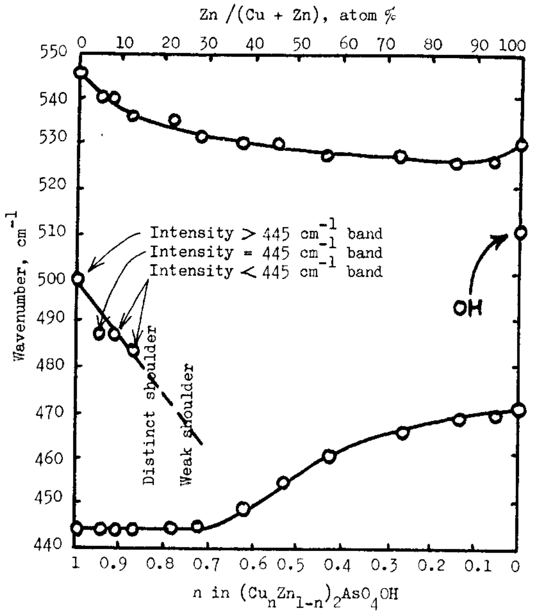


FIG. 7. Positions of absorption maxima in the 440-550 cm^{-1} range in the infrared spectra of members of the olivenite-adamite solid-solution series.

Two absorptions between 440 and 500 cm^{-1} are of considerable analytical value, their relative intensities and wavenumbers varying with composition (fig. 7). These absorptions are unaffected by deuteration and have been assumed to be due to the AsO_4^{3-} ν_4 vibrations, which should lie in this region (Moenke, 1962, 1966; Sumin de Portilla, 1974; Hill, 1976). They persist, however, in the spectrum of pure synthetic libethenite, at 445 and 480 cm^{-1}, and furthermore their changes with composition seem to reflect the ordering discovered by Toman (1978), the 500 cm^{-1} band of olivenite changing position and weakening as Zn replaces Cu in the 5-coordinate sites, while the 440 cm^{-1} band remains constant, only increasing in wavenumber while Zn is replacing Cu in the 6-coordinate sites. This may be coincidence, or these bands may be metal-oxygen absorptions of 5-coordinate Cu(II) and of 6-coordinate metal respectively. Moenke (1962, 1966) assigns these bands for libethenite to the phosphate ν_4 and ν_2 modes respectively.

Summary and conclusions. Infrared spectroscopy can be used, with small samples, as a rapid and facile method for determining the approximate position of a mineral in the olivenite-adamite solid-solution series, and for estimating the amount of phosphate substitution in olivenite.

The method uses a combination of criteria involving (i) the wavenumber of the O-H stretching vibration near 3500 cm^{-1}, (ii) the prominence of the O-H deformation vibration in the 885-945 cm^{-1} region, (iii) the wavenumbers and relative intensities of absorptions in the 440-550 cm^{-1} range, (iv) to a lesser extent, the profile of the arsenate ν_3 absorption band, and (v) in the case of phosphatian olivenites, the relative transmittances of the arsenate and phosphate ν_3 absorptions. In most cases, given reasonable spectra, the method is accurate to within about 10 atom % Zn/(Cu+Zn). In favourable cases, e.g. those composition ranges with sharp spectral changes, somewhat higher accuracies can be obtained.

Table I gives examples of the results obtained for a range of natural specimens.

TABLE I. *Infrared analyses of natural specimens*

Sample no. (RSWB coll.)	Locality	$Zn/(Cu+Zn)$, atom % (approx.)
79-107	Tsumeb, SW Africa	0
64-176	Cap Garonne, France	0
64-161	Wheal Gorland, Cornwall	0
66-408	Wheal Gorland, Cornwall	0
66-492	Wheal Gorland, Cornwall	0
67-246	Wheal Gorland, Cornwall	0
66-282	St. Day United mine, Cornwall	0
67-18	Mina Esperanza, Bolivia	0
(*a*)	Touissit mine, Morocco	12
80-174	Kamariza, Greece	15
67-296	Kamariza, Greece	20
71-109	Zacatecas, Mexico	30
79-108	Kamariza, Greece	40
67-381	Kamariza, Greece	45
81-64	Tsumeb, SW Africa	45
72-309	Kamariza, Greece	55
(*b*)	Kamariza, Greece	60
72-292	Kamariza, Greece	70
72-310	Kamariza, Greece	95
67-298	Kamariza, Greece	95
67-297	Kamariza, Greece	100
74-381	Mapimi, Mexico	100
		Mole % PO_4^{3-} (approx.)
67-246	Wheal Gorland, Cornwall	0
67-18	Mina Esperanza, Bolivia	6
64-161	Wheal Gorland, Cornwall	7
(*c*)	Wheal Gorland, Cornwall	13
66-492	Wheal Gorland, Cornwall	13
66-408	Wheal Gorland, Cornwall	14
66-282	St. Day United mine, Cornwall	15

(*a*) Specimen belonging to H. Corke.
(*b*) Specimen belonging to J. I. Wilson.
(*c*) Unnumbered specimen, collected in 1958.

Note on nomenclature. Toman's revelation of the monoclinic symmetry of olivenites with 0 to about 20 atom % $Zn/(Cu+Zn)$ poses a problem in nomenclature. 'Zincian olivenite' can clearly be used for monoclinic material within this range, but material with between 20 and 50 atom % $Zn/(Cu+Zn)$ is orthorhombic and so is not a variety of 'olivenite'. 'Zinkolivenit' has been used (Koechlin, 1928) for zincian olivenite (of no known provenance and with no analysis reported), but is not a satisfactory name for orthorhombic material as it suggests that it is a variety of olivenite and is easily confused with 'zincian olivenite'. It is undesirable to introduce new names unless absolutely necessary. 'Cuproadamite' (Lacroix, 1910) has long been in common use for adamites containing copper, and Dr M. H. Hey and P. G. Embrey suggest that its definition might be extended to cover orthorhombic members of the series containing appreciable amounts of copper beyond Cu:Zn 1:1 and up to the symmetry changeover point, 'cuprian adamite' being reserved for adamites containing small proportions of copper. As the series is complete there is no theoretical boundary between cuproadamite and cuprian adamite, and the only convenient appreciable gap in the observed composition range of natural specimens, the gap between 70 and 95 atom % $Zn/(Cu+Zn)$, may be a coincidental function of the limited number of analyses available (e.g. see Table I). A value of 80 atom % $Zn/(Cu+Zn)$ might therefore be used as an imperfect but convenient boundary between 'cuproadamite' and 'cuprian adamite'.

Experimental section. The synthetic arsenates were prepared by the method used by Guillemin (1956), Minceva-Stefanova *et al.* (1965) and Toman (1978). Premixed 0.1 M aqueous solutions of carefully measured mixtures of Cu and Zn ions in the appropriate proportions were added slowly to excess arsenate solutions and the mixtures subsequently boiled under reflux. The resulting crystalline solid solutions were analysed by atomic absorption spectrometry and found to have Cu:Zn ratios different from those of the mixtures used for their preparation, despite the order of mixing, designed to avoid this. Solid solutions containing 0, 2.5, 5.5, 8.5, 11.5, 21, 29, 38, 46, 57, 73, 87, 94, and 100 atom % $Zn/(Cu+Zn)$ resulted from mixtures containing 0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90, 95, and 100 atom % $Zn/(Cu+Zn)$ respectively. The preferential precipitation of Cu-rich material suggests that olivenite is more stable than adamite under the conditions of reaction. In contrast with our results, Guillemin (1956) obtained a product with 'Cu:Zn = 1:6' from the reaction of equal moles of Cu and Zn sulphates with sodium arsenate solution, but did not report the conditions used, in particular the critical order of mixing and whether the Cu and Zn solutions were premixed before addition to or of arsenate. Phosphate-containing olivenites were prepared by analogous methods using appropriate mixtures of phosphate and arsenate solutions and subsequently analysed. Analyses showed that the phosphate:arsenate ratios were close to those of the mixtures used in their preparation, products containing 5, 9, 19, and 100 mole % PO_4^{3-} resulting from mixtures containing 5, 10, 20, and 100 mole % PO_4^{3-}.

Deuterated olivenite, adamite, libethenite, and olivenite$_{80}$libethenite$_{20}$ were prepared by separating the initial gelatinous precipitate as far as possible by centrifuging, removing the supernatant liquid, and treating the precipitate with excess deuterium oxide. After several hours the excess liquid was removed by centrifuging and replaced by fresh deuterium oxide. This process was repeated and eventually the precipitate was boiled under reflux for 1 hour (5 hours in the case of deuterated adamite) with fresh deuterium oxide and the resulting crystalline precipitate filtered off and dried in a desiccator.

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