Mcalpineite, $Cu_3TeO_6 \cdot H_2O$, a new mineral from the McAlpine mine, Tuolumne County, California, and from the Centennial Eureka mine, Juab County, Utah[1]

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Abstract

Mcalpineite, ideally $Cu_3TeO_6 \cdot H_2O$, occurs as isolated 0.5 mm-sized emerald green cryptocrystalline crusts on white quartz at the long-abandoned McAlpine mine, Tuolumne County, California, U.S.A. Associated nonmetallic phases are muscovite (mariposite), calcite, goethite, hematite, chlorargyrite, choloalite, keystoneite, mimetite, malachite, azurite, annabergite and a host of unidentified crusts, both crystalline and amorphous. Associated metallic minerals include pyrite, acanthite, hessite, electrum, altaite, native silver, galena, pyrargyrite, sphalerite and owyheeite. The mineral has also been identified at the Centennial Eureka mine, Juab County, Utah, U.S.A., where it occurs as interstitial olive-green coatings and as millimetre-sized dark green-black cryptocrystalline nodules lining drusy quartz vugs. Associated minerals are xocomecatlite, hinsdalite-svanbergite, goethite and several new species including two hydrated copper tellurates, a hydrated copper-zinc tellurate/tellurite, and a hydrated copper-zinc tellurate/tellurite-arsenate-chloride. Mcalpineite is cubic, *P*-lattice (space group unknown), a = 9.555(2) Å, V = 872.4(4) Å. The strongest six lines in the X-ray powder-diffraction pattern [d in Å (I) (hkl)] are:

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4.26(40)(210), 2.763(100)(222), 2.384(70)(400), 1.873(40)(431,510), 1.689(80)(440) and 1.440(60)(622). The average of four electron-microprobe analyses (McAlpine mine) is CuO 50.84, NiO 0.17, PbO 4.68, SiO_2 0.65, TeO_3 39.05, H_2O (calc.) [4.51], total [100.00] wt. %. With O = 7, the empirical formula is $(Cu_{2.79}Pb_{0.09}Ni_{0.01})_{\Sigma 2.89}(Te_{0.97}Si_{0.05})_{\Sigma 1.02}O_{5.90}\cdot 1.10H_2O$. This gives a calculated density of 6.65. g/cm^3 for $Z = 8$. The average of two electron-microprobe analyses (Centennial Eureka mine) is CuO 51.2, ZnO 3.1, TeO_3 39.0, SiO_2 0.2, As_2O_5 0.8, H_2O (by CHN elemental analyser) 7, total 101.3 wt. %, leading to the empirical formula $(Cu_{2.56}Zn_{0.15})_{\Sigma 2.71}$ $(Te_{0.88}Si_{0.02}As_{0.02})_{\Sigma 0.92}O_{5.47}\cdot 1.53H_2O$. The infrared absorption spectrum shows definite bands for structural H_2O with an O-H stretching frequency centred at 3320 cm^{-1} and a H–O–H flexing frequency centred at 1600 cm^{-1}. In reflected light Mcalpineite is isotropic, nondescript grey, with ubiquitous brilliant apple to lime green internal reflections. The refractive index calculated from Fresnel equations is 2.01. Measured reflectance values in air and in oil are tabulated. Reflectance study also shows that cryptocrystalline aggregates are composed of micron-sized sheaves of fibrous or prismatic crystals. Other physical properties include: adamantine lustre; light green streak; brittle; uneven fracture; translucent to transparent and nonfluorescent under both long- and short-wave ultraviolet light. The name is for the first known locality, the McAlpine mine.

KEYWORDS: Mcalpineite, new mineral, McAlpine mine, California, U.S.A., Centennial Eureka mine, Utah, reflectance data, X-ray data, electron-microprobe analyses, infrared-absorption study.

Introduction

THE new mineral species mcalpineite, ideally $Cu_3TeO_6\cdot H_2O$, was first encountered in 1990 by one of us (F.E.C.) during routine megascopic examination of a newly-purchased suite of mineral specimens from a locality in California, U.S.A. This collection of approximately 350 specimens, weighing about 85 pounds, was labelled as 'hessite and petzite with gold' and was originally collected from the McAlpine mine, Tuolumne County, California, U.S.A. Many of the specimens have a colourful variety of small, but distinct, secondary crusts and crystal groupings. They are found perched on and enclosed within massive white quartz and are associated with various metallic phases. Semiquantitative electron-microprobe analyses of representative material submitted to Mr. Bart Cannon (Cannon Microprobe, Seattle, Washington, U.S.A.) confirmed the presence of various Cu- and Ni-bearing tellurates or tellurites, as well as other secondary phases with unusual chemistry. A selected number of specimens was then sent to the senior author for X-ray powder-diffraction (XRD) identification and further mineralogical study.A second occurrence for Mcalpineite was discovered by one of us (M.C.J.) in July 1992 at the Centennial Eureka mine, Juab County, Utah, U.S.A. A suite of secondary minerals from this locality was studied qualitatively using a scanning electron microscope (SEM) coupled with an energy-dispersive spectrometer (EDS). In many cases the EDS spectra could not be satisfactorily matched to any known mineral species. Subsequently, representative unidentified specimens were submitted to the senior author for XRD, and some of these were found to give a powder pattern that is identical to the mineral from California.

The mineralogical study was essentially complete before this second occurrence was discovered; hence, most of the mineralogical data reported here are for the McAlpine mine locality. Only within the chemistry section have we separately reported detailed results of the quantitative chemistry of mcalpineite from Centennial Eureka; this locality provided sufficient material for a quantitative determination for water.

The mineral is named for the first known and type locality, the McAlpine mine. The mineral and the mineral name have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. Type material (McAlpine mine) is preserved at: the Natural History Museum, Great Britain, in polished section as BM 1992,374; within The Systematic Reference Series of the National Mineral Collection, housed at The Geological Survey of Canada, Ottawa, Ontario, Canada as two specimens under catalogue number NMC 67163. In addition, two specimens reside within the private collection of Mr. Forrest E. Cureton II.

Occurrence and associated minerals

Mcalpineite is an extremely rare constituent at the long-abandoned McAlpine mine, Tuolumne County, California, U.S.A. (latitude 37°45′58″N, longitude 120°15′9″W). The two mine shafts have caved in and are now inaccessible, as, with one exception, are all drifts.

Only four McAlpineite-bearing specimens, containing an estimated 1 mg of sample have been identified to date from the McAlpine mine. The mineral is found as isolated 0.5 mm-sized emerald green cryptocrystalline crusts on white well-crystallised quartz, associated with chromian muscovite (locally known as mariposite), and most probably formed from the breakdown of the primary tellurium-bearing ore minerals. Metallic phases identified by a combination of quantitative electron microprobe and X-ray powder diffraction include: pyrite, acanthite, hessite, electrum, altaite, native silver, galena, pyrargyrite, sphalerite and owyheeite. Secondary nonmetallic minerals identified by X-ray powder diffraction and qualitative electron-microprobe study are: chlorargyrite, choloalite, keystoneite (Back *et al.*, 1988), mimetite, azurite, malachite, annabergite, calcite, goethite, hematite, as well as a host of unidentified phases that are both crystalline and amorphous. Further details regarding the mineralogy, geology and geochemistry of the McAlpine mine and surrounding areas are given by Weir and Kerrick (1987).

The second occurrence, the Centennial Eureka mine, is located in the West Tintic district, Juab County, Utah, U.S.A. (latitude 39°56′38″N, longitude 112°07′18″W), about 1.5 km southwest of the historic town of Eureka. The deposit was worked through a large vertical shaft to a depth of 702 m (2281 feet) over an aggregated claim length of 891 m. The property was first discovered in 1876 and became the largest precious metal producer in the district, primarily yielding gold, silver and copper. During the ten years between 1905 and 1914, production peaked at about 100,000 tons annually (Lindgren and Loughlin 1919). Underground mining was probably discontinued at least sixty years ago, and the workings are now essentially inaccessible.

The complex and enormous ore bodies of the Centennial Eureka mine are contained for the most part in The Cambrian-aged Cole Canyon and Opex dolomites and in The Ordovician-aged Ajax limestone, and occur in a series of parallel 'channels' following northerly-trending fracture zones. Primary mineralisation consists mainly of enargite with lesser pyrite, chalcopyrite and galena, hosted in a gangue of quartz (both coarse-crystalline and jasperoidal replacement), bladed baryte and cave-deposit calcite. Oxidation of the ores is relatively complete down to the 10th level (338 m), at which point remnant sulphides together with abundant secondary minerals occur and continue down to the water table at the 18th level (584 m).

A small mining operation, known locally as the Centurion Mines Corporation, recently bulldozed the large dumps of the mine and removed the majority of the material for cyanide heap leaching. A single 'stratigraphic' layer, exposed in one of the upper dump remnants, contains common boulders of mineralised rock. These boulders are characterised by corroded enargite and diverse secondary hydrated arsenate assemblages, all in a gangue of quartz and baryte. Throughout this 'stratigraphic' layer, uncommon boulders of decalcified and brecciated brown-grey limestone occur which possess suites of secondary hydrated copper and copper-zinc tellurite/tellurate minerals that line drusy quartz vugs. On several of these boulders, Mcalpineite occurs as interstitial olive-green coatings and as millimetre-sized dark green-black cryptocrystalline nodules lining drusy quartz vugs. Directly associated minerals include: green spherules of xocomecatlite; two new hydrated copper tellurates, a new hydrated copper-zinc tellurate/tellurite, and a new copper-zinc tellurate/tellurite-arsenate-chloride that are currently under study; hinsdalite-svanbergite crystals; and minor goethite (limonite). A total of perhaps forty mcalpineite specimens have been recovered from this second locality. A listing of many primary and secondary minerals identified at the Centennial Eureka mine has been published by Marty *et al.* (1993). In their paper, Mcalpineite is noted as unknown no.1.

Physical properties

The mineral (McAlpine mine) occurs as isolated 0.5 mm-sized emerald green crusts on white quartz. The lustre is adamantine, the streak light green, and the opacity varies from translucent to transparent. The physical appearance resembles

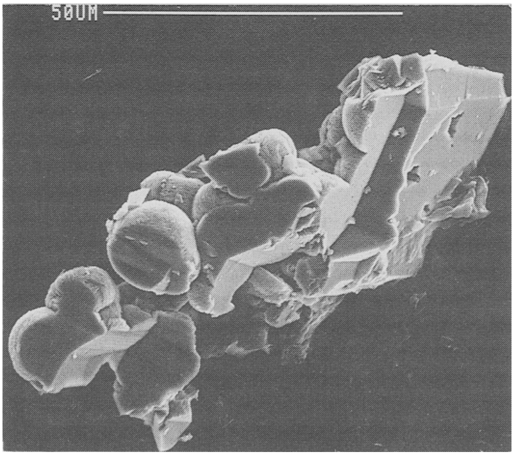

FIG. 1. Scanning electron photomicrograph of an aggregate of mcalpineite 'crystals' from the MeAlpine mine (Scale bar: 50 μm).

that of choloalite except that the latter has a vitreous lustre. The mineral is brittle with an uneven fracture and is nonfluorescent under both long- and short-wave ultraviolet light. SEM study reveals that these crusts are composed of anhedral 'crystals', 20 μm or less in size, which seem to have poorly formed 'faces' (Fig. 1) that are brightly reflecting in transmitted light. However, reflectance study (coupled with the failure of X-ray single-crystal studies) indicates the cryptocrystalline nature of these 'crystals'; they are composed of micron-sized sheaves of fibrous or prismatic crystals. Neither hardness nor density could be determined due to limitations on size of available specimens and dearth of material.

Chemistry

McAlpine mine. An aggregate of Mcalpineite crystallites, roughly 50 by 100 μm in size, was mounted in polished section and chemically analysed with a JEOL 733 electron microprobe utilising an operating voltage of 15 kV, a beam current of 20 nA and a beam diameter of 5 μm. The following standards were employed: natural cuprite (Cu), synthetic nichromite (Ni), natural crocoite (Pb), natural almandine (Si) and synthetic mackayite (Te). An energy-dispersion spectrum indicated the absence of elements with atomic number greater than 9 other than those reported here; F, Cl, S, Sb, Co, Se, Sn and Zn were specifically sought, but not found. The mineral is very stable under the electron beam and does not show any evidence of cathodoluminescence. The average of four analyses gave CuO 50.84(25), NiO 0.17(3), PbO 4.68(17), SiO_2 0.65(2), TeO_3 39.05(20), H_2O (calc.) [4.51], total [100.00] wt. %. A dearth of pure material prevented the acquisition of quantitative values for H_2O by classical chemical methods. However, its presence was confirmed by powder infrared-absorption study and, therefore, it was calculated by difference. With O = 7, the empirical formula is $(Cu_{2.79}Pb_{0.09}Ni_{0.01})_{\Sigma 2.89}(Te_{0.97}Si_{0.05})_{\Sigma 1.02}O_{5.90} \cdot 1.10H_2O$. The type material is a plumboan mcalpineite. The simplified formula is $Cu_3TeO_6 \cdot H_2O$, which requires CuO 55.21, TeO_3 40.62, H_2O 4.17, total 100.00 wt. %. Mcalpineite is very similar to synthetic Cu_3TeO_6 (Bayer, 1967), the structure of which has been described by Hostachy and Coing-Boyat (1968) and by Falck *et al.* (1978). Inspection of the structure of Cu_3TeO_6 (atomic coordinates of Falck *et al.*, ibid.) clearly shows that there is marginally sufficient room (4 Å void) within the structure for the single H_2O molecule. We suspect that the reduction in symmetry from a body-centred lattice to a primitive lattice may be an attempt by the structure to maximise a stable O....O separation for the H_2O molecule. This H_2O molecule is almost completely enclosed within the Cu_3TeO_6 framework and may account for the stability of the mineral under the electron beam. The near-identity of the X-ray powder data for Cu_3TeO_6 and Mcalpineite, coupled with the very similar composition, strongly suggests that the tellurium atom valence state is Te^{6+} (i.e. a tellurate). Unfortunately, without a crystal structure this can not be conclusively proven.

Centennial Eureka mine. A nodule of Mcalpineite was mounted in polished section and chemically analysed using the same instrumentation and operating conditions reported above for the McAlpine mine locality, with one exception; the beam diameter was 10 μm. The standards for Te, Cu and Si were identical; additional standards were: synthetic $ZnSeO_3$ (Zn) and synthetic $AgCo_3H_3(AsO_4)_3$ (As). An energy-dispersion spectrum indicated the absence of elements with atomic number greater than 9 other than those reported here: Ni, Co, Pb, Sn, Sb and Se were specifically sought, but not found. Water was determined on 0.1638 mg of pure sample using a Perkin Elmer model 240 CHN elemental analyser. The sample was heated to approximately 1000 °C in oxygen/helium, followed by purification of evolved gases and detection by thermal conductivity detectors. Calibration and blanks were run both before and after the sample. The calibration substance was melamine. The results give 7(1) wt. % H_2O. The low sample weight coupled with the relatively small water content means that the analysis was performed close to the detection limit of the equipment, hence the low precision of the final H_2O wt. % value. The average of two probe analyses, plus the water determination, give CuO 51.2(2), ZnO 3.1(1), TeO_3 39.0(1), SiO_2 0.2(1), As_2O_5 0.8(1), H_2O 7(1), total 101.3 wt. %. With O = 7, the empirical formula is $(Cu_{2.56}Zn_{0.15})_{\Sigma 2.71}(Te_{0.88}Si_{0.02}As_{0.02})_{\Sigma 0.92}O_{5.47} \cdot 1.53H_2O$. Mcalpineite from Centennial Eureka is a zincian variety with the same idealised formula of $Cu_3TeO_6 \cdot H_2O$. The measured water value of 7(1) wt. % is somewhat higher than that calculated by difference (5.7 wt. %) but, given the limitations mentioned above, is more than reasonable and conclusively shows that the mineral is not anhydrous.

Infrared-absorption study

The infrared spectrum of mcalpineite (McAlpine mine) was obtained using a Spectra-Tech IR-Plan infrared microscope accessory interfaced to a Bomem Michelson MB-120 Fourier-transform infrared spectrometer (FTIR) which utilises a 0.25 mm liquid nitrogen-cooled mercury cadmium telluride detector. A small amount of the pure mineral was mounted in a diamond anvil microsample cell, then pressure was applied to crush the mineral and cause it to spread as a randomly oriented powder; after crushing, the pressure was released. The diamond cell was then positioned in the infrared microscope accessory and the powdered sample masked so as to isolate a circular area measuring 100 μm in diameter which was between 1 and 5 μm in uniform thickness. Two hundred scans were collected and combined at 4 cm^{-1} resolution, from 700 to 4000 cm^{-1}. The transmittance spectrum (Fig. 2) was produced by taking the ratio of the single beam spectrum of the specimen in the diamond anvil cell against a single beam spectrum of the empty diamond anvil cell collected with the same parameters. The spectrum clearly shows absorption bands for structural H_2O. An O–H stretching frequency is centred at 3320 cm^{-1} and a H–O–H flexing frequency is centred at 1600 cm^{-1}. These absorption bands are marked with arrows on Fig. 2.

Optical properties

The same McAlpine mine polished section, previously used for probe analyses, was then submitted for reflectance studies. The carbon coating was removed by abrasion with aluminum oxide paste.

In plane-polarised light, and where the otherwise ubiquitous greenish cast from internal reflections is absent, Mcalpineite is a nondescript grey. The mineral is sensibly transparent: apart from the greenish cast, vari-coloured internal reflections cloud most of the section. Between crossed polars, these are resolved as 'sheaves' of fibrous or prismatic crystals with brilliant apple to lime green internal reflections. Only one area, 8 by 16 μm in size, was sufficiently (but not entirely) free from internal reflections to provide a suitable area for reflectance measurement. This area was isotropic, as, so far as could be determined, given the abundance of internal reflections, was the rest of the section.

The measured field was 4 μm in diameter. It was measured with ×40 objectives, adjusted to effective numerical apertures of 0.26. The reflectance standard was a Zeiss SiC (#472), and the oil used for immersion measurement was Zeiss N_D = 1.515 at 20°C. The results, together with the colour values computed from them, are presented in Table 1 and are graphically represented in Fig. 3. It is stressed that the measured data are from the best area available for reflectance measurement, but even here it was not possible to entirely

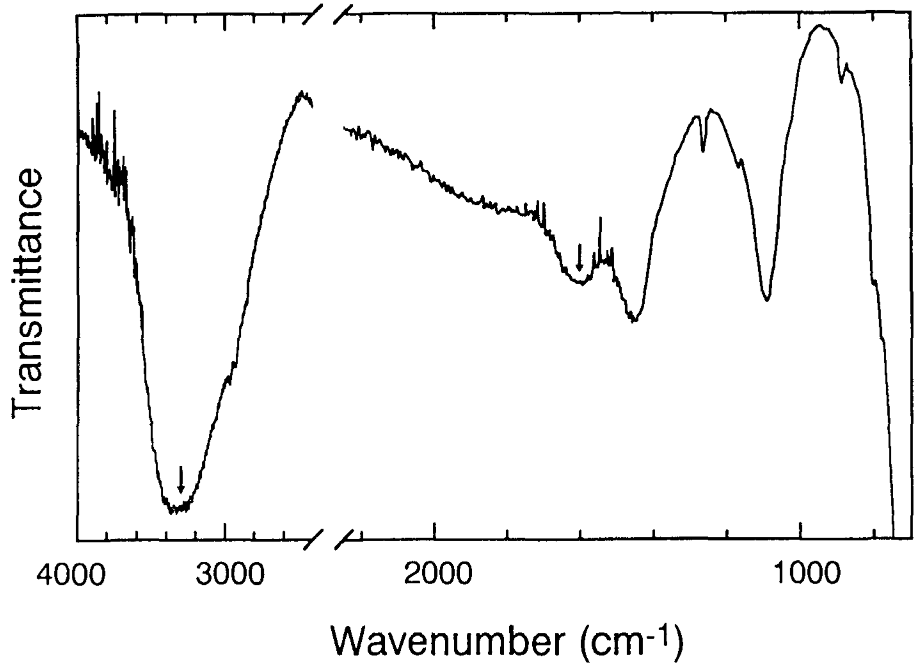

FIG. 2. Infrared-absorption spectrum for mcalpineite (McAlpine mine).

TABLE 1. Reflectance data and colour values for mcalpineite

λnm	R	^{im}R
400	14.4	4.10
420	13.8	3.46
440	13.2	3.04
460	12.9	2.92
470	*12.8*	*2.97*
480	12.5	2.94
500	12.1	2.63
520	11.8	2.35
540	11.6	2.28
546	*11.6*	*2.25*
560	11.6	2.15
580	11.2	2.10
589	*11.2*	*2.05*
600	11.0	2.03
620	11.0	2.00
640	11.1	2.01
650	*11.0*	*2.01*
660	10.95	2.00
680	10.9	1.99
700	10.8	2.01
C colour values:		
x	0.2970	0.2779
y	0.3018	0.2792
Y%	11.5	2.24
λ_d	476	475
P_e%	6.5	16.1
A colour values:		
x	0.4356	0.4177
y	0.4028	0.3923
Y%	11.4	2.17
λ_d	488	486
P_e%	3.1	7.8

TABLE 2. X-ray powder data for mcalpineite

	*I*est.	*d* Å(meas.)	*d* Å(calc.)	*hkl*
	30	4.76	4.78	200
	→40	4.26	4.27	210
	30	3.91	3.90	211
*	→100	2.763	2.758	222
	5	2.640	2.650	320
	5	2.553	2.554	321
*	70	2.384	2.389	400
	5	2.244	2.252	411,330
*	10	2.132	2.137	420
	→5	2.085	2.085	421
*	30	2.038	2.037	332
*	15	1.950	1.950	422
*	40	1.873	1.874	431,510
*	→10	1.772	1.774	432,520
*	10	1.746	1.745	521
*	80	1.689	1.689	440
	3	1.637	1.639	433,530
	5	1.593	1.593	600,442
*	15	1.550	1.550	611,532
	5	1.510	1.511	620
*	20	1.475	1.474	541
*	60	1.440	1.441	622
	5	1.408	1.409	631
*	10	1.380	1.379	444

114.6mm Debye-Scherrer powder camera, Cu radiation, Ni filter (λ Cu-Kα = 1.54178 Å)
intensities visually estimated, not corrected for shrinkage and no internal standard
* = lines used for unit-cell refinement
indexed with a = 9.555 Å

eliminate the effects of internal reflections from the measured signal. Therefore, the data must be interpreted with some caution. The refractive index (at 589 nm) calculated from the two-media measurements using the Koenigsberger equations is 1.98, for which the corresponding absorption coefficient is 0.19. On recalculation of the air and oil reflectances independently, using the Fresnel equations, the refractive indices (for k = 0) are 2.00 (air) and 2.02 (oil). Given the obvious transparency of this mineral, we suggest that the refractive index should be taken as the mean of the air and oil data (2.01) rather than the Koenigsberger-derived value.

X-ray studies

Repeated attempts to obtain single-crystal X-ray precession photographs showed that even extremely small fragments of Mcalpineite from both localities are composed of multiple crystallites. No coherent diffraction nodes were observed on precession orientation photographs. However, the X-ray powder-diffraction pattern from the McAlpine mine specimen (Table 2) is virtually identical to synthetic Cu_3TeO_6 (PDF 22-251) except for four additional medium to weak powder lines (marked with arrows in Table 2). They are always present on powder films and are not due to contamination. These lines can be successfully indexed if the body-centred cubic

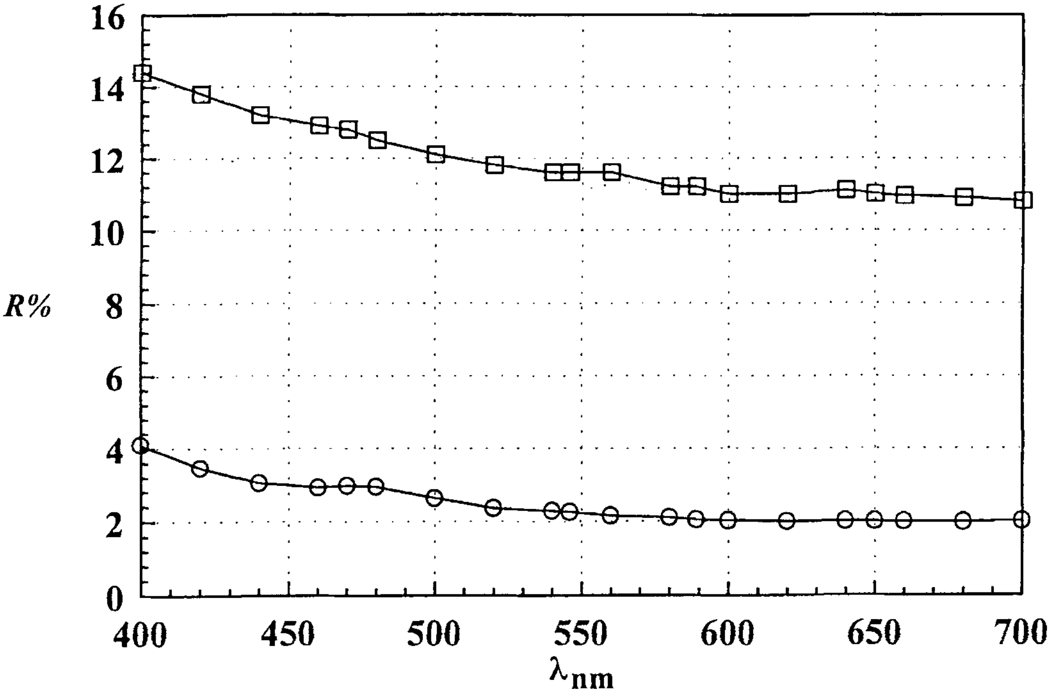

FIG. 3. Reflectance spectra measured in air and in oil (N_d) 1.515) for mcalpineite (McAlpine mine).

lattice of Cu_3TeO_6 (space group $Ia\bar{3}$, a = 9.537(1) Å (Falck *et al.*, 1978)) is symmetry reduced to a primitive cubic lattice. The retention of cubic symmetry is in accordance with reflectance studies which show that the mineral is isotropic.

Mcalpineite is cubic, *P*-lattice (space group unknown) with diffraction aspect *P****. The refined unit-cell parameter, based on 13 reflections between 2.763 and 1.380 Å for which unambiguous indexing was possible, is a = 9.555(2) Å, V = 872.4(4) Å^3. With Z = 8, the calculated density for the empirical formula (McAlpine mine, water calculated by difference)is 6.65 g/cm^3.

Discussion

Mcalpineite represents the seventh known Cu-bearing tellurite or tellurate found in nature. The other six are: balyakinite,$CuTeO_3$; cesbronite,$Cu_5(TeO_3)_2(OH)_6 \cdot 2H_2O$; graemite, $CuTeO_3 \cdot H_2O$; rajite, $CuTe_2O_5$; teineite,$CuTeO_3 \cdot 2H_2O$; and xocomecatlite, $Cu_3TeO_4(OH)_4$. Of these, only xocomecatlite has a Cu:Te ratio of 3:1, but its X-ray powder pattern is totally unlike that of Mcalpineite. Other than the obvious relationship to synthetic Cu_3TeO_6, Mcalpineite bears no similarity with any other inorganic compound found in the literature.

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