

THE LASER RAMAN IDENTITY OF GIBBSITE PSEUDOMORPHOUS AFTER CROCOITE FROM DUNDAS, TASMANIA

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(with three text-figures and three plates)

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Gibbsite both invests and replaces crocoite in late supergene ores of the Dundas district, Tasmania. The laser Raman spectrum of the gibbsite shows strong, well-developed ν -OH stretching bands at about 3370, 3440, 3525, 3620 cm^{-1} , confirming its identity. Crocoite gives bands at 840 cm^{-1} ν_1 , 853 and 825 cm^{-1} ν_3 , 348 cm^{-1} ν_2 , 400, 377, 358, 338 and 326 cm^{-1} ν_4 , and at 179, 135, and 118 cm^{-1} , corresponding to crystal field components of Pb-O vibrations and lattice modes. The chemistry of the late, mineralising fluids is unknown and the relative stabilities of crocoite and gibbsite can not be determined.

Key Words: gibbsite, crocoite, Raman spectra, Dundas, Tasmania.

INTRODUCTION

Crocoite (PbCrO_4) was first described from silver-lead mines of the Dundas district of Tasmania by Petterd (1894). Subsequently, numerous spectacular specimens, not equalled in quality elsewhere, have been collected from the region (e.g. Palache 1896, Petterd 1902, Anderson 1906, Lancaster 1977, Bancroft 1984, Haupt 1988).

The mineral commonly occurs as radiating masses of adamantine to vitreous, vermilion, prismatic crystals, lining vugs and coating fractures in the wall rock and gossan, and frequently intermixed with friable clays. Reported associated minerals include so-called "chromian" cerussite, massicot, chalcophanite, and rarer pyromorphite and dundasite, as well as "limonite" and "wad". Often the prismatic crystals are hollow.

Gibbsite is also abundant in the Dundas mines, "where it encrusts gossan and often coats crocoite crystals" (*Catalogue of the minerals of Tasmania* 1970: 49; Lancaster 1977, Haupt 1988). In crocoite specimens from Dundas in the collection of the Australian Museum, gibbsite not only invests crocoite but also pseudomorphs the hollow prisms, a relationship not previously described. The identity of gibbsite in both habits is confirmed by non-destructive laser Raman microsampling procedures and the textural relationships are clarified by electron microscopy.

gossan, coated with "wad" and sparse pyromorphite(?), and heavily encrusted with radiating, acicular, hollow prisms of crocoite, partly pseudomorphed by gibbsite. The prismatic crystals range from 1-25 mm long and 0.1-4 mm across, with dull scarlet to vermilion bases grading through patchy, pale vermilion to pale orange-yellow crystal walls, to off-white terminations (pl. 2). The prisms are hollow throughout much of their upper extent, and here they have been more or less replaced with gibbsite, including terminations, most of which are missing or damaged (pls 2, 3A,B). Crystal walls are typically c. 0.05-0.2 mm thick, irrespective of the mineralogy. Near their attachment, the crystals are solid but with hollow cores, the inner surfaces of which are also lined by gibbsite (pl. 3C). Throughout all the crystal mass, the surface lustre of the crocoite has been dulled with a dusting of gibbsite. The pale, pseudomorphed portion consists of a mosaic of 10-50 μm diameter, transparent, vitreous gibbsite crystallites (pl. 3D). Replacement renders the hollow crystal walls more translucent and the mosaic structure can be clearly seen in transmitted light, mottled with and outlined in pale orange-yellow. The extent of staining varies, with some close-packed crystallites, forming the upper pseudomorph wall, being pellucid, with only a hint of yellow tinting the crystal mass.

MODE OF OCCURRENCE

Three specimens exemplify the habits exhibited by gibbsite at Dundas, two of which are examined in detail:

D42734 Crocoite with gibbsite, Tasmania. Partly limonitised gossan block, coated with 0.5-10 mm long, 0.1-0.2 mm wide, acicular prisms of vermilion crocoite, invested with tufts and balls of white, microcrystalline gibbsite (pl. 1A).

D46576 Crocoite with gibbsite, Adelaide Mine, Dundas, Tasmania. Matted 5-15 mm long, 0.1-1 mm wide, acicular and bladed prisms of bright vermilion crocoite in cavernous ferromanganese gossan, partly coated by pisolitic stalactites of gibbsite, fingers of which rise 10 mm above the surface and are up to 3 mm thick (pl. 1B).

D44000 Crocoite partly replaced by gibbsite, Adelaide Mine, Dundas, Tasmania. Irregular, 200 \times 250 \times 200 mm mass of

RAMAN SPECTROSCOPY

Gibbsite

Gibbsite was confirmed using laser Raman spectroscopy, employing instrumental conditions given in Cooney *et al.* (1989) and Rodgers *et al.* (1989). The Raman spectra of fragments of the white encrustations and of different areas of the crystal walls were recorded by microsampling, using a Jobin-Yvon U1000 instrument with 514.5 nm Ar^+ as the exciting line. Laser power was 1 W with 100 mW recorded at the sampling lens (an uncoated \times 40 objective of a Nikon microscope). Monochannel Ga-As photomultiplier detectors were employed. Spectra for gibbsite were recorded from 3000-3700 cm^{-1} and 100-1300 cm^{-1} .

Initial determinations were made of a white, 3 mm diameter ball investing a small group of crocoite crystals in specimen *D42734*. A small portion of the ball was crushed,

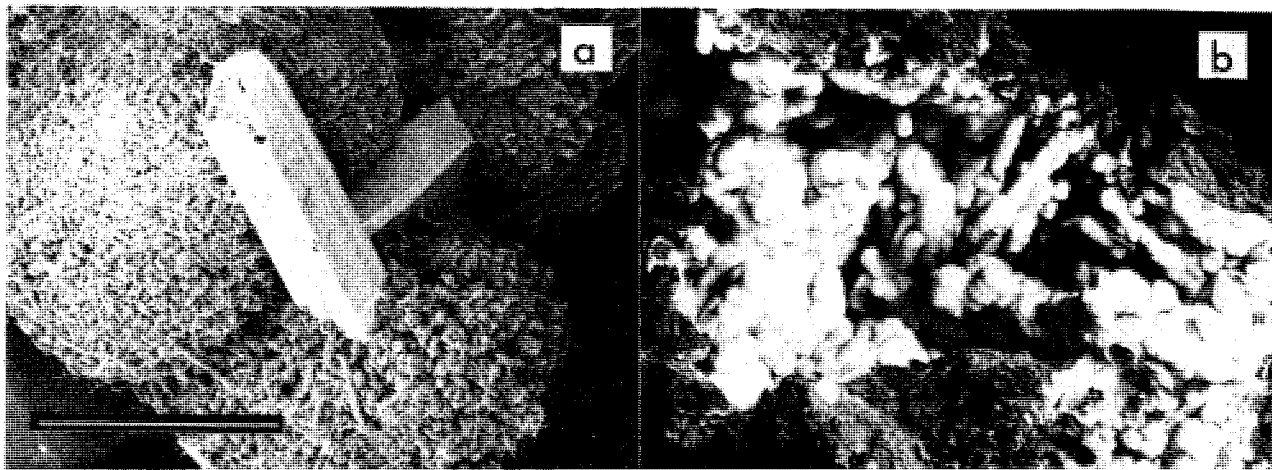


PLATE 1

(a) Scanning electron micrograph of multicrystal balls of gibbsite investing crocoite prisms. In this encrusting mode, crocoite has remained passive throughout precipitation of gibbsite. Haupt (1988: 385) noted that "chemical methods for removing [gibbsite] without harm to the underlying crocoite have been developed." (Surface fibres are fungal hyphae.) Australian Museum specimen D42734, Tasmania. Scale bar: 1 mm. (b) Pisolitic stalactites of gibbsite lining vug in gossan containing abundant bright crocoite needles. Australian Museum specimen D46576, Dundas, Tasmania. Base of photo is approximately 100 mm.



PLATE 2

Prismatic crocoite crystals partly pseudomorphed by gibbsite (white). The prisms are hollow throughout much of their length where they have been more or less replaced with gibbsite, including their former terminations. Near their attachment, the crystals are solid, although having hollow cores whose inner surfaces are also replaced by gibbsite. Australian Museum specimen D44000, Dundas, Tasmania. Base of photo is approximately 45 mm.

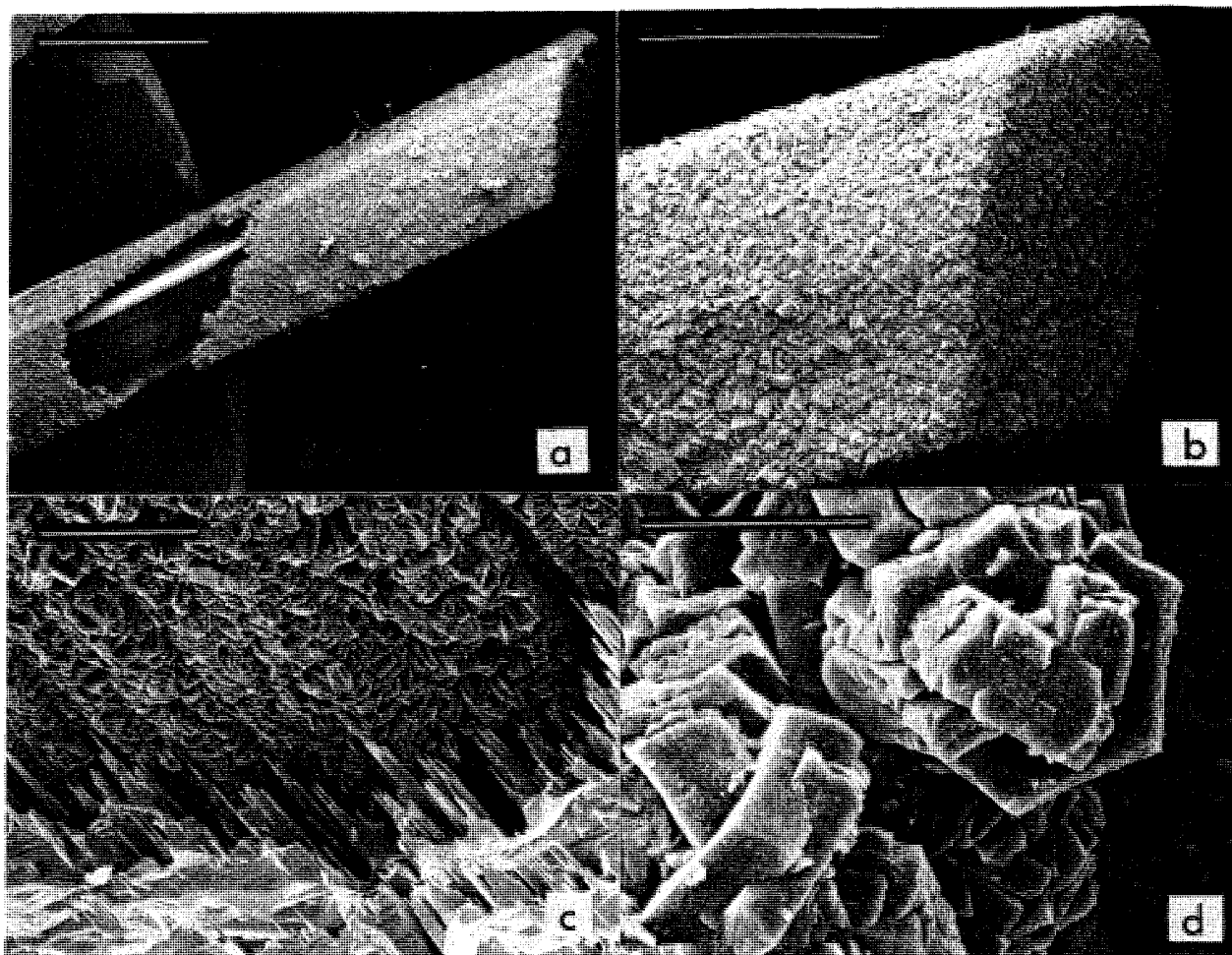


PLATE 3

Scanning electron micrographs of gibbsite-crocoite association, Dundas, Tasmania. Australian Museum specimen D44000. (A) Broken, hollow, prismatic crystal of crocoite with termination totally replaced by crystalline gibbsite mosaic. Original crocoite forming inner wall of the crystal tube can be seen through hole. The portion of crystal below hole is a dull scarlet and the surface here is studded with gibbsite crystallites. Scale bar: 2 mm. (B) Similar termination to that in (A). Scale bar: 500 μm . (C) Crocoite-gibbsite tube broken close to solid crocoite crystal base. Multicrystal gibbsite tube wall above, splintered crocoite below; splinters at margins conforming to grooves in gibbsite aggregate. Scale bar: 200 μm . (D) Aggregate of tabular, pseudohexagonal crystals of gibbsite on broken edge of pseudomorphed termination. Scale bar: 50 μm .

yielding abundant, transparent to partly occluded crystal fragments. Raman spectra recorded using laser power of 1000 mW yielded an excellent gibbsite "fingerprint" with strong v-OH stretching bands at about 3370, 3440, 3525, 3620 cm^{-1} , the results closely approximating those of Huneke *et al.* (1980) and Rodgers *et al.* (1991). The same spectrum was returned by direct laser examination of the remaining original ball surface.

Several pseudomorphed crystals were scanned from D44000; the laser being focused directly on the virgin surface of the crystal prisms. Typical results were demonstrated by the partly broken, off-white termination of one former 15 mm crocoite crystal, which gave a clear gibbsite spectrum with a strong background fluorescence that decreased sharply with increasing wavenumber. A smaller but complete, largely pseudomorphed crystal (similar to that in plate 3B) gave similar results, with signal to noise ratio being improved by increasing the laser power to c. 1500 mW (fig. 1).

Scans of white pseudomorph crystal tips of D44000, showing the least yellow colour, gave good gibbsite spectra

free of any crocoite bands in the region 100–1300 cm^{-1} (fig. 2). Lower on the same prisms, where replaced portions of the crystals are more intensely stained, weak crocoite lines appear in the Raman spectra.

All gibbsite crystallites examined from this large specimen, D44000, appeared similar in size to the focused laser spot.

Crocoite

Unsatisfactory crocoite spectra, but sufficient to confirm the identity of the mineral, were obtained from 100–1200 cm^{-1} from several of the vermilion portions of crystals of D44000, using the green Ar^+ 514.5 nm line. The CrO_4^{2-} ion absorbs strongly over the range 24000–28000 cm^{-1} (Campbell 1965) but transmits in the red and superior results were obtained by macrosampling untreated faces from these same crystals with the red Kr^+ laser (647.1 nm) and an Anaspec-Cary 81 spectrometer. The example shown in figure 3 closely matches the result obtained by Wilkins (1971) for an unlocated Tasmanian crocoite and is broadly

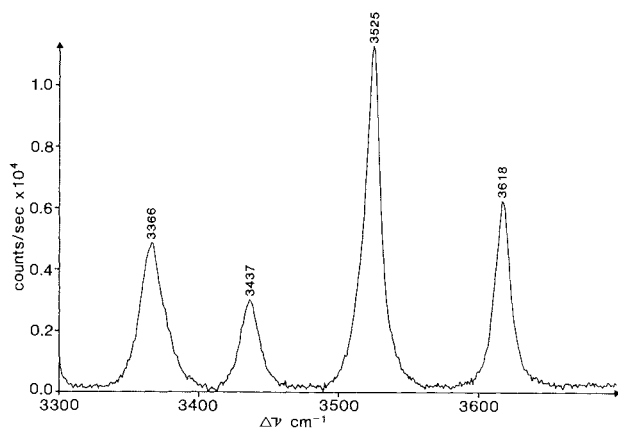


FIG. 1 — Microprobe laser Raman spectrum of Dundas gibbsite, pseudomorphing crocoite from 3330–3700 cm^{-1} . Australian Museum specimen D44000.

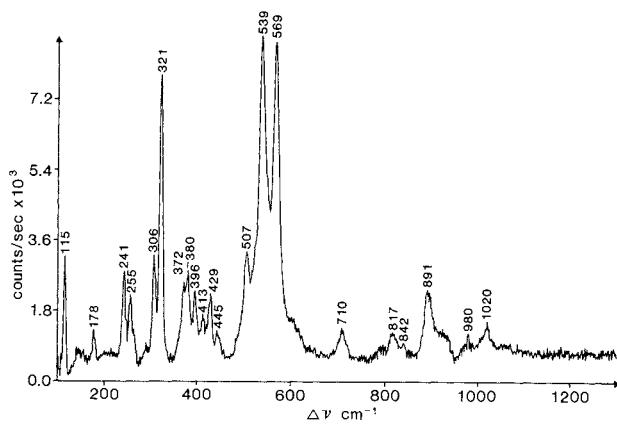


FIG. 2 — Microprobe laser Raman spectrum of Tasmanian gibbsite, investing crocoite from 100–1300 cm^{-1} . Australian Museum specimen D42734.

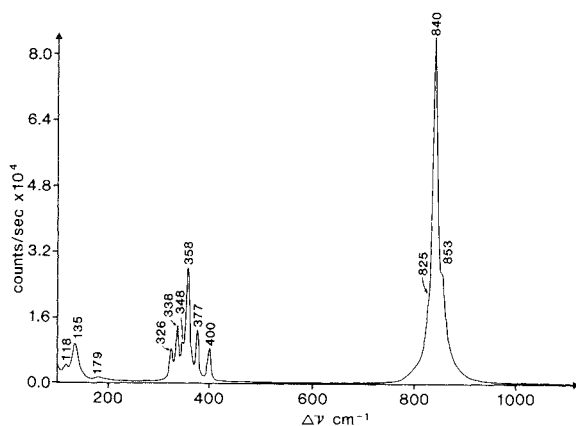


FIG. 3 — Laser Raman spectrum of Dundas crocoite from 100–1200 cm^{-1} . Australian Museum specimen D44000.

comparable to that obtained by Scheuermann *et al.* (1970) from a polished crocoite single crystal cut normal to c . This arrangement avoided scrambling of polarisation of the incident and scattered radiation caused by polycrystalline reflections, and produced a spectrum exhibiting finer structural detail than obtained by Wilkins (1971) or the present study.

Band assignments for crocoite, following Scheuermann *et al.* (1970) and Wilkins (1971), are:

- ν_1 (A_1) 840 cm^{-1} (symmetric stretching of CrO_4^{2-});
- ν_3 (F_2) 853, 825 cm^{-1} (asymmetric stretching of CrO_4^{2-});
- ν_2 (E) 348 cm^{-1} (bending deformation of CrO_4^{2-});
- ν_4 (F_2) 400, 377, 358, 338, 326 cm^{-1} (bending vibration of CrO_4^{2-});
- 179, 135, 118 cm^{-1} crystal field components of Pb–O vibrations and lattice modes.

DISCUSSION

Results obtained here demonstrate the versatility of the laser Raman microprobe in identifying the crystal chemistry of fine-grained compounds in a non-destructive manner. However, the experimental results shed scant light on the late paragenetic history of the Dundas ores.

A complex sequence of mineralisation has affected the Dundas district (Reid 1925, Blissett 1962). Following emplacement of the primary ore, secondary deposition occurred in fissure-replacement bodies. In the main, the secondary minerals within oxidised ore appear to have been derived from the primary minerals, and solution migration of metallic elements has been limited. Crocoite has formed late in a probable supergene sequence, and conventional wisdom regards the mineral as a product of oxidation of primary chromite in serpentinite wall rocks with solution of the chromium, and the subsequent reaction of this species with lead liberated from the primary ore. However, without any information on the chemistry of the mineralising fluids, the late paragenesis of the Dundas ores can only be conjectured.

Existing accounts of mineral paragenesis in the region make little reference to the role of gibbsite within the oxidised gossan ores. Clearly it is late, arguably the latest major mineral in the sequence. Among the wide range of minerals deposited earlier in the Dundas ores, few are aluminous. If aluminium was a component of the mineralising fluids, conditions did not favour it precipitating as part of a solid phase. Slightly acid to neutral conditions favour the precipitation of gibbsite, but it is seldom possible to define the conditions of formation of an aluminium hydroxide deposit from the crystal chemistry of its present day component(s) (Rodgers *et al.* 1991). In the case of Dundas, any attempt to draw conclusions is confounded by gibbsite replacing crocoite in one instance and investing it in another. This apparent dual facility of gibbsite to precipitate upon stable crocoite, as well as to crystallise at the same mineral's expense, may indicate that the stability fields of the two minerals overlap in a manner similar to that deduced by Southwood & Vilgoen (1986) for coexisting crocoite and vauquelinite in a silver–lead deposit in the Transvaal. However, the contrasting textural evidence at Dundas may also reflect the influence of kinetic factors in the formation of gibbsite, rather than purely thermodynamic considerations, as Nickel (1984) demonstrated for a pyrite–sulphur–jarosite pseudomorph assemblage. The investment of crocoite crystals could be consistent with rapid nucleation,

the pseudomorphism of delicate crystals suggesting a more extended gibbsitisation.

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