SHORT COMMUNICATIONS

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Prosopite, doyleite and otavite from Coldstones Quarry, Pateley Bridge, North Yorkshire

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THE Lower Carboniferous (Dinantian) limestones worked at Coldstones Quarry, Pateley Bridge, North Yorkshire [National Grid Reference SE 123 641] are cut by several veins which carry fluorite, baryte, galena and sphalerite. These veins lie immediately north of the North Craven Fault System (Dunham and Wilson, 1985). Where exposed in the quarry the veins are strongly oxidized and the supergene minerals hemimorphite, smithsonite and cerussite are abundant, commonly lining cavities which may represent original pockets of sphalerite and galena. Traces of aurichalcite and rosasite have been reported together with local concentrations of cinnabar of supergene origin (Young *et al.*, 1989). Recent examination of oxidized veinstone, collected from fallen blocks from the Garnet Vein and associated veins exposed in the southern face of the quarry, has revealed the presence of the rare minerals prosopite, doyleite and otavite; all are reported here for the first time from the British Isles.

Prosopite

This basic alumino-fluoride of calcium ($CaAl_2(F,OH)_8$) is most commonly found in association with other aluminium fluoride minerals such as cryolite, in granitic or alkaline intrusive or volcanic environments where it is typically a product of F-rich greisenization and hydrothermal processes (e.g. Scheerer, 1857; Palache *et al.*, 1951; Bailey, 1980). In a review of aluminofluoride minerals Bailey (op cit., p34) suggests that minerals of this sort may also form in supergene environments, though no instances of prosopite in such situations are cited. However,

prosopite reported from Dugway, Torvel County, Utah (Hillebrand, 1899), the blue cuprian prosopite resembling turquoise from Santa Rosa, Zacatecas, Mexico (Dunn and Fryer, 1976) and, more recently that found as small spherules on corroded fluorite at Clara Mine, Schwarzwald, Germany (Walenta, 1990) may be examples of this paragenesis.

At Coldstones Quarry prosopite occurs as white to pale blue-tinted chalky or soft earthy masses up to 10 mm across, always associated with minerals of undoubted supergene origin. Identification was by IR, EDA and powder XRD. Examination by SEM showed the prosopite to consist of aggregates of prismatic crystals 1–5 μm long) (Fig. 1). It is most commonly found embedded in thick, pale brown, often somewhat spongy encrustations on massive fluorite and on 1–3 cm fluorite cubes. Such crusts consist of variable mixtures of smithsonite, halloysite-10 Å, and several not fully characterized aluminium hydroxide and/or silicate phases (some possibly amorphous); the prosopite may be replacing the original components. Similar patches of prosopite occur in irregular open cavities within the encrustations or within the fluorite veinstone. These are lined with iron-stained smithsonite which, together with traces of cinnabar, probably represent original masses of sphalerite. Here prosopite clearly postdates smithsonite. There seems little doubt that all of the prosopite at this locality is of supergene origin. On the specimens examined, prosopite is quite abundant, though its distribution in the vein may be restricted.

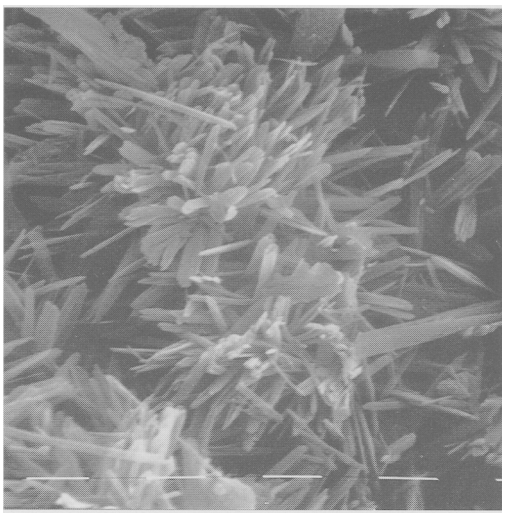

FIG. 1. Prosopite from smithsonite-lined vug in smithsonite-halloysite-Al hydroxides encrustation on fluorite. Scale bars 1 μm.

Doyleite

The aluminium hydroxide mineral doyleite [$Al(OH)_3$] is a rare mineral first described from an altered pegmatite at Mont Saint-Hilaire, Quebec and from silicocarbonatite sills at Francon Quarry, Quebec (Chao *et al.*, 1985). More recently it has been identified at the Clara Mine, Oberwolfach, Baden-Württemberg, Germany, as small crystalline crusts on quartz, associated with kaolinite (Walenta, 1993).

Doyleite has been identified by X-ray powder diffraction of a very soft powdery white mineral filling small (up to 3 mm) cavities in greyish white fluorite. The doyleite is accompanied locally by prosopite as well as by other white, powdery to milky white, translucent, massive minerals which have not yet been fully characterized, though preliminary data suggest that aluminium hydroxides may be the major constituents.

The infrared spectrum of the X-rayed sample of doyleite, however, did not correspond to the published doyleite spectrum (Chao *et al.*, 1985). It is probable that the bulk of the sample consists of amorphous aluminium hydroxides whose infrared absorption masked those of doyleite: gibbsite was not found. Doyleite from Francon Quarry, Quebec, was reported to be generally admixed with an unidentified mineral believed to be an aluminium hydroxide, with an X-ray pattern similar to that of gibbsite (Chao *et al.*, op cit.). Some samples of encrustations on fluorite from Coldstones Quarry also gave powder patterns near that of gibbsite although, according to the infrared evidence, no significant amount of gibbsite can be present.

Otavite

The cadmium carbonate mineral otavite ($CdCO_3$) is a very rare supergene mineral first described from Tsumeb, Otavi, Namibia (Schneider, 1906). A zincian otavite has subsequently been reported from the Mo Ba lead-zinc deposit, Vietnam (Johan, 1962) and a calcian otavite in the cement of Permian cupriferous sandstones in the Orenburg area, Ural Mountains, Russia, has been described (Bur'yanova *et al.*, 1969).

At Coldstones Quarry otavite has been found in one cavity in fluorite veinstone as small, pure white, nodular masses up to 2 mm across, some of which exhibit crude twinned rhombohedral outlines (Fig. 2) perched on well-crystallized hemimorphite, botryoidal smithsonite, or fluorite. It is clearly the last-formed mineral in the cavity. Identification of the otavite was by IR and XRD.

Both the slightly enlarged unit cell and the position of the ν_4 IR absorption peak (721 cm^{-1}) indicated a

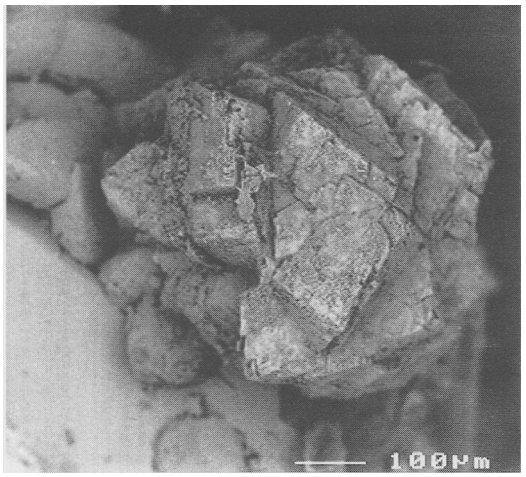

FIG. 2. Calcian otavite, crystal group on fluorite. Scale bar 1 µm.

calcian otavite, with ~27 mol.% $CaCO_3$ estimated from the IR spectrum. EPMA analyses of a polished section of the aggregate shown in Fig. 2 (perpendicular to the interface with the underlying fluorite) revealed alternating high-Ca zones of average stoichiometry $(Cd_{0.58}Ca_{0.35}Pb_{0.04}\ Zn_{0.03})CO_3$, and low-Ca zones averaging $(Cd_{0.66}Ca_{0.26}Pb_{0.04}Zn_{0.03})CO_3$, The average composition of the crystal group was $(Cd_{0.62}Ca_{0.31}Pb_{0.04}Zn_{0.03})CO_3$.

This is the first confirmation of macroscopic otavite from the British Isles, though its presence was inferred in 1987 from the X-ray powder pattern (unpublished Natural History Museum X-ray number 6472F) of very thin, bright yellow powdery crusts on baryte, collected by S.A. Rust from Waterbank Mine, Ecton, Staffordshire. After subtracting lines due to admixed baryte the residual pattern corresponded to that of otavite with a somewhat reduced unit cell, indicating a zincian variety.

Oxidation of sphalerite to form abundant hemimorphite and smithsonite within the veins at Coldstones has, no doubt, released the cadmium required to form otavite. Supergene alteration of sphalerite elsewhere in the Northern Pennine Orefield has typically produced thin crusts of cadmium sulphides, including greenockite (Young *et al.*, 1987) but these have not been observed at Coldstones Quarry.

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