MINERALOGICAL MAGAZINE

JOURNAL OF THE MINERALOGICAL SOCIETY

Vol. 33 June 1963 No. 261

# *Rosasite, aurichalcite, and associated minerals from Heights of Abraham, Matlock Bath, Derbyshire, with a note on infra-red spectra.*

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[Read 27 September 1962.]

*Summary.* Rosasite and aurichalcite occur with other copper, zinc, and also lead minerals in Masson Cavern, Rutland Cavern, and other workings in the Heights of Abraham, Matlock Bath, Derbyshire. Partial analyses of two specimens each of rosasite and aurichalcite show Cu:Zn ratios typical of the respective species. They appear to have been formed by the action of solutions containing zinc on disseminated chalcopyrite. The infra-red absorption spectra of malachite, rosasite, aurichalcite, and hydrozincite, examined by the mull technique, are shown to fall into two groups corresponding with the structural groups established by X-ray work. Twin absorption maxima at O–H stretching frequencies are present in the spectra of malachite and of rosasite.

ROSASITE has been found in Rutland Cavern (a classic British locality for aurichalcite) and, together with aurichalcite, in neighbouring workings in orebodies associated with the Great Rake at the Heights of Abraham, Matlock Bath, Derbyshire. The mines and caves on this part of the Great Rake complex may be divided into three probably connected series one above the other: Masson Cavern, at about 800 ft O.D.; Rutland Cavern, at about 700 ft O.D.; and the lower Nestus mine workings, at about 550 ft O.D. Masson and Rutland Caverns are at present open as show-caves.

In the Carboniferous Limestone of the Heights of Abraham there are a number of caves and abandoned lead mines on the Great Rake and its off-shoots. Near the surface, at the outcrop of the rake, parts of a series of natural hollows and old workings form Masson Cavern (N.G.R.[1] SK/29165866), opened as a show-cave in 1844, and connected to the north with the Black-Ox–High-Loft mine complex.

Below them, Rutland Cavern (N.G.R.[1] SK/29305858) was opened to the public in 1810 by driving a 160 ft adit level into the upper workings of the long disused Nestus mine, formerly extensively worked by shafts from the surface (cf. Adam, 1845). This mine is also known under several variants of the name (e.g. Nestes, Nester's, Nestor's), and an early name associated with the Heights of Abraham is *Nes(s)tow(e)s gro(o)ve* or *Nesthouse grove*, signifying either a grove of trees or a lead mine ('groove') (Cameron, 1959). The history of Nestus mine is obscure. Bryan (1903) suggests that it is to be identified with the 'lead work in Mesterforde' mentioned in the Domesday Book, although it is more probable that a shallower mine in this rich area was then worked. It is also reputed to be a Roman mine, but although lead mines near Matlock were known to the Romans, the effects of a long medieval history of mining in the region make it impossible to identify individual Roman mines (cf. Davies, 1935). Probably only the outcrops were attacked, so that the Masson Cavern workings are more likely to have been exploited than any part of the deeper Nestus mine.

It should be mentioned that Rutland mine or cave appears to have been confused with Cumberland mine or cave, about half a mile to the south (Farey, 1811; Green and Strahan, 1887; Caruthers and Strahan, 1923).

The lower workings of Nestus mine are now less readily accessible. A shaft (N.G.R. SK/29255856), explored by the Kindwr Club in 1912–13 and by Workman and others in 1955, was found to lead to extensive excavations some 150 ft below Rutland Cavern (Nash and Workman, 1955). These included a large worked-out pipe dipping steeply south, and east–west stope workings apparently on the Great Rake. The shaft is here partly blocked, but descends a further 200 ft to the water-table, while smaller shafts that have not been examined lead up towards the Rutland Cavern workings. Farey (1811), by listing separately 'Nester's or Nestus Rake' and 'Old Nester's or Nestus Pipe', was probably distinguishing between the workings associated with what is now Rutland Cavern and these lower workings.

The gangue minerals in all three sections are calcite and fluorite, in accordance with the position of the ore-bodies in the fluorite zone as defined by Wedd and Drabble (1908; cf. Dunham, 1952). The fluorite is mostly colourless; purple fluorite is rare and local, which suggests that the deposits are in the high-temperature sub-zone proposed by Mueller (1954), and may therefore be close to an emanative centre of the lead-zinc mineralization. Colourless platelets of baryte are present occasionally on corroded calcite. Small amounts of chalcopyrite occur dispersed as grains up to 2 mm across, largely altered into dark brown, pitchy material the composition of which has not been established.

The principal ore-mineral is galena, associated with which is some blende; these have been mostly removed by mining, the remaining ore being found in strings, individual grains, and pockets. Secondary lead

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[1] These are the National Grid References of the cave entrances.

minerals are represented by small amounts of cerussite.[1] The most common secondary products derived from the ore-minerals are those of zinc and copper, of which aurichalcite and rosasite are described in detail below. On one sample of the veinstuff from Rutland Cavern bunches of small needles of malachite were found associated with colourless microglobular smithsonite, iron-stained calcite, and fluorite, but aurichalcite and rosasite were absent. In general, smithsonite and hemimorphite are common (cf. Greg and Lettsom, 1858) and often occur in close association with rosasite and aurichalcite; smithsonite forms pale brownish botryoidal crusts or minute colourless globules, and is occasionally found as a white powdery deposit both underlying and coating rosasite; hemimorphite forms bunches and crusts of colourless tabular crystals.

## *Aurichalcite.*

Aurichalcite from Derbyshire was first described and analysed by Connel (1848), who gives Matlock as the locality. Other early authors (Greg and Lettsom, 1858; Hall, 1868; Woodward, 1881) refer to the more precise locality of Rutland mine or Cavern. This may, in fact, have been known earlier as a locality for aurichalcite, since Tooke (1836) lists 'cupriferous calamine' from Rutland Mine, and Adam (1845) mentions among zinc minerals from Rutland Cavern 'that beautiful species of the green carbonate called "cupreous"'. Comparison of hand-specimens of aurichalcite in museums, nearly all of which had been collected long ago, with those that we collected from Rutland Cavern proper and with specimens recently raised from the lower Nestus mine workings strongly suggests that most of the museum specimens originated in the lower workings. In fact, aurichalcite is common and widely distributed in all three series of workings, growing on fluorite and calcite, and often closely associated with rosasite. It forms pale green felted or pearly crusts, or tufts of needles or blades up to 5 mm long.

Two other occurrences of aurichalcite in the limestone of the Derbyshire Dome are known: Golconda mine, Hopton,[2] and Millclose mine,

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[1] A specimen of matlockite (B.M. 54263) in the British Museum collection was for a time attributed to 'Rutland Mine', and this locality has been quoted by F. A. Bannister (Min. Mag. 1934, vol. 23, p. 587). Dr. G. F. Claringbull has very kindly investigated the catalogue entry and labels associated with this specimen, and has found that it originates from 'Arkwright Mine, Cromford, Derbyshire' and not from 'Rutland Mine'.

[2] Cf. two specimens in the British Museum collection: B.M. 1921, 249, aurichalcite associated with hemimorphite and baryte, presented by C. S. Garnett, 1921; and B.M. 1951, 191, aurichalcite from C. S. Garnett collection, bought from Gregory, Bottley, & Co., 1951.

Wensley (Traill, 1939), both in Derbyshire. We have collected aurichalcite also from road excavations at Harp Edge (Matlock Bath parish), near Cromford, Derbyshire, and from dumps at the Dutchman, Good Hope, and Waterbank mines, Ecton Hill, Wetton, Staffordshire.

### *Rosasite.*

Many of the specimens that were collected by the authors in Rutland and Masson Caverns in 1959 and some specimens from the lower Nestus mine workings showed in addition to aurichalcite a green globular carbonate, the X-ray powder pattern of which resembled that of malachite and which proved to be rosasite. The rosasite from this new British locality occurs as pale bluish-green to dark green botryoidal crusts or globules up to 2 mm diameter, and occasionally as clusters of microneedles, on fluorite or calcite. Like the aurichalcite, it is scattered throughout the mineralized portions of the limestone and rarely forms isolated patches of high concentration.

In recent years rosasite has been found at several localities in the British Isles: several mines in the Caldbeck area, Cumberland, and the Grisedale mines, Patterdale, Westmorland (Kingsbury and Hartley, 1957); Chatsworth mine, Grassington Moor, Yorkshire (Hartley, 1959; the present authors have also found rosasite on other parts of Grassington Moor); Snelston mine, Snelston, near Ashbourne, Derbyshire;[1] and Penberthy Croft mine, St. Hilary, Cornwall (Kingsbury and Hartley, 1957). To these we can add two new localities, Red Rake mine, Calver, Derbyshire, and Waterbank mine, Ecton Hill, Wetton, Staffordshire.

Partial analyses of rosasite and aurichalcite from Rutland Cavern (table I) show them to have Cu:Zn ratios typical of the respective species

TABLE I. Partial analyses of rosasite and aurichalcite from Rutland Cavern.

| | CuO. (%) | ZnO. (%) | Cu : Zn. (*atoms*) | CuO+ZnO. (% *found*) | CuO+ZnO. (% *calc.**) |
|---|---|---|---|---|---|
| 1. Rosasite, light green, globular ... | 41·2 | 30·6 | 1·34 | 71·8 | 72·1 |
| 2. Rosasite, dark green, globular ... | 38·1 | 31·2 | 1·21 | 69·3 | 72·2 |
| 3. Aurichalcite, pale green, acicular | 21·4 | 50·0 | 0·43 | 71·4 | 74·0 |
| 4. Aurichalcite, darker, bladed ... | 25·2 | 47·6 | 0·53 | 72·8 | 74·0 |
| 5. Aurichalcite (Connel, 1848) ... | 32·5 | 42·7 | 0·76 | 75·2 | 73·9 |

1–4. Analyst: D. I. Bothwell, 1960. 6–10 mg samples purified by means of $CH_2I_2$; Cu estimated electrolytically as metal, Zn gravimetrically as 8-hydroxyquinolate.

5. '3·16 grains analysed by ordinary methods.' Also $CO_2+H_2O$, 27·5 %; MgO and CaO, tr.; sum, 102·7.

* Calculated assuming the formulae $(Cu,Zn)_2CO_3(OH)_2$ for rosasite and $(Zn,Cu)_5(CO_3)_2(OH)_6$ for aurichalcite, and using the experimental Cu : Zn ratios.

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[1] R. J. King, priv. comm.

(cf. Lauro, 1938; Palache, Berman, and Frondel, 1951). Connel's 1848 analysis, on the other hand, indicates an unusually copper-rich aurichalcite.

## *Formation of aurichalcite and rosasite.*

It appears that in the Masson Hill orebodies aurichalcite and rosasite are formed by the direct action at ordinary temperatures of zinc-bearing solutions on disseminated grains of chalcopyrite (or of the brown pitchy alteration product already mentioned), the residual iron being responsible for the brown staining usually associated with these minerals. In some cases traces of such grains can be seen to form the nuclei of globules of rosasite or of bunches of aurichalcite crystals. No such nuclei of other minerals, e.g. malachite, have been detected. The rarity of malachite and the almost complete absence of 'copper staining', contrasted with the widespread occurrence of smithsonite and hemimorphite, also suggest that the copper is precipitated by mobile zinc ions as rosasite or aurichalcite in the vicinity of the original chalcopyrite grains. It is possible that the conditions (temperature of the solution, nature and concentration of solutes) are such as to render the copper relatively immobile by adsorption on the calcitic matrix, a mechanism that receives some support from the work of Canals, Marignan, and Cordier (1949 *a*, *b*). These authors found that cupric ions are preferentially adsorbed on calcium carbonate from a solution containing $\sim 10^{-7}$ g-ion/l. of both cupric and zinc ions, the difference being more marked as the concentration of the two ions increases.

The paragenesis is therefore somewhat different from that encountered elsewhere, e.g. at Tsumeb, SW. Africa, or in the Altai ore-deposits, Siberia, where malachite acts as a precursor of rosasite and aurichalcite (Schneiderhöhn; Bolgov and Rozybakyeva, 1956). Thus Schneiderhöhn has shown that at Tsumeb malachite, itself pseudomorphous after azurite, is converted by zinc-bearing solutions successively into cuprozincite, paraurichalcite, rosasite, aurichalcite, and hydrozincite. Kernels of residual malachite surrounded by these reaction products occur at Tsumeb.

## *A note on the use of infra-red spectroscopy.*

In these studies we have found infra-red absorption spectroscopy to be a convenient and rapid method for identifying small quantities of secondary minerals, and in particular for distinguishing between rosasite and aurichalcite and between hydrozincite and powdery smithsonite.

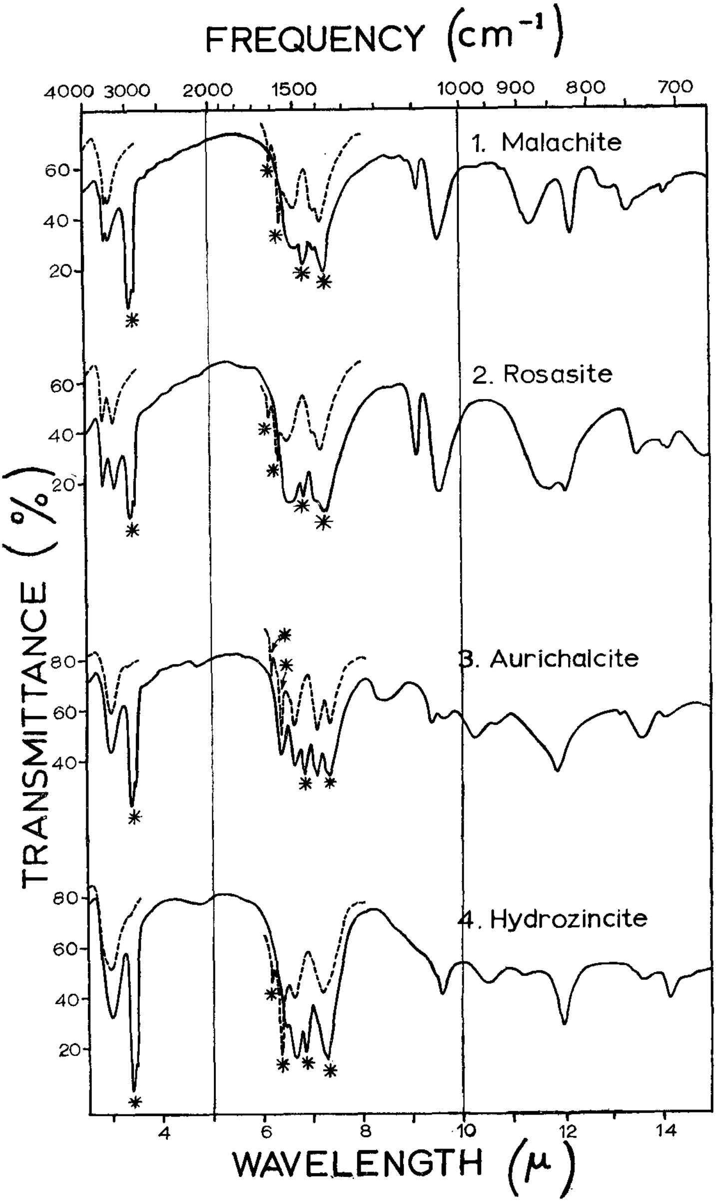

FIG. 1. Infra-red absorption spectra of: (1) malachite, Rutland Cavern; (2) rosasite, Rutland Cavern; (3) aurichalcite, Rutland Cavern; (4) hydrozincite, Van mine, Llanidloes, Montgomeryshire. (—Nujol mull; - - - - hexachlorobutadiene mull; bands due to the suspension media are starred.)

The scope of this technique as applied to inorganic compounds and minerals is apparent from many papers (e.g. Hunt, Wisherd, and Bonham, 1950; Miller and Wilkins, 1952; Launer, 1952; Hunt and Turner, 1953; Takeuchi, 1959; and references cited by these authors). Normal, basic, and hydrated carbonates are among the minerals most readily identified by infra-red spectroscopy, both when pure (cf. Huang and Kerr, 1960; Caillère and Pobeguin, 1960) and when present in mixtures (cf. Pobeguin and Lecomte, 1953; Underwood, Toribara, and Neuman, 1955; Pobeguin, 1960).

The infra-red absorption spectra (fig. 1) of hydrozincite from Van mine, Llanidloes, Montgomeryshire, and of aurichalcite, rosasite, and malachite from Rutland Cavern were taken with a Perkin–Elmer 137 (Infracord) spectrophotometer fitted with a sodium chloride prism, an instrument that is well suited for the routine identification of minerals. The 'mull' technique of supporting the sample in the infra-red beam was used: by placing the sample, finely ground in an agate mortar, in the centre of a sodium chloride plate and covering this with a second plate on which a small drop of the suspension medium ('Nujol' or hexachlorobutadiene) has been put, as little as 0·05 mg of the minerals could be identified. With the minerals described here this procedure gave suspensions showing little scattering at high frequencies and no anomalous effects due to orientation of the particles. The time taken for each identification was less than 15 min.

In addition, a precision spectrophotometer (Perkin–Elmer 21) was used to measure the positions of maximum absorption given in table II. Spectra taken in 'Nujol', in hexachlorobutadiene and in KCl pressed disks showed no significant differences (apart from those due to absorption by the suspension media). Calibration was against polystyrene (Plyler and Peters, 1950). Except in the 3000 $\text{cm}^{-1}$ region (see below), the spectrum of malachite agrees with that published by Huang and Kerr (1960).

TABLE II. Absorption maxima of hydrozincite (1) from Van mine, Llanidloes, Montgomeryshire and of aurichalcite (2), rosasite (3), and malachite (4) from Rutland Cavern (s, strong; m, medium; w, weak; values in brackets denote inflections).

1. 3350 s, (1550 m), 1505 s, 1390 s, 1040 m, 945 w, 890 w, 830 s, 735 w, 705 w.
2. 3340 s, 1560 s, 1505 s, 1415 s, 1365 s, 1060 m, (1035 m), 977 s, (930 m), 835 s, 730 m, (705 w).
3. 3490 s, 3245 s, 1522 s, (1415 s), 1385 s, 1095 m, 1040 s, 843 s, 825 s, 740 w, 705 w.
4. 3400 s, 3305 s, 1495 s, (1425 s), 1390 s, 1095 m, 1045 s, 875 s, 820 s, 770 w, 750 w, 710 w.

The spectra (fig. 1 and table II) fall into two groups, in accord with the structural relationships established by X-ray work between hydrozincite and aurichalcite, on the one hand, and rosasite and malachite, on the other (Lauro, 1938; Ramsdell, 1947; Palache, Berman, and Frondel, 1951). An interesting difference between members of the two groups lies in the nature of the bands in the 3000 $\mathrm{cm}^{-1}$ region, due to O–H bond stretching vibrations. The former pair of minerals shows a single, rather broad band, whereas rosasite and malachite show two widely separated, sharp bands of approximately equal intensity (Huang and Kerr (1960) record a single strong band at 3510 $\mathrm{cm}^{-1}$ in the spectrum of malachite taken in a KBr pressed disk; this band, probably masking the twin malachite bands, is due to adsorbed water and also appears in the spectra of calcium oxide in KBr and of a blank KBr disk). The structural implications of these observations are being investigated. In view of their wide separation (rosasite, 245 $\mathrm{cm}^{-1}$; malachite, 95 $\mathrm{cm}^{-1}$) and since drying of the samples at 105° has no effect, it is reasonable to assign this pair of bands to the two distinct sets of OH groups known to be present in the structure of malachite (Wells, 1951) and, by analogy, in that of rosasite. The bands are shifted in opposite directions when zinc is introduced into the malachite structure, a change that is accompanied by an expansion of the unit cell (Lauro, 1938).

It should be mentioned that the powder infra-red spectra of the reagents 'zinc carbonate, $ZnCO_3.2Zn(OH)_2.H_2O$' and 'cupric carbonate, $CuCO_3.Cu(OH)_2$' given by Hunt, Wisherd, and Bonham (1950) correspond with those of hydrozincite and malachite respectively, except that only one peak in the 3000 $\mathrm{cm}^{-1}$ region is recorded for the 'cupric carbonate'.

*Acknowledgements.* The authors wish to thank Prof. H. Lipson and the staff of the Physics Dept., College of Science and Technology, Manchester, for the use of X-ray equipment; Mr. D. I. Bothwell, Mineral Dept., British Museum (Natural History), for chemical analyses; Mr. A. W. G. Kingsbury, University Museum, Oxford, for samples of authentic rosasite and hydrozincite; and Mr. E. N. Aspey, proprietor of the Heights of Abraham, for his kind permission to study the Masson and Rutland Caverns.

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