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Childrenite in South-West England

R. S. W. BRAITHWAITE

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

AND

B. V. COOPER

Torquay Natural History Museum, Babbacombe Road, Torquay TQ1 1HG

SYNOPSIS

CHILDRENITE $(Fe,Mn)AlPO_4(OH)_2.2H_2O$, the iron-rich end-member of the childrenite-eosphorite diadochic series, was first discovered by Brooke (1823) on specimens from near Tavistock in Devon. Subsequently it has been recorded from a small number of other British localities, mostly in the Tavistock area, and also from near St. Austell in Cornwall, and from one locality in Cumbria. The Sir Arthur Russell collection, now in the British Museum (Nat. Hist.), has specimens from a few additional localities, all near Tavistock, and the Geological Museum, Institute of Geological Sciences, has a specimen from Wheal Jane, near Truro.

Some specimens found in July 1973 and subsequently, on old mine dumps in the Callington-Gunnislake area in Cornwall, a few miles to the west of Tavistock, proved to be of childrenite. These finds prompted a survey of the area between Callington and Dartmoor in order to determine the distribution of childrenite. The results of this survey indicate that childrenite is more widely distributed than formerly supposed, a considerable number of new localities being discovered. Previously recorded localities in the area were also re-examined, including the Tavistock Canal Tunnel, reputed to be the original locality.

Francolite (carbonate-fluorapatite) is a paragenetically related phosphate mineral also classically from this area, and its distribution and paragenetic relationship to childrenite have also been examined.

During the course of this investigation various associated minerals have been observed, the most interesting being chalcoalumite from South Wheal Crebor, near Tavistock. This is the first record of chalcoalumite from Britain, it being recorded previously only from Arizona and recently from Belgium. This find is intended to be the subject of a further paper.

Details of all these occurrences are to be found in the Miniprint section of this paper, and the distribution of childrenite and apatite localities in this area is shown in fig. 1.

Childrenite crystals from four scattered localities in SW England have been analysed by electron probe microanalysis. These analyses are in agreement with older published analyses of childrenite from the area, and are reasonably constant in Fe and Mn values and ratios, independent of locality or country rock. Our analyses of the childrenites all give values between $Ch_{81}Eo_{19}$ and $Ch_{89}Eo_{11}$, the older analyses between $Ch_{85}Eo_{15}$ and $Ch_{90}Eo_{10}$ with one exception of dubious accuracy. P and Al values are near theoretical, leaving no room for diadochic replacement, e.g. with arsenic, common in the main phase of mineralization in the area. Dr M. H. Hey has analysed chemically a number of childrenites from the area, distinguishing between oxidation states, and has found very variable and often considerable proportions of Fe(III), which can even exceed the Fe(II) content. This Fe(III) is almost certainly the result of supergene oxidation.

The infrared spectra of childrenite from several localities, including analysed samples, have been measured and compared with those of eosphorites, one of which was analysed by electron probe microanalysis. The spectra are characteristic and useful for identification purposes, but the differences between the spectra of childrenite and of eosphorite are not sufficient to determine the position of a sample in the series with any appreciable accuracy. The observed splitting of spectroscopic degeneracy of PO_4 absorptions is consistent with a phosphate anion site symmetry of C_s, in agreement with published structural data from X-ray diffraction measurements.

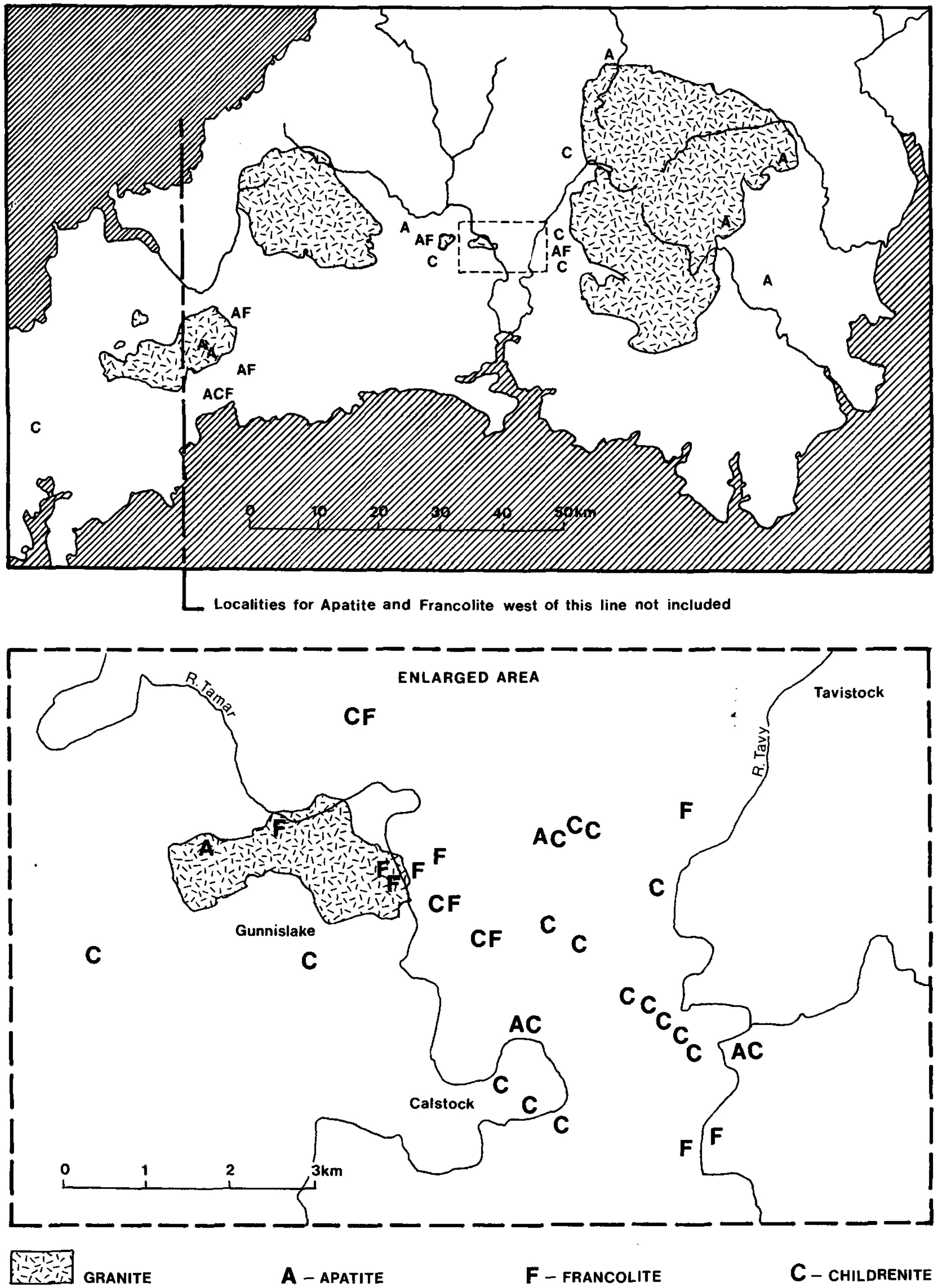

FIG. 1. Distribution of childrenite, 'apatite', and francolite occurrences in Devon and east Cornwall.

The childrenite is always found close to the granite margins. This distribution, which also cuts across the sediments, coupled with the paragenesis and the arsenic-free and constant composition, independent of locality, indicates that it is the result of hydrothermal phosphatization of the metasediments, connected with the intrusion of the granites, but later than the main mineralization. Francolite may take the place of childrenite in this stage of mineralization if conditions are more suitable for its preferential formation.

REFERENCE

Brooke, H. J. A. (1823) *Q. J. Lit. Sci. Art. London*, **16**, 274–5.

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CHILDRENITE IN SOUTH WEST ENGLAND

R.S.W. BRAITHWAITE

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester, M60 1QD

and

B.V. COOPER

Torquay Natural History Museum, Babbacombe Road, Torquay, TQ1 1HG.

CHILDRENITE $(Fe,Mn)AlPO_4(OH)_2.H_2O$, the iron-rich end-member of the childrenite-eosphorite diadochic series, is a rare and classical British mineral, having been first discovered by H.J. Brooke (1823) on three specimens purchased in Tavistock, Devonshire, and said to have been found in ground "perforated for the canal lately completed there". R. Allan (1834), and some later authors, including Greg and Lettsom (1858) and Rudler (1905), ascribe the discovery and naming to Levy. The list of Lévy's publications in the Royal Society Catalogue of Scientific Papers for 1800 - 1863 does not mention any relevant paper other than that of 1837, with its description and drawings of specimens in Heuland's collection. J. Drugman (1914) ascribes the mistake to an ambiguous note in Berzelius's "Jahres-Bericht" (1825). Subsequently, a few further localities have been recorded in the Tavistock area, the best specimens, and those usually seen in museums, hailing from George and Charlotte mine, Tavistock Hamlets (SX 453699), where crystals up to 2 cm long have been reported (R. Talling in Greg and Lettsom, 1858). The other recorded localities in this area are Wheal Crebor (SX 455720)(Greg and Lettsom, 1858) and West Wheal Crebor (SX 450719)(Russell, 1926), Tavistock Hamlets; Russell United mine, Tavistock Hamlets (Centred on SX449710), from where a specimen in Sir A. Russell's collection (not numbered) now in the British Museum (Nat. Hist.) was presented to the Bain collection (of Keynsham) by Captain F. Bray, the mine manager, in 1878 (v. infra); East Wheal Russell, Tavistock Hamlets (Centred on SX 451710) (two un-numbered specimens collected by Sir A. Russell from dumps in 1950 and 1951, and now in the British Museum (Nat Hist.)); Wheal Betsy, Mary Tavy (Centred on SX 510810) (five specimens, un-numbered, collected from old dumps by A. Russell in 1904, and now in the British Museum (Nat. Hist.)). Devon and Cornwall mine, Tavistock, quoted by Collins (1871) and later authors, is a group name, including George and Charlotte mine (v. supra.) and William and Mary mine (v. infra) (Dines, 1956). Virtuous Lady mine, Buckland Monachorum, is discussed as a possible locality below. An early Cornish locality some distance from Tavistock is "Crinnis mine", St. Austell (Greg and Lettsom, 1858; Drugman, 1914); according to Sir A. Russell (notes held in the British Museum (Nat. Hist.)) childrenite was found here, in a copper lode, some time between 1809 and 1823, the actual locality being Crinnis and Carlyon mine (which adjoins the Old Crinnis mine on the south), from a dump of which, on the cliff edge, Russell rediscovered childrenite in 1910. The British Museum (Nat. Hist.) holds a number of specimens from Crinnis and Carlyon mine, a specimen (BM 60697) labelled as from Crinnis mine, acquired from T.H. Holdsworth in 1832, and one (BM 1911,609) labelled as from Old Crinnis mine, given to the Geological Society by T.H. Holdsworth in 1835. A specimen found during the recent reworking of Wheal Jane, Kea, Cornwall is in the collections of the Geological Museum, Institute of Geological Sciences, South Kensington, numbered M.I. 34341, and is discussed below. The only recorded British locality remote from South West England is a vein near Causey Pike, near Keswick, in Cumbria (Kingsbury, 1957), not to be confused with Rammelsberg's erroneous locality "near Callington in Cumberland" (Rammelsberg, 1852; cf Drugman, 1914; Kingsbury, 1957).

Habit. Childrenite crystals from South West England are most commonly of a bipyramidal habit, with forms $\{110\}$ and striated faces of ($\{121\}$ + $\{131\}$) prominent, and $\{100\}$ generally less prominent; or less commonly of a prismatic habit, elongated parallel to c, with $\{110\}$ predominant, and terminated by $\{121\}$ and $\{131\}$, $\{100\}$ being less prominent.

NEW LOCALITIES FOR CHILDRENITE

Lady Ashburton mine, Callington, Cornwall. Very pale creamy-brown bipyramidal crystals of childrenite, averaging 0.25 mm in maximum dimension, sparsely scattered on iron-stained shaly killas adjacent to quartz veining, were found on dumps near SX 368702.

Prince of Wales mine, Calstock, Cornwall. Childrenite is common on the dumps, centred on SX 401706, as pale brown bipyramidal crystals, mostly 0.5 - 1 mm in size, closely clustered on killas, and as pale brown prismatic crystals to 1.3 mm in small vughs in quartz-chlorite veinstuff. Small amounts of green scorodite crystals, and traces of dump-growth brochantite and linarite have also been observed on the dumps, in addition to the recorded minerals (Dines, 1956), but not in any particular association with the childrenite.

Drakewalls mine, Calstock, Cornwall. Childrenite occurs on the dumps, particularly commonly on those near SZ 427707, as small thickly clustered pale brown bipyramidal crystals on brownish killas, and occasionally as larger, fine, clear, brilliant, brown pipyramidal crystals to 1.5 mm or more on fracture surfaces in killas, sometimes coated with a black manganese oxide film.

Okeltor mine and its vicinity, Calstock, Cornwall. Clear, sharp, very pale creamy-brown bipyramidal childrenite crystals, averaging about 0.3 mm in length were found, closely packed on fracture surfaces in chloritic killas on dumps centred on SX 445689.

Iron-stained, very pale brown 0.25 mm bipyramidal childrenite crystals, some with opaque granular cores, were found thickly scattered on somewhat iron-stained fracture planes in grey slaty killas on a small dump at SX 44656927, beside a track near Ferry Farm, between Okeltor and Harewood Consols mines.

Small, very pale brown childrenite crystals were observed on killas forming part of a wall at SX 435693, about 200 m west of Calstock church, and probably derived from nearby dumps. No childrenite was found, however, on the partly grassed-over remains of some small dumps in the immediate vicinity.

Wheal Anna Maria, Tavistock Hamlets, Devon. Small, very pale brown bipyramidal crystals to 0.2 mm were found investing botryoidal siderite collected from the dumps by Mr. S. Fairchild in January, 1979.

Gawton mine, Tavistock Hamlets, Devon. Deep reddish brown, sharp, translucent bipyramidal childrenite crystals to 0.2 mm were found, richly sprinkled on iron-stained killas adjacent to quartz veining on dumps near SX 452689.

South Wheal Crebor (= New East Russel mine), Tavistock Hamlets, Devon. Childrenite has been found in situ in an adit level near SX 465714, in an interesting mineral association. The childrenite, of composition $Ch_{85}Eo_{15}$ (v. infra), occurs as almost colourless prismatic and bipyramidal crystals 0.5 to 1 mm long, thickly sprinkled on fracture surfaces in grey killas containing decomposing pyrite and chalcopyrite. The childrenite, which sometimes forms compact matted layers, is overlain by supergene copper minerals, notably native copper in branching crystals altering to cuprite, brochantite, and a pale blue to almost colourless radiating mineral giving an infrared spectrum identical with those of chalcoalumites from Bisbee and Grandview mines, Arizona. Chalcoalumite has only been recorded from Arizona (Larsen and Vassar, 1925; Williams and Khin, 1971; Leicht, 1971) and recently from Belgium (du Ry et al, 1976).

Little Duke (= North Tavy) mine, Tavistock Hamlets, Devon. Very pale brown bipyramidal childrenite crystals, averaging 0.2 mm, were found thickly clustered on chloritic killas from dumps near SX 471695, particularly on those of Gill's shaft. Small anatase crystals were among other species found here.

Sortridge Consols mine, Whitchurch, Devon. Small, clear, very pale brown, but heavily iron-stained bipyramidal childrenite crystals, mostly about 0.25 mm in size, closely packed on killas heavily invaded by arsenopyrite and chlorite, were found on dumps near SX 510707. We have also found greenish coatings of beaverite here.

Furzehill (= Furzehill Wood) mine, Walkhampton, Devon. Pale yellowish-brown bipyramidal crystals of childrenite, about 0.5 mm long, on tourmalinised quartz-killas veinstuff, were collected from dumps near SX 518692.

The old Tavistock to Bere Alston railway line traverses the district from N. to S., and exposes the country rocks in cuttings and a tunnel. These exposures were examined, and childrenite was found as pale brown bipyramidal crystals, mostly thickly scattered in iron-stained fractures in grey slaty killas adjacent to hydrothermal quartz-chlorite veins, at three places: (a) SX 466700, adjacent to William and Mary mine, as crystals to 0.1 mm, (b) SX 469699, adjacent to William and Mary and Virtuous Lady mines, as crystals to 0.2 mm, (c) SX 470697, adjacent to Little Duke mine, as crystals to 0.25 mm. No childrenite was found in other parts of the track.

Wheal Jane, Kea, Cornwall. The specimen in the Geological Museum referred to earlier from this locality was collected by one of the mine geologists in about 1970, and presented to the Institute of Geological Sciences by Mr. K.E. Beer. It bears the acquisition number M.I. 34341, and is labelled as from "New Shaft, 120' below collar, Wheal Jane, Baldhu, Chasewater, Cornwall". It consists of clear greyish-brown crystals of tabular habit, mostly about 0.5 mm in length, richly sprinkled on white vein quartz. The crystals are tabular parallel to [100], which is the dominant form, {110}, {121}, and {131} being the other forms present. X-ray powder diffraction (by the Institute of Geological Sciences), shows that the material is a member of the childrenite-eosphorite series, but is unable to place its position in the series. The colour, and particularly the habit of these crystals are notably different from those from the other localities dealt with in this paper, and the occurrence is much further to the W. The composition of this material, is, however, similar to that of the other samples from the area that have been analysed (see Table 2), and is near $Ch_{81}Eo_{19}$.

REEXAMINATION OF SOME KNOWN LOCALITIES OF PARTICULAR INTEREST

The Tavistock Canal Tunnel. It is probable that the original locality for childrenite - the ground "perforated for the canal" near Tavistock - is the Tavistock Canal Tunnel (Taylor, 1817; Toll, 1948; Dines, 1956; Barclay et al MSS describing visits in 1923, 1931 and 1933), driven 1803 - 1818, which runs from SX 462723 to SX 449703 and cuts a number of lodes in the Wheal Crebor and East Wheal Russell setts. The Wheal Crebor lodes were discovered in the driving of the tunnel, and started being worked in 1810. A specimen presented to the Royal Albert Memorial Museum, Exeter, by Mrs. R.L. Berry in 1874, accession number 4544, was labelled "Calamine (carbonate of zinc), Tavistock Canal, Devon", but consists of dark brown bipyramidal childrenite crystals, mostly 0.3 to 0.4 mm in size, closely clustered together, associated with "francolite" (carbonate-fluorapatite), hexagonal short prismatic crystals to 0.5 mm, and siderite, on quartz with pyrite and chalcopyrite. The childrenite is later than the francolite, which postdates the siderite, which is later than the quartz and sulphides.

The tunnel workings were explored during the dry summer of 1976, and childrenite was found in a crosscut, the 45-fm level of East Wheal Russell, which was worked from the tunnel. This childrenite forms pale brown brilliant crystals of prismatic habit, typically 0.5 x 0.25 x 0.18 mm, richly sprinkled on crevice surfaces coated with a black manganese oxide, in killas. These specimens have little resemblance to the Exeter Museum specimen referred to above, which therefore probably came from elsewhere in the workings, possibly Georgina lode of Wheal Crebor.

Wheal Crebor and West Wheal Crebor, Tavistock Hamlets, Devon. These mines worked a series of lodes coursing E. 20°N. (Dines, 1956). Georgina lode was discovered in, and worked from, the Tavistock Canal Tunnel; the other lodes were worked from shafts and adits. The dumps were examined, and childrenite was found on those of Gill's shaft (SX 455721), Rundle's shaft (SX 453720), and those around West Wheal Crebor engine house (SX 450719). Specimens in the British Museum (Nat. Hist.) acquired between about 1850 and 1890 are labelled "Wheal Crebor", as is a specimen from Sir A. Russell's collection (ex Warburton collection) acquired in 1964; specimens collected or acquired between 1926 and 1964 are labelled "West Wheal Crebor"; two of these, collected by A.W.G. Kingsbury in 1936 and 1945 respectively are labelled "from dump by Engine House".

The childrenites from here form small, pale brown bipyramidal crystals, most about 0.3 to 0.4 mm long, and some short prismatic crystals to 0.7 mm, closely packed on killas, quartz veining, and chloritic "peach" with scattered sulphides.

William and Mary mine, Tavistock Hamlets, Devon. Once part of Devon and Cornwall United mine, the workings straddle the Tavistock to Bere Alston railway line near SX 464701 between George and Charlotte and Virtuous Lady mines. The Sir A. Russell collection in the British Museum (Nat. Hist.) has two specimens of childrenite from here, collected by Sir Arthur in 1920 from a dump. One of us (B. V. C.) has collected childrenite in situ in the adit, on fracture surfaces in a shatter zone in chloritic schistose killas. The childrenite forms clear, sharp, pale brown bipyramidal to short prismatic crystals, mostly 0.2 to 0.5 mm long, with occasional clusters of clear honey-brown crystals to 1.5 mm. As previously mentioned, childrenite has also been found in railway cuttings in the vicinity.

Virtuous Lady mine, Buckland Monachorum, Devon (SX 473698). The British Museum (Nat. Hist.) holds three specimens of childrenite with localities labelled as "Virtuous Lady mine": BM 34259, acquired from R. Talling in 1862, and BM 96867 and BM 96868 from the Alan Greg collection, acquired in 1860. The late Mr. A. W. G. Kingsbury examined these specimens closely, and from their matrix, associated minerals, and general appearance concluded that they are all derived from George and Charlotte mine, and not Virtuous Lady mine. We have not found childrenite on the dumps, but B. V. C. has visually identified tiny crystals of childrenite on an unlabelled "Lady's slipper" from an old collection, which probably came from Virtuous Lady mine. The occurrence of childrenite at this mine has yet to be confirmed, but would not be surprising in view of its occurrence at other mines in the vicinity.

Russell United mine, Tavistock Hamlets, Devon (centred on SX 440713). The British Museum (Nat. Hist.) holds one specimen from here, in the Russell collection, referred to in the introduction. We have not confirmed the occurrence of childrenite here, but have found small crystals of francolite. Barclay and Toll (MS, 1922), repeated by Dines (1956) report the presence of scorodite underground here. It is just possible that the "scorodite" could have been confused with childrenite, with which some brownish crystals have a superficial resemblance.

East Wheal Russell, Tavistock Hamlets, Devon (SX 450710). The British Museum (Nat. Hist.) has two specimens, in the Russell collection, collected by Sir Arthur from an old dump of this mine, and referred to in the introduction. In addition to the material collected in the 45 fm. level from the Canal Tunnel (v. supra) we have collected childrenite from the dumps of Murchison's shaft, and of the deep adit (portal at SX 437708).

George and Charlotte mine, Tavistock Hamlets, Devon (SX 453699). This is the classical locality for the finest childrenites collected in Britain, referred to in the introduction.

An old adit has recently been reopened, and widened in readiness for visits by tourists. Good specimens of childrenite have been found among the debris resulting from this operation.

Wheal Betsy, Mary Tavy, Devon (centred on SX 510810). As stated in the introduction, Sir A. Russell collected several specimens of childrenite from the dumps of this old lead mine in 1904. We have examined the dumps and descended the shaft to a stoped-out area about 80 feet below the shaft collar, without finding childrenite.

Crinnis and Carlyon mine, St. Austell, Cornwall. Sir Arthur Russell rediscovered childrenite on a dump at SX 052520, on the cliff edge near the hotel. We have also collected childrenite from exposures in the highly distorted Lower Devonian shales at the foot of the cliff near SX 054520 on the east side of the headland, and have found childrenite and francolite on separate specimens on an overgrown dump at SX 05555235, just north of the railway line.

LOCALITIES FOR FRANCOLITE IN THE AREA (See Fig. 1).

The relationship between the occurrences of childrenite and of francolite (carbonate-fluorapatite) as competing phosphates is of interest, and is discussed later. The francolites have been identified by refractive index measurements and by infrared spectroscopy.

Recorded localities for "apatite". Some of the apatites in the area are of high-temperature, pegmatitic origin, e.g. those from Luxulyan, Meldon, Bittleford Down and Bovey Tracey. Others are of francolite paragenesis, and may well be francolite, but have not been checked. East Cornwall (within National Grid square SX): Colcerrow quarry, Luxulyan (Kingsbury, 1958); Crinnis and Carlyon mine, St. Austell* (Rudler, 1905); Fowey Consols mine, Tywardreath* (Collins, 1871); Gready quarry, Luxulyan (Busz, 1905); Wheal Maudlin, Lostwithiel* (Miers, 1897); Pitt Farm, Stoke Climsland (Russell, notes held in B.M.(N.H.)). Devon: Bittleford Down, Widecombe (Brammall and Harwood, 1924); Bovey Tracey (Greg and Lettsom, 1858; Wolleigh Farm, Kingsbury, 1964); Chudleigh (probably the Bovey Tracey locality) (Hall, 1868; Collins, 1871); Wheal Franco, Walkhampton* (Greg and Lettsom, 1858); George and Charlotte mine, Tavistock Hamlets* (members of the fluorapatite to francolite series, Embrey and Fejer, 1969); Haytor, Ilsington (specimen in the British Museum (Nat. Hist.)); Meldon, Okehampton (McLintock, 1924); Tornewton Cave (collophane, Proudfoot, 1958); Virtuous Lady mine, Buckland Monachorum (Dines, 1956).

Unpublished or new localities for "apatite". Hingston Down quarry, Gunnislake, Cornwall; Hawks Wood mine, North Hill, Cornwall; Holmbush mine, Stoke Climsland, Cornwall (G. Ryback, Priv. Comm., 1955); West Wheal Crebor, Tavistock Hamlets, Devon (J. Gliddon, Priv. Comm. 1978).

Recorded localities for francolite. East Cornwall: Fowey Consols mine, Tywardreath** (Greg and Lettsom, 1858); Wheal Maudlin, Lostwithiel** (Kingsbury, 1961). Devon: Wheal Franco, Walkhampton** (Greg and Lettsom, 1858); George and Charlotte mine, Tavistock Hamlets** (Embrey and Fejer, 1969).

Unpublished or new localities for francolite. East Cornwall: Crinnis and Carlyon mine, St. Austell**; Gunnislake Clitters mine, Gunnislake; Old Gunnislake mine, Gunnislake; East Gunnislake mine, Calstock, associated with libethenite; Holmbush mine, Stoke Climsland** Devon: South Bedford mine, Tavistock Hamlets; Wheal Crebor, Tavistock Hamlets; Devon Great Consols mine, Tavistock Hamlets; Ding Dong mine, Tavistock Hamlets; Lady Bertha mine, Buckland Monachorum; Russell United mine, Tavistock Hamlets; East Wheal Russell, Tavistock Hamlets; Tavistock Canal Tunnel, Tavistock Hamlets; Tavy Consols mine, Tavistock Hamlets.

*Also locality for francolite.

**Also locality for "apatite".

INFRARED ABSORPTION SPECTROSCOPY

The infrared spectra of childrenites from George and Charlotte mine, South Wheal Crebor, Drakewalls mine, Prince of Wales mine and Sortridge Consols mine, in "Nujol" mulls, were measured in the 670 - 4000 cm^{-1} region, using a Perkin-Elmer 137 spectrophotometer with sodium chloride optics, calibrated against polystyrene. The spectra are all very similar, and that of one sample from South Wheal Crebor was measured over a wider wavenumber range (380 - 4000 cm^{-1}), in "Nujol" mull, between KBr plates, using a Perkin-Elmer 397 grating spectrophotometer, and over the 200 - 800 cm^{-1} range, using a Perkin-Elmer 621 spectrophotometer, calibrated against polystyrene, using CsI plates, to give greater accuracy in wavenumber. and to cover a wider range to include the regions of the PO_4^{3-} ν_2 and ν_4 absorptions.

The infrared spectra of eosphorites from Taquaral, Brazil; Joao Modisto, Brazil; North Carolina; and Palermo, New Hampshire, were measured over the 670 - 4000 cm^{-1} region, and that of the Taquaral specimen also over the 380 - 4000 cm^{-1} and 200 - 800 cm^{-1} regions, using the same apparatus and conditions described above for the childrenites.

The spectra are illustrated in Fig. 2, and absorptions and probable assignments are tabulated in Table 1.

All the childrenites gave very similar spectra over the 670 - 4000 cm^{-1} region, as did all the eosphorites. The differences between the spectra of childrenite and of eosphorite in this region are mainly small. Somewhat wider differences were observed in the 200 - 700 cm^{-1} range, but not sufficient to be likely to be useful in determining the position of a sample in the diadochic series with any accuracy. These differences can be seen in Fig. 2 and Table 1.

The spectra of both minerals show two OH stretching absorptions: a strong and very sharp one near 3450 cm^{-1} indicating a freely vibrating O-H bond, and a broader, weaker band near 3300 cm^{-1} indicating a hydrogen-bonded O-H vibration. In both cases the H-O-H "scissor" bending mode is near 1630 cm^{-1}. The presence of the forbidden ν_1 P-O symmetrical stretch in the 940 - 950 cm^{-1} region, coupled with the multiplicity of ν_2, ν_3 and ν_4 absorptions due to the removal of spectroscopic degeneracy, indicate phosphate anion site distortion in the lattice. The maximum number of three absorptions each appear for the ν_3 and ν_4 modes, and two absorptions appear in the ν_2 region. This combination points to C_s site symmetry, in agreement with that derived from published X-ray structure data (Hanson, 1960; Wykoff, 1965).

ANALYSES

Four childrenite samples, and the eosphorite used for detailed infrared spectroscopy were analysed by Mr. C. Guilford, in the Geology Department, University of Manchester, using a Cambridge Geoscan Microprobe Analyser, fitted with an energy dispersive analyser.

The electron probe microanalyses and the older published chemical analyses of childrenites from scattered localities in South West England are remarkably constant (see Table 2). Church's (1873) analysis of material from "Tavistock" is somewhat anomalous, being low in Al, and high in Mn.

Apart from Church's material, the Fe and Mn values and ratios show little variation, and Fe - Mn zoning within the crystals was looked for, but not detected. Substitution by other diadochic elements is small; a little Ca is present, and Church reports a little Mg. The P and Al values are near the theoretical values, indicating little if any diadochic replacement of these elements, in an area where As is common in the high temperature hydrothermal veins. Dr. M.H. Hey informs us that he has detected appreciable amounts of Zn in childrenite from the area. Unfortunately, Zn was not looked for in our electron probe microanalyses.

The electron probe analyses do not of course distinguish between oxidation states. Church's analysis shows 2.45% Fe(III) (3.51% Fe_2O_3) in his material. Dr. M.H. Hey informs us that his chemical analyses of childrenite from the area indicate the presence of considerable

TABLE 1 WAVENUMBERS AND ASSIGNMENTS OF INFRARED ABSORPTION MAXIMA OF CHILDRENITE AND OF EOSPHORITE.

ABSORPTION MAXIMA, cm^{-1} CHILDRENITE	EOSPHORITE	ASSIGNMENTS
$Ch_{85}Eo_{15}$ South Wheal Crebor, Devon. Off RSWB 75-387.	$Ch_{36}Eo_{64}$ Taquaral, Brazil. Off RSWB 73-318.	
300 m	300 m	Al-O ?
323 m	323 m	
368 m	366 m, shoulder	
393 s, sh	393 s, sh	
453 ms	448 ms	PO_4^{3-} ν_2 bend
470 ms, shoulder	472 ms	PO_4^{3-} ν_2 bend
578 s, sh	572 s, sh	PO_4^{3-} ν_4 bend
616 s, sh	602 s	PO_4^{3-} ν_4 bend
630 s, shoulder	---	Fe-O ?
663 s, sh	652 ms	PO_4^{3-} ν_4 bend
710 s, sh	680 m	Metal-O ?
930 s	910 s	Metal-O ?
950 s	940 s, shoulder	PO_4^{3-} ν_1 symmetrical stretch
978 s, shoulder	984 s, shoulder	PO_4^{3-} ν_3 asymmetrical stretch
1032 vs, sh	1035 vs, sh	
1078 s, sh	1080 s, sh	
1169 ms, sh	1165 ms, sh	
1630 m, br	1625 m, br	H-O-H "scissor" in-plane bend
1800 - 2000 vw, vbr	1800 - 2000 vw, vbr	
3280 ms, br	3310 m, br	H-bonded O-H stretch
3430 s, sh	3450 s, sh	O-H stretch, not H-bonded
3540 w, shoulder	3540 w, shoulder	O-H stretch

w = weak, m = medium, s = strong, v = very, sh = sharp, br = broad.

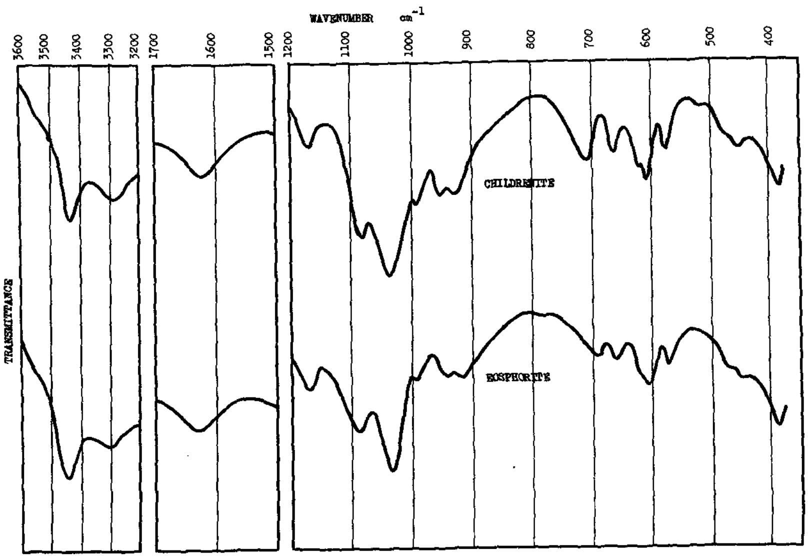

FIG. 2. INFRARED SPECTRA OF CHILDRENITE $Ch_{85}Eo_{15}$ AND EOSPHORITE $Ch_{36}Eo_{64}$

amounts of Fe(III), sometimes even exceeding the Fe(II) values. For example a childrenite (off BM 52432) from George and Charlotte mine gave Fe_2O_3, 16.1; FeO, 10.1%. Dr. Hey kindly offered to analyse some of our material, and smaller proportions of Fe(III) were found (see Table 2). In contrast to Fe:Mn, Fe(III):Fe(II) is very variable, and is almost certainly a result of supergene oxidation. The absence of blue or similar coloration in these oxidised childrenites indicates that charge transfer does not take place between these ions.

DISCUSSION

All the localities known in the area for childrenite and for francolite are close to granite margins, and are concentrated along the approximately W - E Kit Hill to Dartmoor axis, around the Kit Hill and Gunnislake cupolas (see Fig. 1). The localities cut across the sediments from Lower Devonian to the Mid-Carboniferous 'Culm' measures, and so are directly related to the granites rather than the sediments.

TABLE 2. ANALYSES OF CHILDRENITES AND AN EOSPHORITE. Weight %

	1	2	3	4	5	6	7	8	9	10	11
Fe (total)	24.30	-	22.00	22.20	20.63	20.68	20.9	21.3	20.5	19.1	7.6
Fe(III)	-	-	-	-	-	2.45	-	3.92*	1.82*	-	-
Mn	-	23.99	2.59	2.41	3.77	5.99	3.5	2.7	3.5	4.5	13.4
Al	11.73	11.78	11.22	11.34	11.20	8.39	11.1	11.0	11.2	10.9	10.9
P	13.48	13.53	13.00	13.06	13.17	13.37	13.1	13.2	12.9	12.7	13.3
Ca	-	-	0.64	0.46	0.86	-	0.32	0.42	0.23	0.34	1.74
Mg	-	-	-	-	-	0.62	n.f.	n.f.	n.f.	0.25	0.60
Si**	-	-	-	-	-	-	n.f.	n.f.	0.1	n.f.	n.f.
Na	-	-	0.19	0.28	-	-	n.f.	n.f.	n.f.	n.f.	n.f.
K	-	-	-	-	-	-	n.f.	n.f.	n.f.	n.f.	n.f.
Formula***	Ch	Eo	$Ch_{90}Eo_{10}$	$Ch_{90}Eo_{10}$	$Ch_{85}Eo_{15}$	$Ch_{75}Eo_{25}$	$Ch_{86}Eo_{14}$	$Ch_{89}Eo_{11}$	$Ch_{85}Eo_{15}$	$Ch_{81}Eo_{19}$	$Ch_{36}Eo_{64}$

*Determined microchemically by Dr. M.H. Hey. **Detection limit 0.08% ***From Fe:Mn, *ignoring* Ca, Mg, *etc.*

n.f. Not found.

1. Childrenite, theoretical. $FeAlPO_4(OH)_2.H_2O$.
2. Eosphorite, theoretical. $MnAlPO_4(OH)_2.H_2O$.

Older published chemical analyses, recalculated to atom weight %.

3. Childrenite, Crinnis mine, Cornwall (Drugman, 1914).
4. Childrenite, Crinnis mine, Cornwall (Otto, 1935).
5. Childrenite, George and Charlotte mine, Devon (Penfield, 1880).
6. Childrenite, "Tavistock", Devon (Church, 1873).

New, electron probe microanalyses.

7. Childrenite, Drakewalls mine, Cornwall. Off RSWB 74-140. Average of three similar analyses.
8. Childrenite, Tavistock Canal Tunnel (E. Wheal Russell), Devon. Off RSWB 76-183. Average of three similar analyses.
9. Childrenite, South Wheal Crebor, Devon. Off RSWB 75-387. Average of three similar analyses.
10. Childrenite, Wheal Jane, Cornwall. Off Inst. Geol. Sci. specimen M.I. 34341. Average of four similar analyses.
11. Eosphorite, Taquaral, Brazil. Off RSWB 73-318. Average of four similar analyses.

The composition of the childrenites is remarkably constant, suggesting a common origin. The childrenite is clearly post-metamorphism, post-fracturing, and although associated with the areas of metallic mineralisation, and usually found in or close to the often As-rich mineral veins, the childrenite is As-free and postdates the primary metalliferous minerals. It is therefore not directly connected with the main mineralisation phase. The childrenite predates supergene oxidation, being formed under low E_h conditions, but sometimes being partly oxidised itself. This paragenesis is clearly shown on specimens from South Wheal Crebor, in which the childrenite occurs on fractures in primary mineralised vein material, and is overlain by a series of supergene oxidation minerals. Apart from francolite, which shows the same paragenetic relationships, childrenite is the only mineral of its generation on all the specimens studied. Childrenite and francolite only occasionally occur at the same locality, and are rarely found on the same specimen. They are seen together on the Exeter Museum specimen from the Tavistock Canal Tunnel, on which childrenite overlays fresh-looking francolite, which itself coats siderite, the childrenite not being an alternation product of the francolite. Francolite is most commonly found in direct association with carbonates, particularly siderite. Synthetic work shows that carbonate-apatite can be formed by the action of phosphate-bearing solutions on calcium carbonate (a normal component of killas) (Ames, 1959), and is not formed by mixing calcium, phosphate, and carbonate ions in aqueous media (Klement. Hüter and Köhrer, 1942). Although this suggests an "outside" source of phosphate, perhaps magmatic, for francolite and presumably also childrenite formation, it does not exclude the possibility of hydrothermal mobilisation of bigenetic phosphate from the metasediments. Stable isotope work might be of interest in this context. The Fe and Al required for childrenite formation are normal components of killas. Childrenite and francolite appear to occupy the same "ecological niche" as competing phosphates but requiring slightly different conditions (pH and/or ion availability) for their preferential formation. Thus in the case of the Exeter Museum specimen referred to above, francolite was formed initially, but was superseded by childrenite when conditions changed.

We conclude that the childrenite and the francolite were formed by late-stage hydrothermal phosphatisation of the metasediments, probably representing the "last gasp" of granitic hydrothermal activity.

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