

CROOKESITE, TlCu_7Se_4 , FROM LITTLEHAM COVE, DEVON: THE FIRST MINERAL CONTAINING ESSENTIAL THALLIUM FROM THE BRITISH ISLES

Mike S. RUMSEY

Department of Earth Sciences, Natural History Museum, Cromwell Road, London, SW7 5BD

Ian DOSSETT

Gaia House, Peel Hall Park, Ashton Keynes, Chester, CH3 8AZ

David I. GREEN

Honorary Research Associate, Amgueddfa Cymru – National Museum Wales, Cathays Park, Cardiff, CF10 3NP

Jens NAJORKA and John SPRATT

Facilities Department, Natural History Museum, Cromwell Road, London, SW7 5BD

The rare thallium copper selenide crookesite occurs as dark grey metallic needles in at least two cavities in a nodule collected from cliffs at Littleham Cove, Budleigh Salterton, Devon. This is the first report of a thallium mineral from the British Isles. The small crystal size, confusion in the mineralogical literature and the need to preserve as much of the specimen as possible for future study, made the identification particularly challenging. Thallium minerals have a very limited worldwide distribution. They are almost entirely restricted to unusual low temperature epithermal deposits.

The discovery of crookesite in nodules in a Permian red bed environment is, therefore of significant interest.

Thallium minerals do not appear to have been reported in this geological setting before.

INTRODUCTION

Minerals which contain thallium as an essential component of their crystal structure are relatively rare in comparison to other elements with comparable or smaller crustal abundances; they number about 60, and account for less than 1.5% of the 5046 currently accepted species (www.ruff.info, retrieved 15/9/2015). Strong geochemical affinities with members of group I of the periodic table, and a comparatively low crustal abundance (0.07 ppm, according to Guberman, 2010) means that thallium most commonly substitutes for chemically similar but more abundant elements of similar charge and size, particularly potassium (Goldschmidt, 1954). As global demand for thallium and its compounds is relatively low, it is obtained as a by-product of the mining of lead, zinc and copper ores (Guberman, 2010).

Controversy surrounds the discovery of thallium. It is generally accepted that Sir William Crookes (1832–1919) of the Royal College of Science in London was the first to realise that a green line in the emission spectrum of impure sulphuric acid was produced by a new chemical element. He named it thallium, but was slow to investigate further. The French physicist Claude-August Lamy (1820–1878) made the same discovery and produced a small ingot of pure thallium metal in 1862. He was credited by the French Academy of Science as the true discoverer. Claims and counter-claims followed, but both men are now credited as co-discoverers (Brock, 2008). Trace quantities of thallium are widespread in the natural environment; it is commonly associated with potassium minerals in clays, soils and granite and found at low concentrations in natural spring water and in plants.

The first mineral with essential thallium was discovered at Skrikerum Mine in Sweden in 1866 and named crookesite in honour of Sir William Crookes (Nordenskiöld, 1867). Crookesite is one of the most common thallium minerals, but to put the general rarity of thallium species in context, it is noted from only 12 locations worldwide (www.mindat.org, retrieved 15/9/2015).

This paper describes crookesite from the central cavity of a dark coloured nodule found in argillaceous red beds of Permian age at Littleham Cove, Budleigh Salterton, Devon. This appears to be the first report from this geological environment and it is the first occurrence of crookesite (or any mineral containing essential thallium) from the British Isles.

GEOLOGY

Littleham Cove lies about 3 km west of Budleigh Salterton on the south coast of Devon (Figure 1). It is a significant and interesting locality due to the presence of vanadium- and uranium-rich nodules in the Permian red beds. The cove falls within the Jurassic Coast World Heritage Site and is situated just outside the Budleigh Salterton SSSI, which is designated for its Triassic pebble beds. It should be noted that nodules are present in many red bed deposits in the surrounding area; they are not restricted to Littleham Cove. There are reports of similar nodules from cliffs between Budleigh Salterton and Exmouth, from nearby inland clay-pits (Carter, 1931) and from similar sequences as far east as Sidmouth (DIG, *personal observations*). However, the specimens described herein were collected near Littleham Cove [SY 044 808] where nodules are very common.

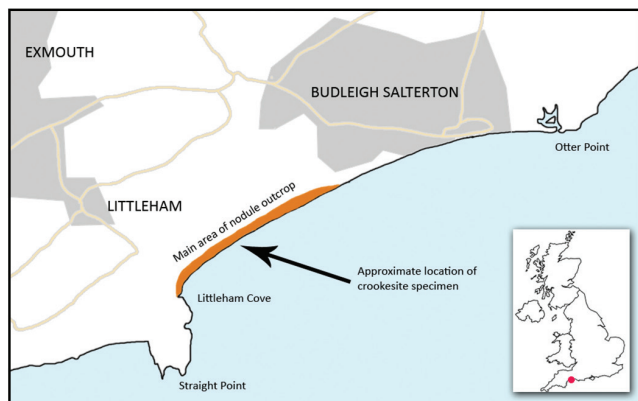


Figure 1. A map of the southern coast line in Devon showing the position of Budleigh Salterton, Littleham Cove and the approximate position of the nodules that were found to contain crookesite.

The nodules were first documented by local archaeologist and geologist George Carter (Carter, 1931) who noted the presence of significant concentrations of vanadium and smaller amounts of uranium, nickel and cobalt. Mineralogical investigations have been reported subsequently in a number of disparate publications and various mineral phases have been either identified or suggested, to account for their unusual geochemistry. The primary minerals within the nodules are typically poorly crystallised and are relatively difficult to identify even by modern techniques.

In a relatively recent study (Milodowski *et al.*, 2000), it was noted that in addition to 22 claimed species, the nodules contain a significant number of phases that have not been fully characterised. Unfortunately the characterisation of these phases was beyond the scope of their study and additional data is still required for the confident verification of some of their claimed 22 species. It is, therefore, impossible to describe the full mineralogical diversity of the nodules, which is clearly underestimated in current publications and warrants a detailed study in the future.

Milodowski *et al.* (2000) also note that the mode of formation of the nodules is poorly understood. The nodules have a global distribution and commonly contain significant concentrations of elements of geochemical interest, notably arsenic and uranium. As such, systematic examination of the mineral assemblages might provide insights into important geochemical questions.

CROOKESITE SPECIMEN

The crookesite-bearing specimen, now registered in the Natural History Museum (NHM) as BM 2013,125, was collected by one of the authors [ID] on a Russell Society field trip in September 2001. The specimen is one of two nodules that were found to contain dark grey, metallic needles. Both were collected in-situ from an exposure in the cliff where they formed part of a band of nodules running approximately parallel to the local bedding, about 5 to 6 m above the beach (Figure 2). Unlike the nodules found on the beach, those collected *in situ* in the cliff exposure had a ‘fresher’ appearance, with fewer cracks and less



Figure 2. The Permian red beds, showing distinctly lighter bands from which the crookesite containing nodules were collected. The Permian red beds, showing the distinctly lighter bands from which the crookesite containing nodules were collected. This photo was taken around the time of collection and it should be noted that this cliff face no longer exists as it is shown here, having suffered from considerable erosion during recent storms

surface alteration to supergene phases, which were visually identified as pinkish erythrite and yellowish pascoite.

The crookesite crystals occur in small cavities in the cores of the nodules. They are typically about 0.02×0.02 mm in cross-section with a maximum length of about 0.9 mm, although most are between 0.2 and 0.5 mm long. The needles are commonly slightly curved. They are present in two of the ten visually similar cavities that were exposed when the nodule was broken in half. Associated minerals in the cavity include unidentified black vanadium oxide(s), colourless prismatic calcite, yellow-orange crusts of pascoite, an unidentified brown vanadium-bearing clay mineral, an unidentified dark grey sub-metallic phase with a pale grey overgrowth and a platy micro-crystalline, blue-grey metallic tarnish on the crookesite needles, which is especially abundant on the larger needles towards their terminations. Unfortunately, the majority of these phases have not been characterised. Due to their small size and position, it was not possible to remove material satisfactorily from these phases for analysis without risking complete destruction of the specimen (Figure 3, see p. 50).

The other cavities on the specimen contain similar mineral assemblages, dominated by a brown vanadium-bearing clay mineral, black vanadium oxide(s) and colourless prismatic calcite crystals up to about 0.5 mm long. In some of the cavities in which crookesite is absent there are tiny (around 10μ) metallic, hexagonal plates that are rich in Cu and Se, it is likely that these are klockmannite crystals which we know have formed post-collection.

CHEMICAL ANALYSIS

Initial analyses by energy-dispersive spectrometry on a scanning electron microscope at the University of Manchester revealed the presence of Cu, Se, Tl and Mo in the metallic needles. Subsequent analyses at the NHM on a different set of needles revealed only Cu, Se and Tl;

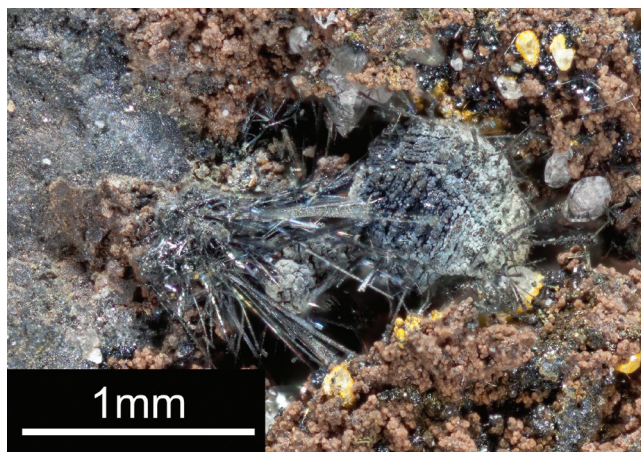


Figure 3. Crookesite specimen BM 2013,125. The crookesite occurs as thin grey metallic needles growing in and around a sphere of a pale grey unidentified mineral. The whole cavity is lined with a brown vanadium-bearing clay group mineral and crystals of calcite (white) and pascoite (yellow) can be seen in association. Tiny black specks throughout the clay group mineral are thought to be various (undetermined) vanadium oxides.

no Mo was detected, but traces of Ni were found. In view of the variation in elemental composition between the two analyses and the presence of an overgrowth on the metallic needles, it was decided that quantitative analyses on the interior of the crystals were required.

A number of needles were carefully removed, mounted in epoxy and polished using an aluminium oxide abrasive. The resulting probe block was carbon coated to ensure better conductivity and analysed by wavelength dispersive spectrometry (WDS) on a Cameca SX100 electron microprobe at the NHM. This probe block is registered in the collections as P16781 and is part of specimen BM 2013,125.

The analyses showed Cu, Se and Tl to be the dominant constituents of the metallic needles, and revealed a heterogeneous bimodal compositional variation. One cluster of results has Cu>Se>Tl and the other Se>Cu>Tl. The first cluster shows a good correlation with the composition of crookesite, while the second remains to be fully understood.

Although the data show a good match to crookesite, a literature review also revealed another phase with a similar chemical composition, *sabatierite*, Cu_6TlSe_4 (Johan *et al.*, 1978). It is recorded that crookesite can be Cu deficient, and has an empirical formula that is more usefully written as $\text{Cu}_{7-x}\text{TlSe}_4$ in which $x < 1$ (Berger, 1987a). Therefore, crookesite cannot be easily distinguished from *sabatierite* on the basis of chemical data alone. Furthermore, a number of synthetic Cu-, Se- and Tl- bearing phases are also known and complicate the identification yet further (Berger, 1987b).

STRUCTURAL ANALYSIS

To determine whether the metallic needles from Littleham Cove are *sabatierite*, crookesite, or equivalent to one of the synthetic Cu-, Se- and Tl-bearing phases noted in the foregoing text requires both structural and chemical data.

At this point, it is important to note that the published data on *sabatierite* has been called into question. Berger (1987a) suggested that *sabatierite* may be identical to a synthetic tetragonal phase with a formula, Cu_4TlSe_3 . Unfortunately the type *sabatierite* specimen has not been re-analysed and whether or not it corresponds to tetragonal Cu_4TlSe_3 , or something else, is not known.

Fortunately, the crystal symmetry and unit-cell parameters of crookesite are not disputed: crookesite is tetragonal, with $a = 10.435 \text{ \AA}$ and $c = 3.954 \text{ \AA}$ (Berger, 1987a) and importantly, these values are different from any of the synthetic or natural possibilities that might correspond to *sabatierite*.

Due to the paucity of material on the specimen (Figure 3), it was inappropriate to run an experiment using standard X-ray powder diffraction techniques as most of the unknown would be destroyed. The recent acquisition of a modern four circle diffractometer by the NHM presented an opportunity to make a more sophisticated structural analysis, including unit-cell parameters and crystal symmetry, from which powder diffraction data could be calculated.

A needle measuring $0.014 \times 0.017 \times 0.360 \text{ mm}$, with slight curvature along its length was removed from the specimen and mounted on a carbon fibre, which was in turn mounted on a glass fibre (Figure 4) for analysis. Data were collected for 51 hours on an XcaliburE, four circle diffractometer equipped with an Eos CCD detector. Analysis was not straightforward as the needle was found



Figure 4. The single crystal of crookesite that was mounted for study on the XcaliburE four circle diffractometer, note the small size of this specimen.

to be an aggregate of smaller crystallites, each with a slight angular offset. A detailed discussion of the data reduction is beyond the scope of this article; however it proved possible to determine space group and unit-cell parameters which are almost identical to those reported for crookesite (Table 1). From these data, the relative intensity and position of the lines in the X-ray powder diffraction pattern could be calculated; these are compared to published data in Figure 5. The similarity to crookesite is striking.

DISCUSSION

Fourteen years after its collection and following eight years of intermittent study at two different institutions, a combination of chemical and crystallographic data has conclusively identified crookesite, the first mineral containing essential thallium from the British Isles.

	Space Group	“a” parameter	“c” parameter
Crookesite (of Berger 1987a)	I/4m	3.954	10.435
Crookesite (this study)	I/4m	3.926	10.430

Table 1. The symmetry and unit-cell parameters of crookesite from Budleigh Salterton, compared with reported data (Berger, 1987a).

Neither the chemical data nor the crystallographic data were sufficient to identify the mineral to species level. The task was complicated by uncertainty surrounding the closely related species sabatierite. Here problems of nomenclature were generated by improvements in instrumentation and subsequent new ideas, racing ahead of the confirmative analyses on the type specimen that is held as an ultimate reference for this exact reason. The nomenclature problems surrounding sabatierite could probably be resolved by a modern investigation of the type specimen. It is unfortunate that this specimen was not re-examined in 1987 when the sabatierite validity was first questioned; it is equally regrettable that a re-examination of this species was beyond the scope of this project. Fortunately, however, the type specimen has been preserved in the collections at the École de Mines in Paris and should be available for future re-examination (www.smmp.net/IMA-CM/ctms_s.pdf, retrieved 15/9/2015).

It is important that such specimens are conserved, recorded in the literature and held within safe, stable, internationally recognised museums. It is also important that these institutions and their curators are able to make competent value judgments to allow researchers access to such specimens so that scientific knowledge can develop in line with advances in instrumentation.

The analytical difficulties associated with the identification of crookesite from Littleham Cove also demonstrate the importance of patience. When the specimen was first submitted to the NHM an in-house

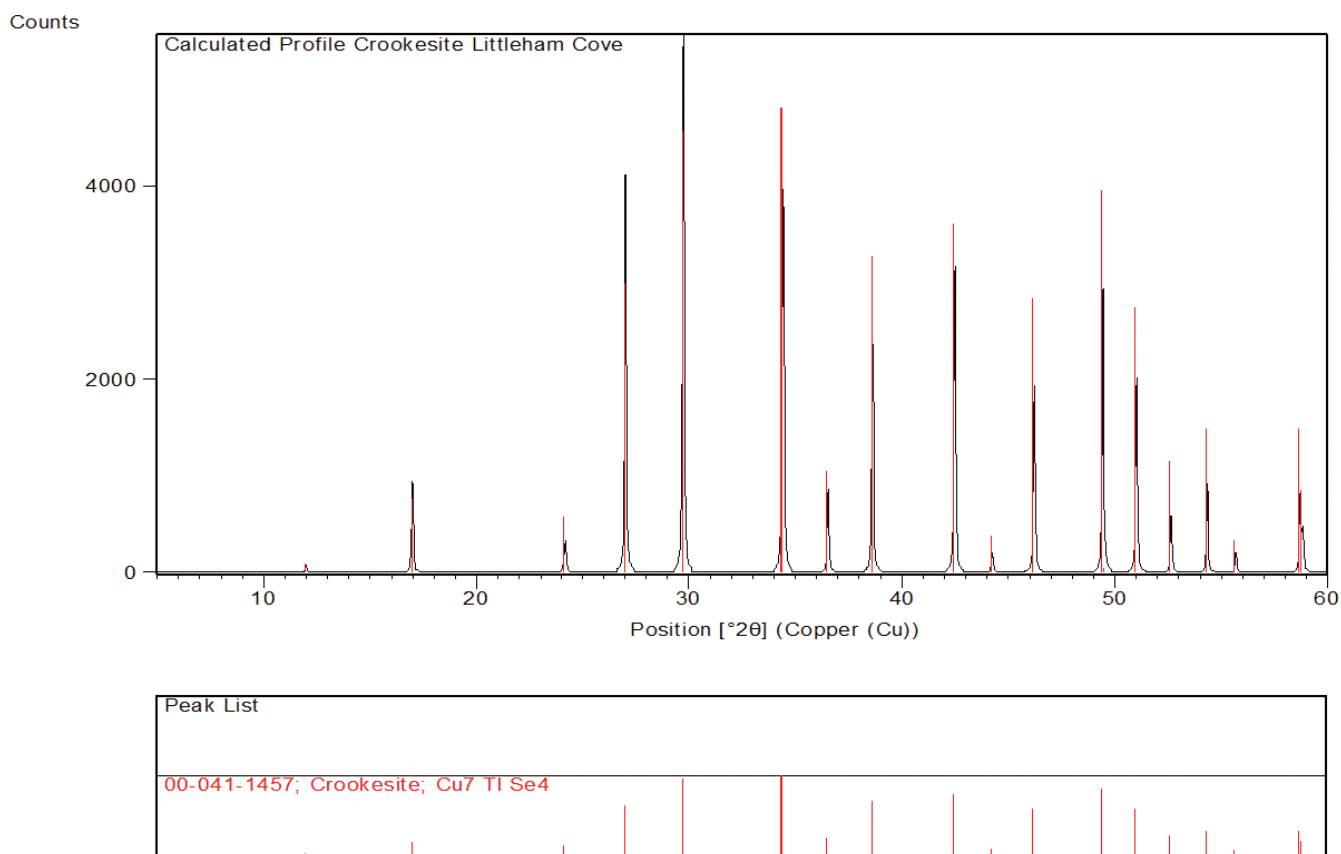


Figure 5. The diffraction pattern of crookesite, calculated from the single crystal data, together with the JCPDS crookesite reference pattern (00-014-1457)

identification by powder XRD would have required the near complete destruction of the unknown, leaving precious little available for future study. A decision was made to wait for a more appropriate technique, which was not available to the institution at the time due to operational constraints. When an appropriate instrument became available, the project was completed in the knowledge that most of the specimen would be preserved for future study.

The occurrence of a thallium mineral in the nodules at Littleham Cove is of significant geochemical interest. Thallium occurs in univalent and trivalent states; the first of these is most important in nature due to the high redox potential required to produce Tl^{3+} . Univalent thallium has considerable geochemical similarities to the larger alkali metals and it commonly substitutes for potassium in mineral structures. Similarities with potassium and other group I elements mean that, despite its crustal abundance, thallium almost always occurs as a substituent in common rock-forming minerals. It is only found as an essential constituent of minerals in very unusual circumstances. Thallium minerals are almost entirely confined to rare low temperature epithermal deposits. The mechanism by which the concentration of thallium has risen sufficiently to produce crookesite in a Permian red bed deposit is, therefore, of very considerable interest and deserves further study. It is hoped that a more complete mineralogical analysis of the locality, the nodules and all the mineral associations will produce a better geochemical understanding of this phenomenon.

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