The occurrence of uranium in association with cassiterite, wolframite, and sulphide mineralization in South-West England

P. K. SWART* AND F. MOORE†

Department of Geology, King's College, University of London, London WC2R 2LS

ABSTRACT. The U content of cassiterite (SnO_2), wolframite $(Fe,Mn)WO_4$, and various sulphides from two localities in the Cornubian batholiths of south-west England has been investigated. Cassiterites showed concentrations of U between 0 and 6 ppm with the higher concentrations corresponding to the darker colour bands. Sulphides contained no detectable U using the fission-track method, but high concentrations relate to micro-veining. This veining was also evident in associated wolframite and appeared to have a composition similar to an iron-arsenate mineral associated with the alteration of arsenopyrite. Wolframite exhibited a wide range of U concentrations with sharp zonation and several generations of ore deposition within one crystal. The U was not, however, associated with either the iron- or manganese-rich phases.

A PRELIMINARY investigation of the U content of sulphide minerals, cassiterite, and wolframite from St. Michael's Mount and Cligga Head, Cornwall, revealed that these minerals contained heterogeneous U distributions (Moore and Swart, 1979). In this paper we present more detailed work which has shown both systematic and irregular variations of this element in the minerals investigated.

Methods

Polished thin sections of the minerals and associated wall-rock alteration were irradiated in a thermal neutron flux (4×10^{16} neutrons cm^{-2}) using Lexan plastic as an external detector. Glass standards, the composition of which had been determined previously by neutron activation were positioned every five sections. After the irradiation, the detectors were etched in a solution of $6N$ NaOH at 75–80 °C for 90 seconds. Track densities could then be related to the thin section by superposition.

* Present address: Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge.
† Present address: Department of Geology, University of Shiraz, Shiraz, Iran.

Detection limits of this technique are approximately 0.01 ppm. In total ten sections of wolframite and cassiterite and six sections of sulphide assemblages were examined. A more detailed description of the method can be found in Simpson et al. (1976).

Results and discussion

Wolframites. In an earlier investigation (Moore and Swart, 1979) it was suggested that the anomalous patterns of U concentration were related to either the Mn- or Fe-rich phases of the wolframite shown by Moore and Howie (1978). Further research, however, has shown that U is associated with wolframite in at least two phases. First, there are distinctly zoned areas of U within the wolframite itself (fig. 1) in which the uranyl ion (UO_2^{2+}) is probably interstitially substituted for either the Fe^{2+} or Mn^{2+} ions. The concentration of U in these areas varies from less than 0.5 to approximately 22 ppm (Table I), with the boundaries between the differing concentrations sharply defined (fig. 2).

Secondly, U is situated in a multitude of microfissures crosscutting the entire crystal. Although the precise composition of these is not known, electron microprobe analyses have shown the presence of Fe and As and they could be similar to the U-rich hydrated iron oxides shown by Simpson et al. (1976). These veinlets do not crosscut the Li-rich micas or associated quartz (fig. 1), but they do traverse the areas of U zonation in the wolframite. This indicates that either the mica and quartz were deposited after this final phase of alteration or that the stresses which caused the microfissures in the wolframite did not cause such structures in the mica and quartz. This latter theory appears to be favoured by the alteration of the micas at their margins, indicated by the higher concentrations of fission tracks (fig. 3).
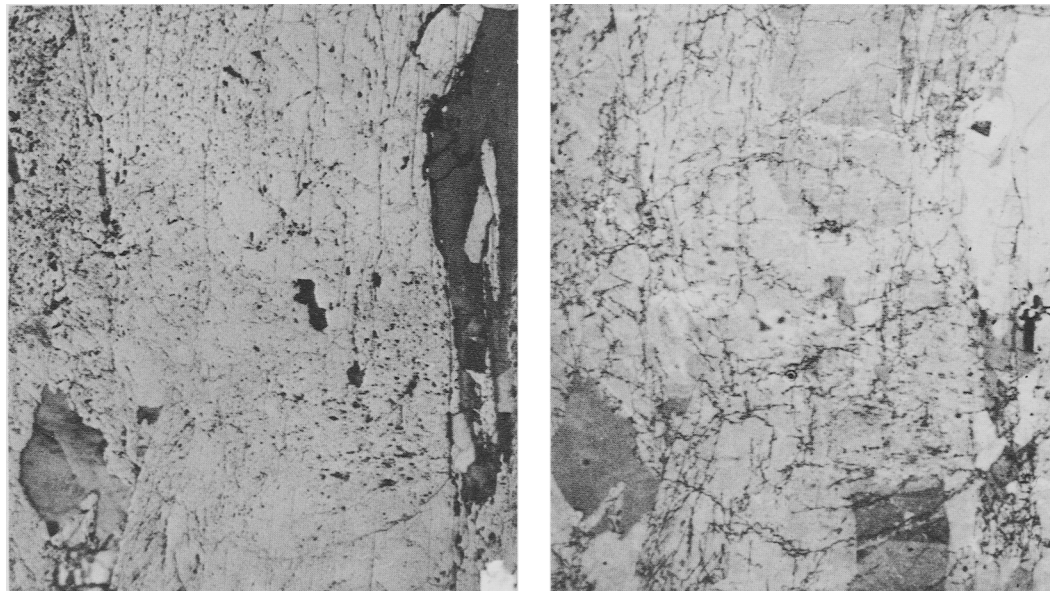
FIG. 1. (a, left) Reflected light micrograph of a section of wolframite and associated gangue minerals. (× 6.2). (b, right) Fission-track print of micrograph shown in 1a. Colour variation is a result of different densities of tracks arising from the fission of ^{235}U and α-tracks from boron and Li decay. In the wolframite distinct and multiple zonation of the U may be seen.

TABLE I. *Uranium concentration in ore minerals and associated minerals*

| Ore minerals	Conc. (ppm)	Comments
Cassiterite	0–6	Higher concentrations in darker bands
Wolframite	0.4–22	Distinct zonation. All crystals contained late fissure-fill U-rich phases
Sulphides (löllingite, arsenopyrite, stannite, kesterite, pyrite, and chalcopyrite)	—	Late fissure-fill U-rich phases

Associated minerals	Conc. (ppm)	Comments	Association
Quartz	0.1	Only in very late fissures	WCS
Topaz	—		C
Tourmaline	—	Conc. associated with pleochroic haloes	C
Lithionite mica	2	Only along altered margins	WCS
Apatite	65	Similar conc. in associated greisens	W
Pharmocosiderite	125	Cryptocrystalline	W
Clay mineral	70	Late infill	CSW

W = wolframite, C = cassiterite, S = sulphides

The micas must therefore have been in place before the deposition of the final U-rich fissure fill. Fluid-inclusion data on the cassiterites and associated quartz vein material (Moore and Moore, 1979) show that the cassiterites were deposited at a higher temperature (400 °C uncorrected for pressure) than most of the associated quartz. The evidence presented in this paper agrees with the conclusions of these researchers, that fluid inclusion temperatures of associated quartz are not reliable geothermometers of the associated mineralization. At the margins of the quartz there are occurrences of an iron-arsenate mineral, relatively rich in U (Table I). This mineral, although being cryptocrystalline, is euhedral in shape and therefore probably replaced a mineral emplaced before quartz deposition. Electron microprobe analyses of this mineral (fig. 4) show it to have a composition similar to scorodite ($FeAsO_4 \cdot 2H_2O$) or possibly pharmocosiderite ($6FeAsO_4 \cdot 2(OH)_3 \cdot 12H_2O$). Such minerals are often formed by the oxidation of arsenopyrite (Palache et al., 1951) and in some sections examined, such oxidation was in an intermediate condition (fig. 5).

A series of point analyses was made using the electron microprobe from the high to low U-rich areas of the wolframite. None of these scans showed any relationship between the Fe, Mn, or U contents (fig. 6).
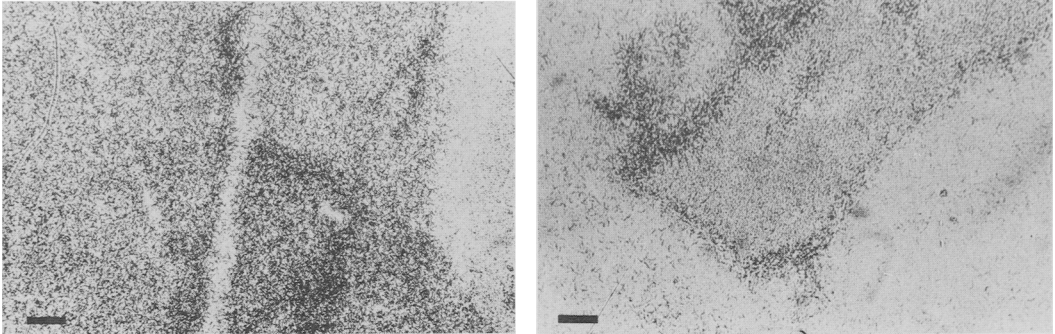
FIGS. 2 and 3. FIG. 2 *(left)* High-power fission-track print of part of fig. 1b. The concentration of U varies between 22 and 0.4 ppm. Scale bar = 50 μm. FIG. 3 *(right)* Fission-track print of a Li-rich mica showing alteration along the margins. Both α- and fission-tracks may be seen. Scale bar = 185 μm.

Variations in Fe and Mn occur at random throughout the crystal whereas U zonation occurs parallel with the crystal growth surfaces. It is probable that while the U zonation reflects the growth of the crystal, changes in the hübnerite/ferberite ratio may be a result of one or more of the following processes proposed by Moore and Howie (1978): (1) Rapid changes in the composition of the mineralizing solutions as a result of wall-rock reactions. (2) Subsequent diagenetic effects. (3) The affinity of either Fe or Mn for other available phases in the hydrothermal solutions.

Sulphides. As reported previously (Moore and Swart, 1979) all the sulphides analysed showed an absence of U at the detection limit of the fission track method. However, associated microveinlets, as seen in the wolframite, contained similar concentrations of U to those occurring in the wolframite. In situations where wolframite and sulphide mineralization are adjacent, such veinlets crosscut from one mineral to another.

Cassiterite. Cassiterite exhibited variable U concentrations with darker zones containing higher track densities than the lighter zones. Cassiterite crystals collected from the two localities in Cornwall all exhibited similar relationships. These
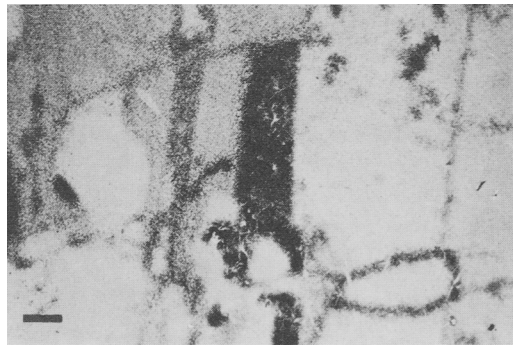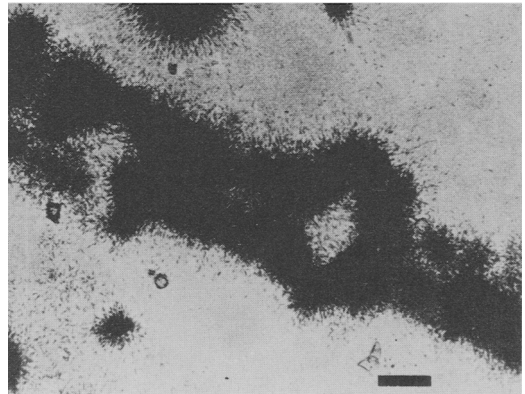

FIG. 4. Fission-track print of pharmocosiderite, situated between wolframite and Li-rich mica. Scale bar = 185 μm.

FIG. 5. *(a, top)* Photomicrograph of arsenopyrite surrounded by pharmocosiderite and mica. *(b, bottom)* Corresponding fission track print showing alteration of arsenopyrite. Scale bars = 185 μm.

results are in agreement with those of Berzina and Dolomanova (1967) on cassiterite from Russia.

Colour zoning in cassiterite has been the subject of controversy for many years (see Cuff, 1979). Attempts by researchers to establish a relationship between differences in chemical composition and the coloration of different zones have resulted in diverse explanations. Zoning has been attributed to differences in Nb, Ta, Mn, and Fe contents (Pecora et al., 1950). Other workers have also reported increases in a variety of elements in the darker zones (Noll, 1949; Goncharov and Filatov, 1971). These elements include Sn, Ti, Nb, Fe, Mn, W, Ba, Sc, and Be. Siddiqui (1964) and Greaves et al. (1971) ascribed the colour zoning to increases of up to 2 % in iron content in the dark zones, yet subsequent researchers found no such relationship between the individual zones (Edwards and Lyons, 1957; Grubb and Hannaford, 1966; Moore and Howie, 1979). Grubb and Hannaford concluded from the Mossbauer spectra of dark magnetic and colourless non-magnetic cassiterite from Malaya, that the ratio of Fe^{2+}/Fe^{3+} was almost six times greater in the dark cassiterite. Subsequently, however, Banerjee et al. (1970) found that cassiterite from the major occurrences of the world, including Cornwall, did not show such a relationship, and deduced that both Fe^{2+} or Fe^{3+} may predominate in dark or light cassiterite.

In the majority of minerals, colour is commonly caused by the absorption of light in the visible regions (4000–7000 Å) through electron transfer processes (Burns, 1970). These may be induced by internal or inter-element electron transitions, crystal imperfections, or band-gap transitions. Electron transfer induced by crystal structure

imperfections can be a result of two processes: (1) The mineral itself may contain lattice defects; (2) The lattice defects can be induced by the presence of radioactive minerals or elements in the structure. In the case of cassiterite, lattice imperfections probably result from structural damage caused by fission of ^{238}U or recoil from the alpha decay of ^{238}U; alpha particles do not register damage in the lattice of most minerals (Fleischer et al., 1975).

In view of these observations and the ability of U to cause lattice defects, it is suggested that the presence of coloured zones in the cassiterite crystals is due to variation in U concentration, analogous to pleochroic haloes in micas and other minerals. Colour variations, possibly due to lattice imperfections, were proposed by Goncharov and Filatov (1971), Gotman (1939), and Grigorev and Dolomanova (1951). However, there is no consistent relationship between elemental variation described by these workers and colour bands. It has also been suggested that varying U concentrations in zoned cassiterite resulted from irregular decay of U (Berzina and Dolomanova, 1967). It is more likely that the crystallization conditions were responsible for this heterogeneity. In a previous study it was seen that magnetic cassiterite is more uraniferous than non-magnetic varieties (Moore and Swart, 1979), which was attributed to the presence of wolframite inclusions. However, no connection is observed between colour banding and the presence of inclusions in this study.

General conclusions

(1) U associated with the ore minerals occurs either substituted for one of the major mineral components, or in late accessory mineral phases, deposited in microfissures in the wolframite and sulphides. (2) U in wolframite and cassiterite occurs as distinct zonation parallel to the crystal growth surfaces. In wolframite U zonation bears no relationship to changes in Fe or Mn. (3) Colour zoning in cassiterite can be attributed to variations in U content and consequent structural damage. (4) In all the generations of sulphides examined, U was present only in late-stage micro-fissures.
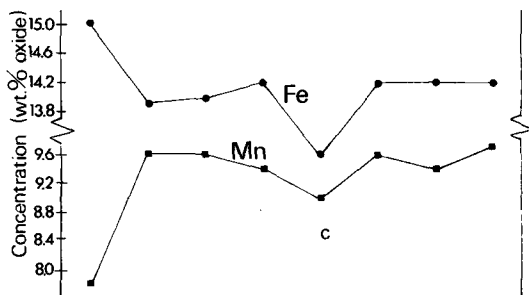
FIG. 6. A series of point analyses from a U-rich (left) to U-poor region of the section shown in fig. 1. Ten such series of analyses were made and all showed there to be no statistically significant change in either the Fe or Mn content (within the sensitivity limits of the probe). Each spot is approximately 10 μm apart; the c represents a microfissure and is the boundary between the two regions.

REFERENCES

Banerjee, K. S., Johnson, C. E., and Krs. M. (1970) *Nature* **225**, 173–5.

Berzina, I. G., and Dolomanova, Y. I. (1967) *Dokl. Acad. Sci. U.S.S.R., Earth Sci. Sect.* **175**, 114–18.

Burns, R. G. (1970) *Mineralogical application of crystal field theory.* Cambridge University Press.

Cuff, C. (1979) In *Geology of tin deposits*, R. G. Taylor (ed.). Elsevier.

Edwards, A. B., and Lyons, P. J. (1957) *Proc. Austral. Mining Metall.* **181**, 93–145.

Fleischer, R. L., Price, P. B., and Walker, R. M. (1975) *Nuclear tracks in solids.* University of California Press.

Goncharov, G. N., and Filatov, S. K. (1971) *Geochem. Int.* **8**, 268–75.

Gotman, Ya. D. (1939) *C.R. Acad. Sci. USSR*, **23**, 470–2.

Greaves, G., Steveson, B. G., and Taylor, R. G. (1971) *Econ. Geol.* **66**, 460–87.

Grigorev, I. F., and Dolomanova, E. I. (1951) *Trudy Mineral. Muz. Akad. nauk SSR*, **3**, 73–92 [English Abstract: Chem. Abst. 49 (1955).

Grubb, P. L. C., and Hannaford, P. (1966) *Mineral. Deposita*, **2**, 148–71.

Moore, F., and Howie, R. A. (1978) *Mineral. Deposita*, **13**, 391–7.

——— (1979) Ibid. **14**, 103–7.

—— Moore, D. J. (1979) *Trans. Inst. Mining Metall.* B, **88**, 57–60.

—— Swart, P. K. (1979) *Proc. Ussher Soc.* **4**, 432–6.

Noll, W. (1949) *Beitr. Mineral. Petrog.* **1**, 593–625.

Palache, C., Berman, H., and Frondel, C. (1951) *The System of Mineralogy*, **2**, J. Wiley & Sons, New York.

Pecora, W. T., Switzer, G., Barbosa, A. L., and Myers, A. Y. (1950) *Am. Mineral.* **35**, 889–901.

Siddiqui, S. F. A. (1964) Unpublished Ph.D. thesis, University of London.

Simpson, P. R., Plant, J., and Cope, M. J. (1976) In *Geology, mining and extractive processing of Uranium.* M. J. Jones (ed.). London: Institute of Mining and Metallurgy, 126–39.