

## COMPUTER AIDED ANALYSIS OF X-RAY IMAGES IN MUDSTONE CONCRETIONS FROM BUDLEIGH SALTERTON, DEVON.

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The examination of fine-grained concretions such as the uranium and vanadium enriched mudstones of Budleigh Salterton, Devon presents difficulties because of the sub-micron size of their mineral grains. We have attempted to address this problem by collecting X-ray images of thin sections of these concretions using a Jeol 8600 electron microprobe.

Techniques were developed in this study using "Image 1.54" and "Photoshop 3.0" to process individual element maps and produce a composite image in which the degree of opacity of each layer can be varied. This allows rapid determination of the distribution of elements and their associations. The technique does not identify minerals as such, but gives an insight into element relationships from which mineral compositions can be deduced.

The concretions, which are of Upper Permian age, were collected from the cliffs of Budleigh Salterton in Devon. They contain moderately high concentrations of uranium, vanadium and copper. They are also cobalt, nickel, lead and arsenic enriched. For example, cobalt occurs in the concretions as an arsenide mineral, a sulphur arsenic mineral, a sulphide and a cobalt nickel sulphide. The observed mineralization occurs as metal-rich coatings around quartz and other primary grains and as a replacement in areas where calcite has dissolved. Examples of other metal sulphides and other associated mineralization are also discussed.

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### INTRODUCTION

Budleigh Salterton is located on the south-east coast of Devon, between Exmouth and Sidmouth. Metal-enriched concretions are found in the Littleham Mudstone Formation, which is exposed at Littleham Cove [040 803], at the western end of Budleigh Salterton Beach. The mudstones are of Upper Permian age, and contain a variety of authigenic minerals (Harrison, 1975). These minerals are largely composed of the elements uranium, vanadium, copper, lead, nickel and cobalt, associated with sulphur, arsenic or oxygen. The minerals are thought to be replacement products that formed by diffusive processes after calcite was partially dissolved. This occurred due to an acidic reduction environment created when ferric oxide was reduced to ferrous oxide. The replacement process was triggered by the decay of organic matter. The concretions are composed of silt size quartz grains (approximately 8 mm) with occasional mica and feldspar grains of similar size, contained in a clay mineral matrix (approximately 2 mm). The microscopic grain size of these concretions makes mineral identification by X-ray diffraction (e.g. Durrance and George, 1976), electron microprobe and reflected light microscopy very difficult. We have developed a method that uses X-ray images generated on a Jeol 8600 electron microprobe. The images were transferred into the computer packages "Images 1.54" (Perceptics) and "Photoshop 3.0" (Adobe) which allows element associations to be shown from which mineral phases can be deduced.

### LITTLEHAM MUDSTONES

The Littleham Mudstone Formation overlies the Exmouth Sandstones and Breccias, and is the uppermost unit of the Permian. The formation is up to 275 m thick, and was either deposited in flood-basin and overbank conditions (Selwood *et al.*, 1984), or may possibly represent a playa mudflat deposit (Mader, 1985). The reddish brown, mainly structureless mudstones, are composed of quartz grains and occasional feldspars, set in silt and clay. The clay, which is essentially composed

of illite with some kaolinite and chlorite, makes up 40-70% of the mudstone. The silt content ranges from 30-50% and fine-grained sand accounts for 2 to 7% (Selwood *et al.*, 1984). The red colour of these sediments is caused by haematite coating the grains. Layers and lenses of olive-green silty sandstones and sandy siltstones, which are up to 0.6 m thick, occur in these mudstones. The olive-green colour is caused by the localised reduction of ferric to ferrous oxide. Some calcite cementation is also present.

### CONCRETIONS

Reduction haloes found in the Littleham Mudstones sometimes contain metal-enriched cores known as nodules or concretions, having diameters of 50 to 200 mm. They show enrichments of U, V, Cu, Pb, Co, Ni, As and S (Harrison, 1975). The concretions were first described by Carter (1931), who noticed that these concretions were rich in vanadium and radioactive, in as much as they fogged a photographic plate. Later workers include Perutz (1939), who classified the concretions on the basis of their external shape as follows (I) irregular, (II) spheroidal-asteroidal, and (III) spheroidal-concentric. Harrison (1975), noted the enrichment of elements such as Co, Ag, Cr, V, and U and reported several minerals. Durrance and George (1976) suggested that reduction mechanism was caused by oxidation of organic matter. Hofmann (1991) compared these reduction spheroids with similar ones from around the world, and Kemp *et al.* (1993; 1994a; 1994b and 1995) presented microprobe data, U/Th ratios, REE patterns, Eh-pH diagrams and the results of leachate experiments, which showed that the enriched elements were transferred in solution as acidic sulphate and chloride complexes.

### IMAGE ANALYSIS

X-ray images were collected from thin sections taken from concretions for 17 elements (Si, Al, Fe, Ti, Ca, Mg, K, P, Co, Ni, U, V, Cu, Pb, Ba, As and S) (Figure.1) on a Jeol 8600 electron microprobe.

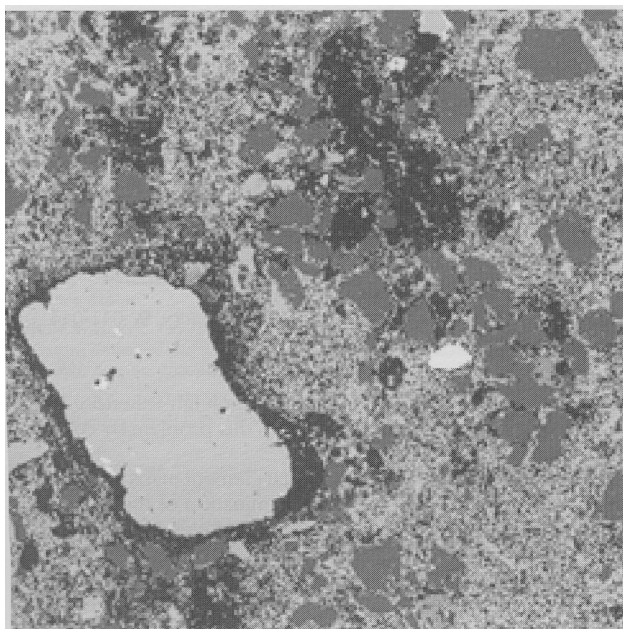


Figure 1. Composite X-ray of seventeen elements. Pale grey areas represent aluminosilicate minerals and clay matrix (large grain is feldspar). Mid grey areas represent quartz, and the dark-grey areas are where the sulphide mineralization occurs. Associated with the sulphide mineralization is uranium.

The image represents a 1 mm<sup>2</sup> area of the concretion.

The individual element map images were saved as TIFF files. These images were taken into "Images 1.54", where background noise was removed, the images cleaned up, a colour spectrum (in which point count levels are converted into RGB (red, green, blue) colour values) was applied to each image and the brightness adjusted to give the best view of the distribution of each element. At this stage the concentration of each element was quantified by calibrating the RGB values by comparing these with the original point count levels, so as to determine which colour most accurately corresponded with the different concentrations of each element.

The resulting images were then opened up separately in "Adobe Photoshop 3.0", and the colour which best corresponded with the spread of the element selected. These selections were then incorporated as separate layers each with a transparent background, into a composite image made up of the 17 individual elements. Using the "Adobe Photoshop 3.0" package individual layers (one for each element) can be made visible or invisible or have their degree of opacity (density of colour) adjusted to reveal the underlying layer or layers. Using this technique we were able to determine, with a high degree of accuracy, the relative distribution of the elements and in what combination they occurred. This technique does not identify minerals as such but gives accurate element relationships from which minerals or mineral groups can be deduced.

## IMAGE INTERPRETATION

Copper is observed to associate with arsenic to form a copper arsenide mineral. Known copper arsenide minerals include algodonite (Cu<sub>6</sub>As), which has been reported from the Littleham Formation by Harrison (1975). Domeykite, Cu<sub>3</sub>As, is another possible copper arsenide mineral. As these minerals were formed under reducing conditions the lower oxidation state of copper is more likely (i.e. algodonite). In addition domeykite is a very rare mineral that is usually associated with hydrothermal deposits (Duda and Rejl, 1986).

Copper also associates with sulphur to form a copper sulphide mineral. Possible copper sulphide minerals include covellite (CuS). This mineral can also have varying amounts of Fe, Se, Ag and Pb in its

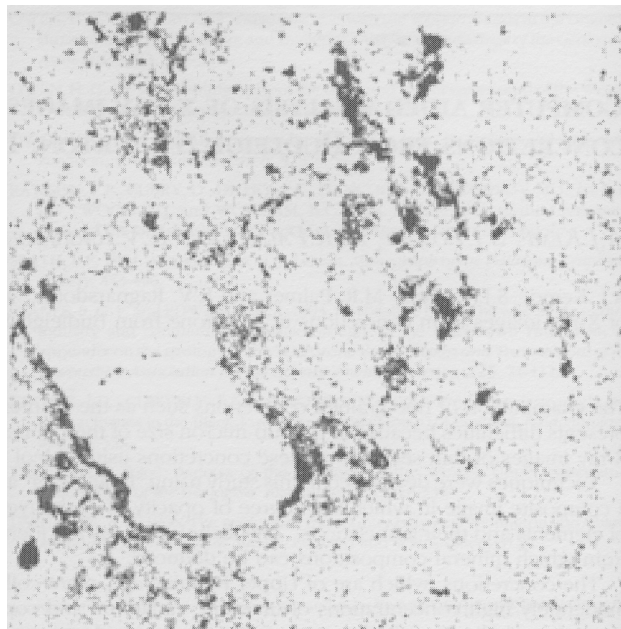


Figure 2. X-ray of copper and sulphur. The pale-grey areas represent copper unassociated with sulphur. The dark-grey areas represent areas of association of copper and sulphur. It can be seen that copper sulphide mineralization is coating the feldspar grain in the bottom left hand corner of the image, as well as filling voids vacated by the decomposition of calcite. The image represents a 1 mm<sup>2</sup> area of the concretion.

structure. In general covellite is found in zones of cementation associated with other sulphide minerals, including bornite, chalcocite, chalcopyrite and enargite (Duda and Rejl, 1986). Chalcocite (Cu<sub>2</sub>S) is also a candidate for the copper sulphide mineral and can contain Ag and Fe in its structure. It is found in the south-west of England as a primary mineral in the granites of Devon and Cornwall (Duda and Rejl, 1986), but if it is present in the concretions it would occur as a secondary mineral. Both covellite and chalcocite have previously been reported from the Budleigh Salterton concretions (Harrison, 1975) (Figure 2).

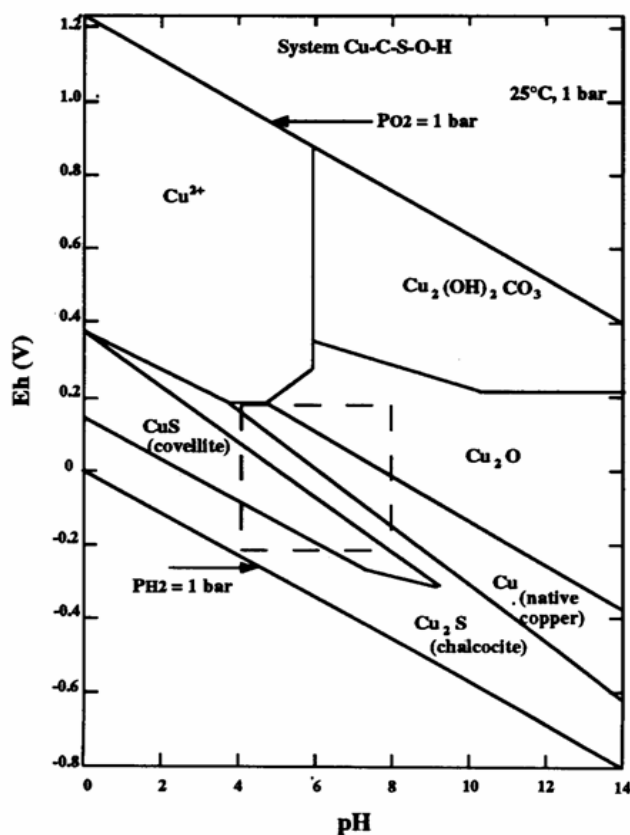
Eh-pH diagrams confirm that covellite and chalcocite are stable under the conditions likely to have existed when the concretions formed (Figure 3).

Copper furthermore associates with arsenic and sulphur to form a sulphur arsenide mineral, which could be enargite (Cu<sub>3</sub>AsS<sub>4</sub>). This is a common copper mineral which is generally found in association with galena, tetrahedrite, sphalerite and quartz in sulphide deposits (Duda and Rejl, 1986).

Cobalt is associated with As, possibly as CoAs<sub>2</sub>, (safflorite). This mineral is deposited under hydrothermal or low temperature aqueous conditions (Duda and Rejl, 1986). It has not previously been reported from the Budleigh Salterton concretions.

Cobalt is also associated with As and S, possibly as CoAsS, (cobaltite). This mineral can often contain iron, which changes the formula to (Co,Fe)AsS. Cobaltite is often found in vein deposits with other arsenide and sulphide minerals (Duda and Rejl, 1986).

Cobalt also occurs solely with sulphur possibly as Co<sub>3</sub>S<sub>4</sub>, (linnaeite). There is possibly an association of these elements with iron in some small areas. Cobalt occurs together with lead in some places and with phosphorus, calcium and titanium in other areas. There is also an association of Co-Ti-Fe. In areas of high K there is a slight enrichment of Co, but in general Co is not strongly associated with K, Si or Al, hence Co is not strongly adsorbed onto clay minerals. Some of these Co mineral assemblages are intergrown with barite (BaSO<sub>4</sub>). Cobalt also shows strong associations with U and Cu. In some areas there is also some relationship of cobalt with iron and



**Eh-pH diagram for part of the system Cu-C-S-O-H**  
 The assumed activities of dissolved species are  $\text{Cu} = 10^{-3} \text{ M}$ ,  
 $\text{S} = 10^{-3} \text{ M}$  and  $\text{C} = 10^{-3} \text{ M}$   
 [ ] most common Eh-pH range of local groundwaters

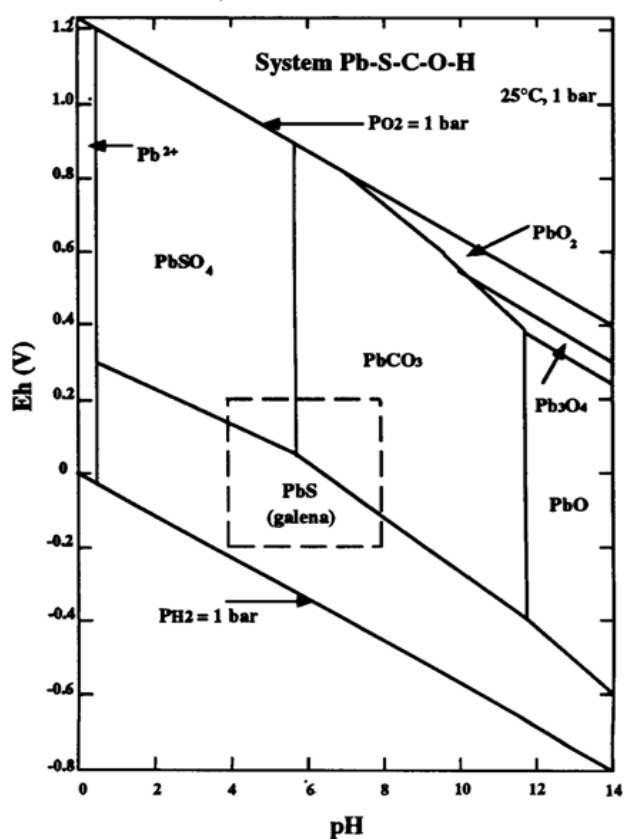
Adapted from Brookins, 1988.

Figure 3. Eh-pH diagram for copper. The boxed area represents the most likely local groundwater conditions during diagenesis. Covellite, chalcocite and native copper can all form under these conditions. All three minerals have been previously reported from the concretions (Harrison, 1975).

and with iron and magnesium in others. These minerals may be remnants of primary mafic material derived from weathering of the early Permian volcanics of the Exeter region. Lastly, cobalt overlaps large areas rich in calcium and potassium, but there is only a slight overlap of cobalt with vanadium and titanium.

Lead is found in association with sulphur to form the mineral galena (PbS). The occurrence of galena in these concretions has not previously been reported. The small areas of lead that are not associated with sulphur are most probably in the clay mineral matrix, either adsorbed onto the surface or substituting for potassium. Eh-pH diagrams show that lead can precipitate from aqueous solutions to form galena (PbS), under the conditions that formed the concretions (Figure 4).

Uranium exists as uraninite, ( $\text{UO}_2$ ) (Figure 5). The uraninite is associated with the arsenide and sulphide mineralization, coating grains and filling areas of veins vacated by the partial dissolution of calcite. There is also evidence for the association of U with Si, which suggests that coffinite ( $\text{USiO}_4$ ) is also present. Previous leachate work indicates that uranium was transported in solution as a sulphate complex (Kemp *et al.*, 1994b). Hence upon reduction it would tend to be precipitated with the sulphide minerals.



**Eh-pH diagram for part of the Pb-S-C-O-H.**  
 The assumed activities of dissolved species are  $\text{Pb} = 10^{-4} \text{ M}$ ,  
 $\text{S} = 10^{-3} \text{ M}$  and  $\text{C} = 10^{-3}$   
 [ ] most common Eh-pH range of local groundwaters

Adapted from Brookins, 1988.

Figure 4. Eh-pH diagram for lead. The boxed area represents the most likely groundwater conditions. The only sulphide of lead to form under these conditions is galena.

Eh-pH diagrams show that under the conditions in which the concretions formed, uraninite is the most likely uranium mineral to form. The presence of uraninite and coffinite has also been confirmed by electron microprobe analysis (Figure 6).

## DISCUSSION

The work presented here suggests that the Littleham Mudstone concretions were created under reducing conditions that were most likely generated by oxidation of organic matter. The oxidation of organics would have reduced ferric to ferrous oxide (Durrance and George, 1976), thus lowering the pH. This resulted in partial dissolution of calcite cement. These reactions created a secondary porosity into which diffused the metals U, V, Cu, Pb, Ni and Co. They were precipitated as oxides, arsenides and sulphides. These metals were leached out of the surrounding oxidized mudstones by sulphate- and chloride-rich porewaters at relatively low pHs. The new minerals filled veins and partially coated grains of feldspar and quartz and are also found in association with calcite and barite.

Harrison (1975) found a variety of minerals including bornite, chalcopyrite, maucherite, niccolite and rammelsbergite as well as the minerals suggested by X-ray image analysis in this study. In addition

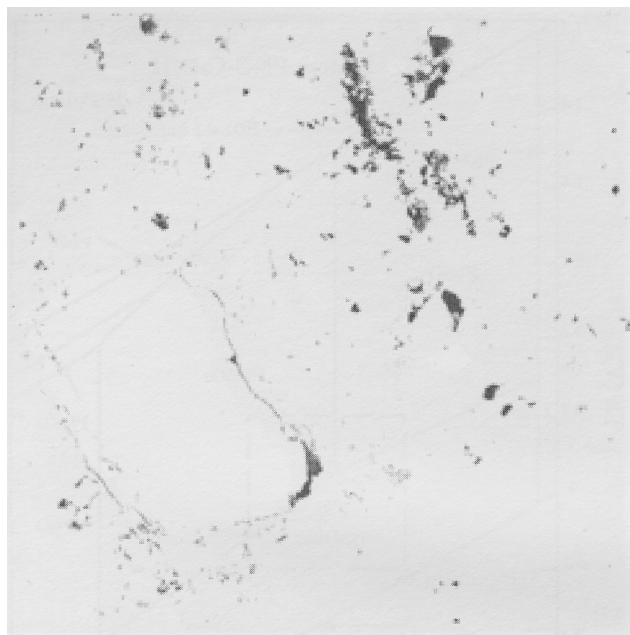


Figure 5. X-ray image of uranium. It can be seen that U occurs in association with the sulphide mineralization. The image represents a 1 mm<sup>2</sup> area of the concretion.

to these minerals the element associations suggest that some of the following minerals may also be present; enargite (Cu<sub>3</sub>AsS<sub>4</sub>) safflorite (CoAs<sub>2</sub>), cobaltite (CoAsS), linnaeite (Co<sub>3</sub>S<sub>4</sub>), and galena (PbS).

## CONCLUSIONS

The imaging method presented here provides a means of identifying the chemical composition of minerals that are too small to be identified by conventional means. From these element associations it is possible to deduce the composition of minerals. The study of the mineralogy and geochemistry of microscopic grains is aided by Eh-pH diagrams which provide further evidence for the possibility of the existence of some of these minerals by delineating their stability ranges.

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## REFERENCES

- BROOKINS, D.G. 1988. Eh-pH diagrams for geochemistry. *Springer-Verlag, New York*: 176p.
- CARTER, G. E. L. 1931. An occurrence of vanadiferous nodules in the Permian beds of South Devon. *Mineralogical Magazine* **22**, 609-613.
- DUDA, R. and REJL, L. 1986. Minerals of the World. *Hamlyn, Twickenham*, 520p.
- DURRANCE, E.M and GEORGE, M.C. 1976. Metatyuyamunit from the uraniferous-vanadiferous nodules in the Permian marls and sandstones of Budleigh Salterton, Devon. *Proceedings of the Ussher Society* **3**, 435-440.
- HARRISON, R. K. 1975. Concretionary concentrations of the rarer elements in Permo - Triassic red beds of South - West England. *Geological Survey of Great Britain, Bulletin* **52**, 1-26.
- HOFMANN, B.A. 1991. Mineralogy and geochemistry of reduction spheroids in red beds. *Mineralogy and Petrology*, **44**, 1-2, 107-124.
- KEMP, A.J., RAGNARSDOTTIR, K. V. and LANES, J. 1993. Permo-Triassic nodules from Budleigh Salterton east Devon. *TERRA Abstracts*, **5**, 652.
- KEMP, A.J., PALMER, M.R., and RAGNARSDOTTIR, K.V. 1994a. The Uranium-Thorium and Rare Earth Element Geochemistry of Reduced Nodules from Budleigh Salterton, Devon. *Proceedings of the Ussher Society*, **8**, 214-218.
- KEMP, A.J., PALMER, M.R., and RAGNARSDOTTIR, K.V. 1994b. Leaching Efficiency of different anions on powdered haematite: Implications for formation of Uraniferous concretions. *A.G. U. Abstracts (EOS)*, V12B-03.

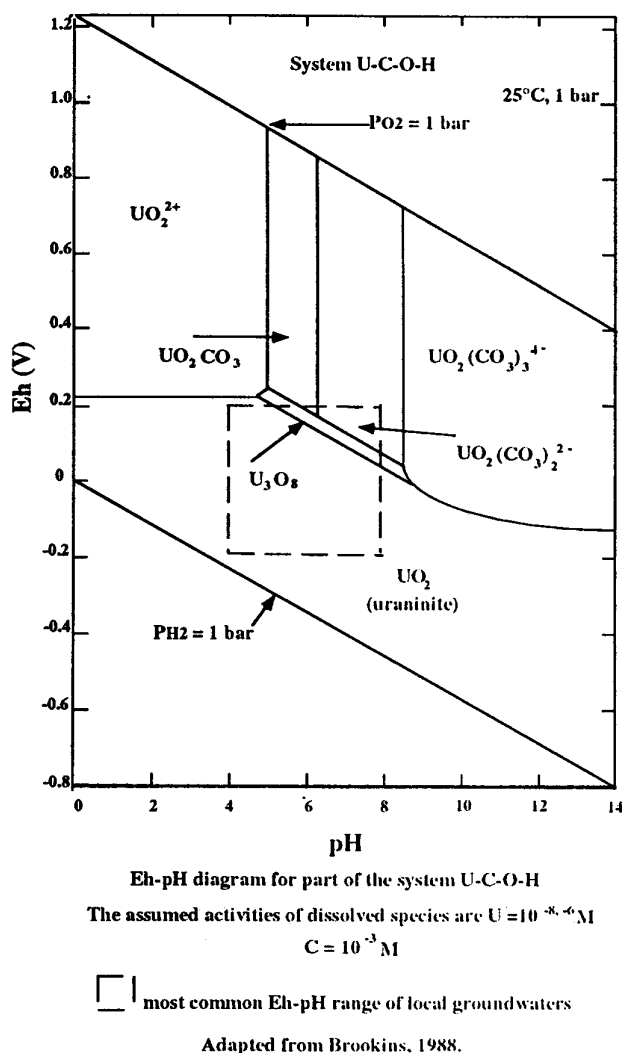


Figure 6. Eh-pH diagram for uranium. The boxed area represents the most likely local groundwater conditions. Uraninite forms under these conditions.

- KEMP, A.J., RAGNARSDOTTIR, K.V. and PALMER, M.R. 1995. Possible metal complexes that existed in groundwaters from the Permo-Triassic of south east Devon, U.K. *TERRA Abstracts* **7**, VII-1 (11P).
- MADER, D. 1985. Braidplain, floodplain and playa lake alluvial fan, aeolian and paleosol facies composing diversified lithogenetical sequence in the Permian and Triassic of South Devon. (England). In D MADER. Aspects of the fluvial sedimentation in the lower Triassic Bundsandstein of Europe 15-64. Springer-Verlag, Berlin.
- PERUTZ, M. 1939. Radioactive nodules from Devonshire, England. *Mineral. Petrog. Mitteil* **51**, 141-161.
- SELWOOD, E. B., EDWARDS, R. A., SIMPSON, S., CHESHER, J. A., HAMBLIN, R. J. O., HENSON, M. R., RIDDOLLS, B. W. and WATERS, R.A. 1984. Geology of the country around Newton Abbot, Memoirs of the Geological Survey of Great Britain, London.