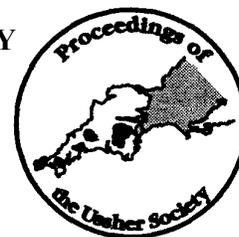


THE URANIUM-THORIUM AND RARE EARTH ELEMENT GEOCHEMISTRY OF REDUCTION NODULES FROM BUDLEIGH SALTERTON, DEVON

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Metal-rich nodules occur at the Permian-Triassic boundary at Budleigh Salterton on the south east Devon coast. The nodules are present in reduced haloes within the otherwise oxidised Littleham Mudstones. The trace element geochemistry of the nodules and the surrounding mudstones and sandstones have been analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). High accuracy data are available for U, Th and the rare earth elements (REE). In addition, semi-quantitative analysis has also been carried out for another 50 elements. The nodules contain high levels of a number of elements, particularly vanadium, uranium and copper. A preliminary model describing the formation of the nodules is presented.

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INTRODUCTION

Vanadium, uranium, copper and other redox sensitive elements occur as mineralized zones, layers and, to a lesser extent nodules, throughout geological time and in many different rock types from around the world (Rich *et al.*, 1977). Amongst the largest and most productive are sandstone hosted deposits. Although the enrichment of these elements can, in some instances, be caused by circulating hydrothermal fluids (Rich *et al.*, 1977), stratabound types (including the nodules) are generally thought to have been formed or enriched in metals by the deposition of minerals from relatively low-temperature circulating groundwaters (Lisitsin, 1962; Rich *et al.*, 1977; Langmuir, 1978; Wanty *et al.*, 1987). Uranium and other redox sensitive elements (such as vanadium) are reduced to form minerals, and in some cases, the native element, e.g copper and silver. The reduction may occur in response to changes in the Eh-pH of the environment arising from the oxidation of organic matter, or bacteria may actively utilize certain inorganic ions as an energy source (Andreyev and Chumachenko, 1964; Haji-Vassiliou and Kerr, 1973; Lovley *et al.*, 1991; Lovley *et al.*, 1993). A large variety of authigenic minerals can form under these conditions; more than 45 have been reported worldwide (Hofmann, 1991). In the Littleham Formation at Budleigh Salterton these minerals include malachite, coffinite, algodonite, niccolite, bornite, vanadinite, rammelsbergite, covellite, chalcocite, chalcocyanite, roscoelite, freirinite, maucherite, calcioconite, rauvite, native silver and native copper. Secondary mineralization due to recent oxidation results in tyuyamunite and metatyuyamunite (Perutz, 1939; Harrison, 1975; Durrance and George, 1976; Hofmann 1991).

GEOLOGY

Permo-Triassic sedimentary rocks are exposed along the south Devon coast from Torbay eastwards to Seaton, and the succession contains some of the best examples of Permian non-marine deposits in Western Europe (Figure 1, and Laming, 1982). The sediments were formed by erosion of the Cornubian Massif, including the Dartmoor granite, and possibly rocks from Brittany. Angular debris and coarse sand were washed down from the high ground into the Dorset Basin, to form alluvial and delta-fan deposits. Post-depositional weathering turned the sediments red by oxidizing the iron (Laming, 1982). The sediments were deposited under semi-arid conditions, with occasional flash flooding. The succession contains breccias, aeolian and fluvial sandstones, conglomerates, mudstones and river gravels. Owing to the poor fossil record, stratigraphic correlation relies heavily on lithological similarities. The Permian-Triassic boundary has been

placed at the base of the Budleigh Salterton Pebble Beds. The metalliferous nodules found at Littleham Cove, Budleigh Salterton occur in the reddish marls known as the Littleham Mudstones, which lie immediately below the Pebble Beds (Figure 1).

NODULES

The nodules are found in reduced mudstone haloes that exist within the oxidised reddish brown mudstones. Carter (1931) first described these nodules and he noted that they were rich in vanadium and fogged a photographic plate, indicating that they were radioactive.

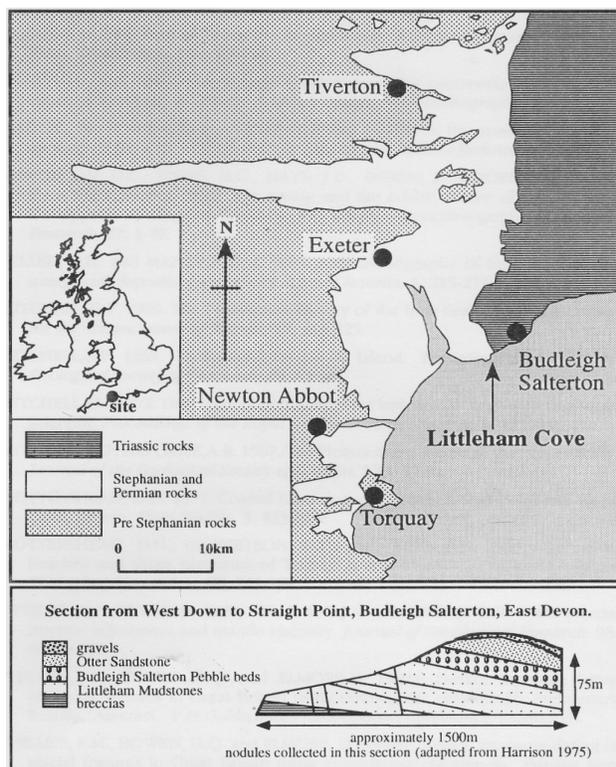


Figure 1. Locality map of Littleham Cove, Budleigh Salterton and Stratigraphic section of the Permo-Triassic exposed from West Down to Straight Point, Budleigh Salterton Beach.

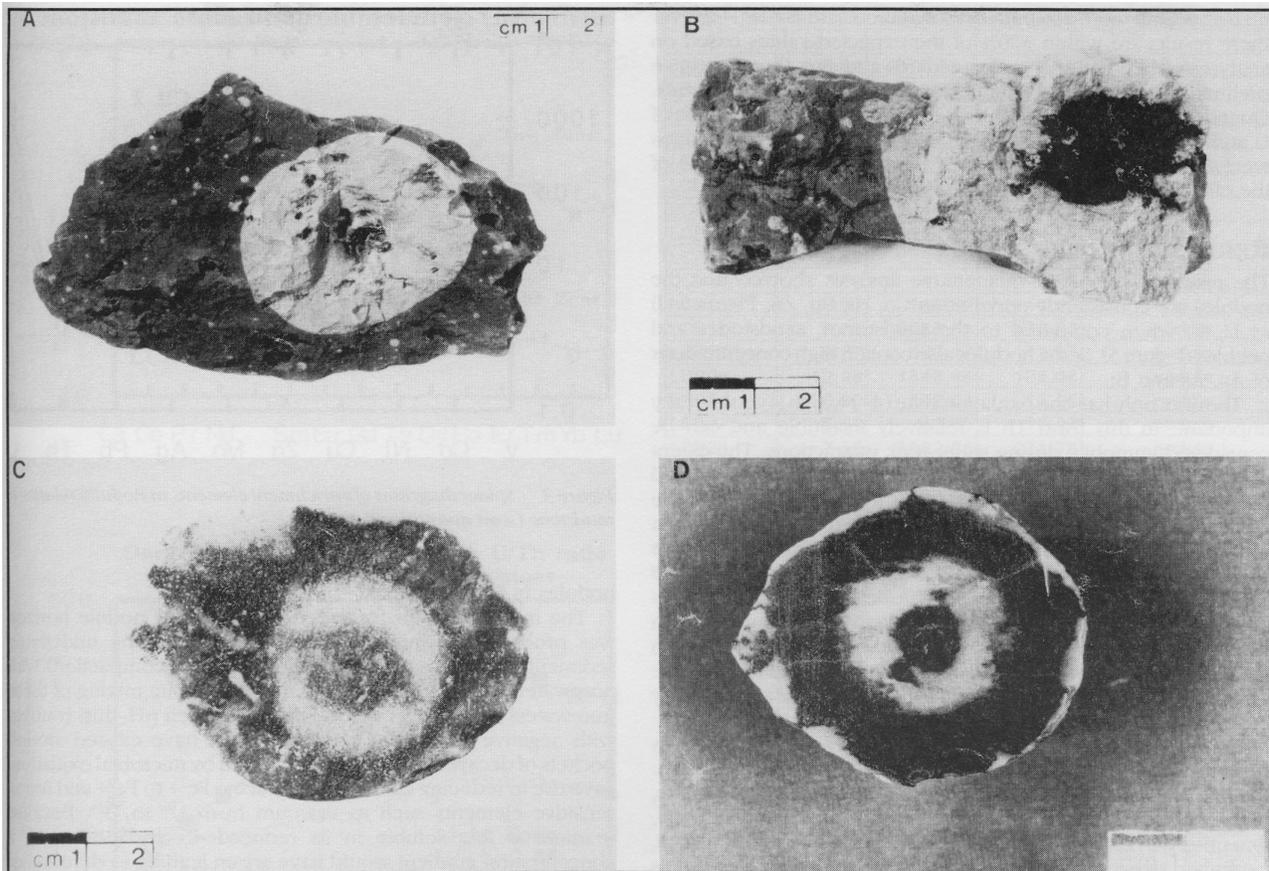


Figure 2. Photographs of nodules.

A. Specimen containing a small nodule medium dark grey N4, in the centre of a reduction halo yellowish grey SY7/2, surrounded by oxidized mudstone pale reddish brown 10R5/6. Contains pockets of soft material in both oxidized and reduced areas, possibly intraformational clay clasts derived from flood plain during channel migration.

B. Specimen containing a nodule, dark grey N3, surrounded by reduced mudstone yellowish grey SY7/2, and finally oxidized mudstone pale reddish brown 10R 5/4, containing several small reduction halos.

C. Nodule brownish grey 5YR 4/1, in hard band of reduced mudstone yellowish grey 5Y 7/2, approximately 1 metre thick, towards the top of the cliff. (highest concretion succession?)

D. Specimen containing a greyish black N2 central core, surrounded by a band of yellowish grey 5Y 7/2 reduced mudstone, enclosed in a dark grey N3 zone, with a thin rim of reduced mudstone 5Y 7/2.

Later studies classified them on their main external features as (I) irregular, (II) spheroidal-asteroidal, (III) spheroidal-concentric (Perutz, 1939). Harrison (1975) in his detailed study of the area, concluded that metallic elements such as Cu, Ag, Ni, Co, Cr, V and U were precipitated as arsenides, sulphides and in some cases native elements. His idea was that the metal enrichment within the nodules resulted from the post-depositional percolation of acidic mineral solutions through the red beds, with precipitation of the minerals occurring preferentially at permeable/impermeable interfaces. He believed the ultimate source of the metalliferous solutions may have been geothermal springs. On the other hand Durrance and George (1976) believe that the precipitation of the metallic elements is governed by redox processes associated with the oxidation of fragments of organic matter buried within the New Red Sandstone sediments.

The nodules can vary in size from a few mm in diameter to approximately 30 cm (Figure 2). Chemical analyses have shown that there are at least three types of nodules (I) uranium-vanadium rich (Carter, 1931), (II) nickel-cobalt rich, (Harrison, 1975), (III) a type with several varieties of copper minerals (Harrison, 1975). Previous studies showed that the nodules contain high concentrations of V, U, Ni, Cu, Co, As, and Ag. The sporadic occurrence of Cu-dominant concretions appears to be unconnected with both the V-dominant and the Ni-As-dominant concretions. The distribution of these nodules

throughout the 270 m (maximum thickness) of Littleham Mudstones led previous workers to suggest, that either the accumulation of these heavy metal-rich concentrations extended over a long time interval, or the enrichment event occurred by post-depositional migration of metal-rich fluids throughout the mudstone beds.

ANALYTICAL METHODS

Crushed dry samples (61) of nodules, mudstones, sandstones and pebbles were acid-digested for analysis by a Fisons Instruments Plasmaquad 2 Plus Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), by the method of Bailey *et al.*, 1993. 200 mg of the dried sample was weighed into a P.T.F.E beaker, and moistened with 2 ml of 18MΩ water, 3 ml of 40% v/v hydrofluoric acid and 2 ml of concentrated nitric acid were added. The beaker was then placed on a hot plate at 210°C and the solution was evaporated just to dryness before being removed from the hotplate. 30 ml of 5% v/v nitric acid was added to the cooled beaker and the beaker returned to the hotplate to dissolve the cake. The sample was made up to 100 ml with 5% v/v nitric acid. Semi-quantitative ICPMS determinations were performed for 50 elements, using indium as an internal standard, the elements of most interest are shown in Figure 3. The semi-quantitative values shown in this figure reflect concentrations normalized to a local oxidized mudstone. No firm conclusions will be drawn from data obtained for these elements until more accurate determinations are

made. However these results are within $\pm 20\%$ of the expected values based on analyses of international rock standards and can, therefore, give preliminary indications of the expected geochemical trends. Quantitative (accurate to within 5%) measurements were made of U and Th (Bailey *et al.*, 1993) and from these results their ratios were calculated. Quantitative measurements were also made of the rare earth elements (REE) (Kemp *et al.*, 1994).

RESULTS

The results of our semi-quantitative analysis showed that the nodules are consistently enriched in Co, Ni, Cu, Zn, Pb, as well as U, V, when compared to the mudstones, sandstones and pebbles (Figure 3). Some nodules also contain high concentrations of Ag, As and Bi.

Thorium only has one oxidation state (4+) which is geologically important. In this form Th is relatively insoluble and can be considered immobile during water-rock interactions. The extent of uranium enrichment in the nodules can, therefore, be determined from a comparison of the Th/U ratio in the nodules and the mudstone. Any variation of the ratio is an indication of uranium enrichment or depletion (Zielinski, 1978). The Th/U ratio (Table 1) for sandstones worldwide is relatively constant at ~ 1.6 -2.8 (Wedepohl, 1978). Analyses of sandstones, mudstones, pebbles and nodules from Budleigh Salterton clearly show that uranium has been depleted in the overlying sandstones and enriched in the nodules. The nodules are also enriched in all the REE (Figure 4) when compared to the surrounding mudstone. This is particularly evident for the heavy REE.

Electron microprobe analyses were carried out on thin sections of several of the nodules which were coated with carbon. Preliminary investigations indicate the presence of malachite, barite, calcite, anatase, quartz, feldspar, uraninite, coffinite, ilmenite, tyuyamanite, metatyuyamanite, carnotite, chlorite, illite, kaolinite, smectite and several, as yet, unidentified minerals consisting largely of copper and sulphur (Kemp *et al.*, 1993).

DISCUSSION

Weathering of the granite masses, volcanics, pre-Permian sediments and limestones in south-west England generated sediments containing relatively high levels of uranium and other lithophile elements. Seasonal variations caused periods of wet and dry weather patterns when these sediments were deposited. Sparseness of plant material allowed the pH of the surface water to remain high. This, combined with aerobic conditions, maintained a high Eh and oxidising conditions prevailed, causing ferrous oxide to be oxidized to ferric oxide. This ferric oxide precipitated as hematite coatings on the sediment grains at and near the surface. This cyclic process continued over a long period of time, building up a great thickness of red sediments. These sediments also contained localised concentrations of organic matter, as shown by the presence of reduced mudstones in the Littleham Mudstone Formation, which hosts the nodules.

The nodules, which contain metal enriched centres, are surrounded by iron reduction halos and occur in 3 distinct horizons within the Littleham Mudstone Formation. Horizon 1 lies within a few metres of the base of the mudstone and horizons 2 and 3 are within a few metres of the top of the mudstone. The lowest is adjacent to the basal boundary with the Exmouth Breccias and Sandstones. These nodules contain more nickel and cobalt than the two higher horizons. However, the nickel and cobalt concentrations are only of the order of a few hundred ppm and no minerals of Ni and Co have been observed by microprobe analysis. One explanation for higher Ni and Co concentrations in these lower horizon nodules, may be related to fragments of volcanic material, which are observed in several breccia horizons within the sedimentary rocks which occur below the Littleham Mudstones (possible sources for this material are the Pocombe and Hatherleigh volcanic series). Ni and Co are relatively enriched in mafic rocks, so that pore water percolating up through the Exmouth Breccias and Sandstones may have enriched the overlying nodules in these elements.

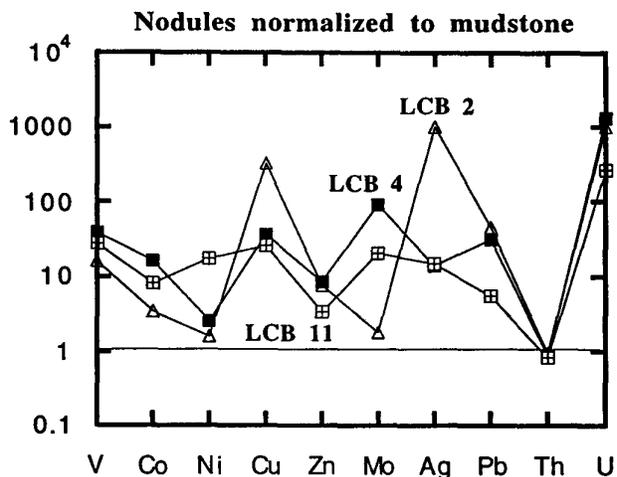


Figure 3. Spider diagrams of enrichment elements in nodules relative to mudstone (semi quantitative data).

The mechanism for formation of this lower nodule horizon was probably the mixing of porewaters from the underlying sediments (on de-watering as they underwent compaction) with porewaters contained within the mudstone. The mixing of these porewaters most likely caused a change in their pH; this, coupled with negative Eh conditions which must have existed around pockets of decayed organic matter caused by microbial oxidation, gave rise to reducing conditions, reducing Fe^{3+} to Fe^{2+} and redox sensitive elements such as uranium from U^{6+} to U^{4+} . Because uranium is less soluble in its reduced 4^+ oxidation state, a concentration gradient would have arisen leading to diffusion of uranium (Klinkhammer and Palmer, 1991) from the surrounding oxidised porewaters. The solubility of uranium in the porewaters would have been enhanced by high concentrations of carbonate ions in the porewaters (Brookins, 1979, 1982; Langmuir, 1978; Taylor and McLennan, 1988) resulting from the dissolution of weathered Devonian carbonates that occur nearby. The presence of high dissolved carbonate complexes is also suggested from the enrichment of heavy REE, which form stronger carbonate complexes than the light REE (Millero, 1992). The REE also show a negative gadolinium anomaly when normalised to the local red mudstone, which may be caused by organic ligand complexing (Lee and Bryne, 1993). Although the REE are clearly enriched in the nodules, further work is required to identify whether they are hosted in specific minerals, or are disseminated throughout the reduced zone of the nodules.

On all but one of our visits to Littleham Cove, this nodule horizon has been covered by beach pebbles, therefore most of the work in this study has been carried out on nodules assumed to have originated from the upper mudstone horizon. The nodules collected from this upper mudstone horizon were not in situ, but were collected, over several visits, from material that had fallen from the cliffs, which frequently undergo minor collapses and falls.

We have recently collected samples from the reduced sandstone band which hosts the third nodule horizon. The sandstone blocks collected contain several metal enriched spheroids. Only semi-quantitative analysis has been obtained for the nodules in these sandstones at present. The upper mudstone horizon and the metre-thick reduced sandstone horizon that make up zones 2 and 3, occur near the boundary of the Littleham Mudstones with the overlying Budleigh Salterton Pebble Beds.

We postulate that the upper mudstone nodule horizon developed from groundwaters derived from the overlying sandstones and pebble beds. These groundwaters carried soluble uranium and vanadium carbonate complexes and, later, soluble copper sulphate complexes, into the upper few metres of the Littleham Mudstones. This is feasible despite the low permeability of the mudstones, as the rocks are

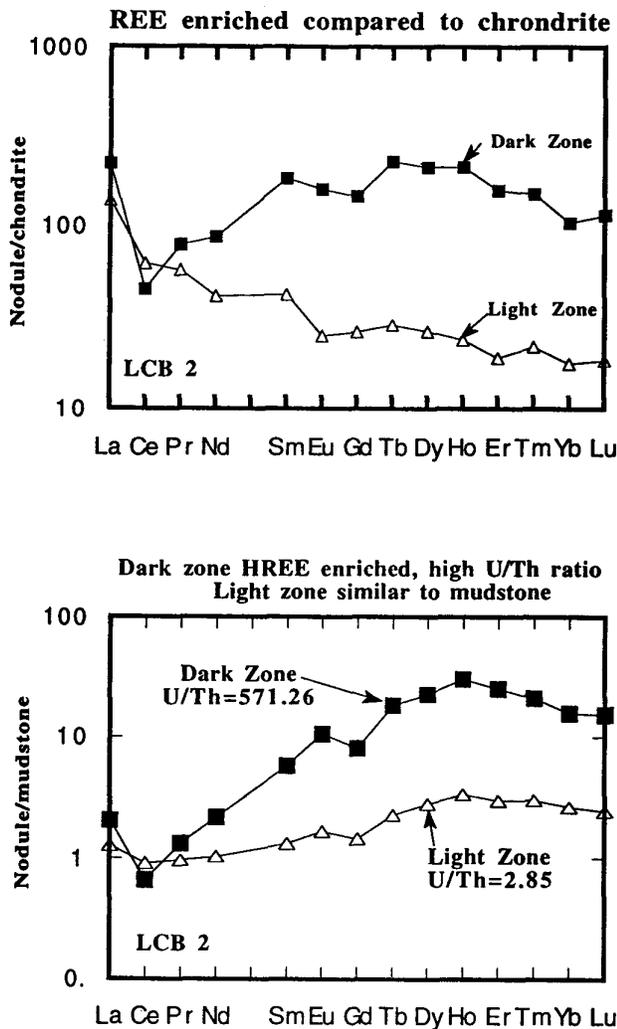


Figure 4. REE patterns in nodules relative to mudstones and chondrite

faulted and jointed throughout. In addition, the nodules appear to be restricted to the upper few metres of the Littleham Mudstones and the porewaters would have been in diffusive contact with the overlying sandstones and Pebble Beds. Here the groundwater mixed with porewater from the mudstone. Where favourable conditions existed (e.g. pockets of decayed organic matter) reduction of iron occurred. Redox sensitive elements that were present in this porewater/groundwater mixture, would have been precipitated as oxides, sulphides, arsenides and occasionally the native element. The mechanism for formation of the nodules is similar to that which formed the nodules in the lower horizon.

As the greenish grey spherical iron-reduced haloes that surround the metal enriched cores of these nodules are radially symmetrical, their formation cannot be attributed to fluid flow, as fluid flow would produce reduction halos elongated in the flow direction. Therefore it is likely that diffusive processes were involved. This could either be outward diffusion of carbon or inward diffusion of oxygen (Mykura and Hampton, 1984).

The radial symmetry of the nodules suggests that they formed after the sediments were initially compacted. The formation of the nodules may have ceased when all the organic carbon had been oxidised. The presence of dark organic matter in the centre of some nodules suggests, however, that redox reactions may have been diffusion-limited by the supply of electron acceptors.

Examination of the nodules shows that there are several distinct types. They all, however, contain well-worked quartz grains if various

Sample	Thorium ppm	Uranium ppm	U/Th ratio	sample type
LCB1	5.64	4676.58	829.18	nodule
LCB1A	7.95	6945.38	873.63	nodule
LCB2A	8.6	11864.45	1379.59	nodule
LCB2B	8.53	8413.76	986.37	nodule
LCB4B	8.8	8144.44	925.5	nodule
LCB4D	6.94	9823.16	1415.44	nodule
LCB11B	8.25	2846.88	345.08	nodule
LCB11C	9.19	2211.82	240.68	nodule
LCB13	9.83	2354.59	239.53	nodule
LCB16A	7.59	41.74	5.5	nodule
LCB16B	8.97	146	16.28	nodule
LCB16C	9	3888.63	432.07	nodule
LCB16D	8.77	102.17	11.65	nodule
LCB20	12.38	1548.46	125.08	nodule
LCB26	6.6	102.61	15.55	nodule
LCB27	5.66	62.65	11.07	nodule
LCB28	7.59	2062.66	271.76	nodule
LCB29	7.49	44.67	5.96	nodule
LCB31	9.6	44.5	4.64	nodule
LCB32	9.65	294.26	30.49	nodule
LCB43	9.18	2704.62	294.62	nodule
LCB50	9.14	4881.51	534.08	nodule
LCB53	8.6	2942.44	342.14	nodule
LCB56	8.39	7881.69	939.41	nodule
LCB57(1)	7.28	3671	504.26	nodule
LCB57(2)	7.69	5495.15	714.58	nodule
LCB58	8.48	5303.63	625.43	nodule
LCB59	8.44	3867.95	458.29	nodule
LCB60	9.25	2832.06	306.17	nodule
LCB62	8.6	8644.48	1005.17	nodule
LCB63 (1)	9.06	1015.24	112.06	nodule
LCB63 (2)	9.34	2203.83	235.96	nodule
LCB 3	1.73	3.27	1.89	quartz pebble
LCB 5	3.08	3.52	1.11	yellow sandstone
LCB 40	7.62	1.03	0.44	coarse sandstone
LB 1	12.1	3.63	0.3	green sandstone
LB 2	16.37	5.37	0.33	red sandstone
LB 3	14.38	2.21	0.15	brown sandstone
LB 4	18.1	3.68	0.2	orange sandstone
BS 1	1.36	1.11	0.81	red sandstone
BS 2	0.98	0.74	0.76	fine red sandstone
BS 8	3.72	1.22	0.33	red sandstone
BS 9	3.54	2.83	0.81	red sandstone
OP 1	2.22	1.15	0.51	red sandstone
OP 2	4.01	2.31	0.58	white sandstone
BS 5	23.75	6.17	0.26	sandstone cement
BS 3	4.33	2.43	0.56	red sand lens
BS 6	0.54	1.64	3.03	light sandy lens
BS 7	1.7	0.79	0.46	darker sandy lens
LCB2C	9.5	53.21	5.6	reduced mudstone
LCB4A	9.68	75.66	7.82	reduced mudstone
LCB 6	5.02	2.4	0.48	reduced mudstone
LCB11A	7.89	530.79	67.27	reduced mudstone
LCB 41	5.51	2.75	0.5	reduced mudstone
LCB 46b	21.78	4.07	0.19	reduced mudstone
LCB 47a	13.6	9.59	0.71	reduced mudstone
LCB 7	17.2	3.65	0.21	oxidized mudstone
LCB 12	10.92	4.11	0.38	oxidized mudstone
LCB 47b	14.19	5.02	0.35	oxidised mudstone
BS 4	19.02	4.05	0.21	dark mudstone
LCB 10	8.18	2.6	0.32	fossil soil

Table 1. Uranium/thorium ratios.

sizes and have cavities filled with minerals enriched in uranium, titanium, copper and other elements, that are embedded in a clay matrix enriched in vanadium. In some cases uranium is present in its oxidized form as a coating on exposed fracture surfaces of nodules in the form of discrete minerals such as tyuyamunite, suggesting that partial oxidation of the nodules has occurred during recent weathering after the nodules had become exposed to the atmosphere.

Other minerals that have been identified within the nodules include; malachite, barite, calcite, chlorite, and several Cu-S, Cu-U-S, Cu-V-U-S, combinations (work in prep). Analyses by microprobe and ICP-MS show low concentrations of nickel and cobalt, so that none of the nickel and cobalt minerals described by Harrison (1975) have yet been identified.

We suggest that the metal enrichment in the nodules occurred in several stages. Initially carbonate-rich groundwaters percolated through the sediments, carrying with them elevated levels of uranium and other soluble elements such as vanadium. Microbial oxidation of organic matter produced reducing conditions within local areas which acted as nuclei for the precipitation of reduced uranium-rich mineral phases and enrichment of vanadium in the clay matrix of the nodules. Copper and zinc are relatively immobile in carbonate groundwaters, so the enrichment most likely resulted from later transport by sulphate-rich groundwaters, formed from the oxidation of sulphide minerals derived from weathering of the granites. This sulphate would be reduced to sulphide around the nodules and result in the precipitation of some of the transition elements as insoluble sulphides. We have not identified a separate category of nickel- and cobalt-rich nodules (cf. Harrison, 1975),

CONCLUSIONS

From our preliminary analysis, we believe that uranium, vanadium and other similar elements were dissolved from the surrounding sediments and transported to the sites of reduction by carbonate-rich ground water. The reducing conditions were induced by the presence of decaying organic matter. As the sulphide minerals in the sediments weathered down, the ground water became enriched in sulphate ions. Copper, zinc and other transition elements became mobile and were also carried to the sites of reduction. The heavy rare earth element enriched patterns, show a Gd anomaly and indicate transport of REE by carbonate and organic complexes. Like Harrison (1975), we also believe the nodules formed after compaction of the enclosing sediments.

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