SHORT COMMUNICATIONS

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Rhenium and tungsten in nickeliferous lateritic profiles

THE geochemical distribution of several elements through three nickeliferous lateritic profiles has been described by Ahmad and Morris (1978). In the present article results for rhenium and tungsten are presented. Hitherto, little has been known concerning the occurrence of these two trace elements in laterites formed as a consequence of tropical weathering of ultrabasic rocks. Neutron-activation analysis (NAA) has been used for the determinations. Such a method, which offers very high sensitivity, was essential, because the abundance of rhenium in igneous rocks is of the order of 0·1-1·0 $\times 10^{-3}$ p.p.m. (Morris and Short, 1969). The relatively few data for tungsten in ultramafic rocks indicate a content of 0·1-0·8 p.p.m. (Krauskopf, 1970).

The lateritic deposits investigated by us are in Guatemala, New Caledonia, and Indonesia. Aspects of the geology, mineralogy, and chemistry of these profiles on serpentinized peridotite have been discussed previously, and descriptions of the samples analysed for rhenium and tungsten are given in the earlier article (Ahmad and Morris, 1978). Distribution of major elements in the residuals conforms with the usual pattern of lateritic weathering of ultrabasic rocks: loss of silica and magnesia results in the marked concentration of iron and of several minor and trace elements. Each of the three occurrences is worked commercially for nickel.

Analytical methods

Rhenium. A radiochemical method involving carrier chemistry and NaI(Tl) γ-scintillation counting of ^{186}Re ($t_{\frac{1}{2}} = 90{\cdot}6$ h) was employed. Full details will be reported elsewhere. The separation scheme, which was based largely on liquid-liquid extractions, yielded the radionuclide in a radiochemically pure state, as was confirmed by decay measurements. Chemical yields were determined by spectrophotometric analysis. The corrected final count rates were compared with those of solutions resulting from dilute perrhenic acid standards irradiated alongside the geological samples. It was shown in previous studies (Ahmad, Ahmad, and Morris, 1977) that the use of such dilute solutions for comparison controls did not give rise to self-shielding problems in the NAA of laterites.

The irradiations were performed in the nuclear reactor HERALD at the Atomic Weapons Research Establishment, Aldermaston, usually with a thermal neutron flux of $2{\cdot}5 \times 10^{12}$ neutrons cm^{-2}s^{-1}. After irradiation for 28 h, the activities of the samples were allowed to decay for 5 days before radiochemical processing.

Values of $0{\cdot}7_2$, $0{\cdot}7_0$, $0{\cdot}7_0$, $0{\cdot}7_1 \times 10^{-3}$ p.p.m. Re were obtained by the method for the international reference rock, basalt ('diabase') W-1. These are in satisfactory agreement with those obtained by Morris and Fifield (1961), namely (0·56-0·84) av. $0{\cdot}71 \times 10^{-3}$ p.p.m.

Tungsten. The procedure followed was essentially that of Lustenhower *et al.* (1976) in which W$^{\text{VI}}$ is adsorbed on charcoal from an acid solution as an 8-hydroxyquinolate complex. The charcoal was counted with a coaxial Ge(Li) semiconductor detector connected to a 4096-channel analyser. Tests with ^{187}W, and also spectrophotometric measurements, showed that the chemical procedure consistently gave a yield of 99%; hence no correction for recovery was required.

In our determinations 0·4 g samples of laterite in polythene tubes were irradiated in the reactor HERALD in a thermal flux of $2{\cdot}5 \times 10^{12}$n cm^{-2}s^{-1} for 4-6 h. Along with the samples, dilute aqueous solutions of ammonium tungstate (VI) were irradiated as comparison standards.

It was found that the photopeak corresponding to $E_\gamma = 0{\cdot}686$ MeV of ^{187}W ($t_{\frac{1}{2}} = 24$ h) was the most suitable for measurement, although analogous results were obtained with the peak from $E_\gamma = 0{\cdot}479$ MeV. Confirmation that the activities could be measured free from interference was gained from decay measurements.

Analyses of the standard rock W-1 in this work showed 0·42, 0·40, 0·41 p.p.m. W; these results agree well with those found by Atkins and Smales (1960), namely (0·41-0·47) av. 0·43 p.p.m.

TABLE I. *Distribution of rhenium and tungsten as a function of depth through lateritic profiles*

Profile	Sample no.	Depth (m)	Description	Re (p.p.m.)	W (p.p.m.)
Guatemala	L1	1·5–2	Surficial laterite	8·9, 9·2 × 10^{-3}	0·16, 0·16, 0·14
	L2	2·5–3	Plastic laterite	6·8, 6·2	0·14, 0·11
	L3	3·5–4	Saprolite	1·9, 2·7	0·38, 0·27
	L4	5·25–5·75	Boulders in saprolite zone	1·3, 1·2, 0·9	0·10, 0·11
	L5	8–8·5	Weathered rock	1·9, 1·0, 1·2	0·03, 0·02, 0·05
	L6	8–8·5	Fines of weathered rock	1·7, 2·0	0·08, 0·08
	L7	10·25–10·75	Rock	1·0, 1·1	0·03, 0·03
New Caledonia	BNC1	0–2	Ferricrete	1·8, 1·7, 1·8, 1·9	0·26, 0·26
	BNC2	2–7	Limonite	0·6, 0·8, 0·9	0·08, 0·08
	BNC3	7–11	Limonite	8·0, 9·0, 6·0	0·13, 0·12
	BNC4	11–13	Limonite	1·6, 1·9	0·13, 0·16
	BNC5	13–14	Limonite and asbolite	1·6, 1·8	0·11, 0·12
	BNC6	14–17	Limonite and asbolite	0·7, 0·9	0·22, 0·16
	BNC7	17–20	Saprolite	0·8, 0·8	0·13, 0·13
Indonesia	BIP1	11–13	Limonite and asbolite	4·5, 5·3, 4·4	0·07, 0·08
	BIP2	13–17	Saprolite	3·1, 3·9	0·06, 0·05, 0·06
	BIP3	18–19	Saprolite and quartz boxwork	1·1, 1·0	0·05, 0·05

Results and discussion

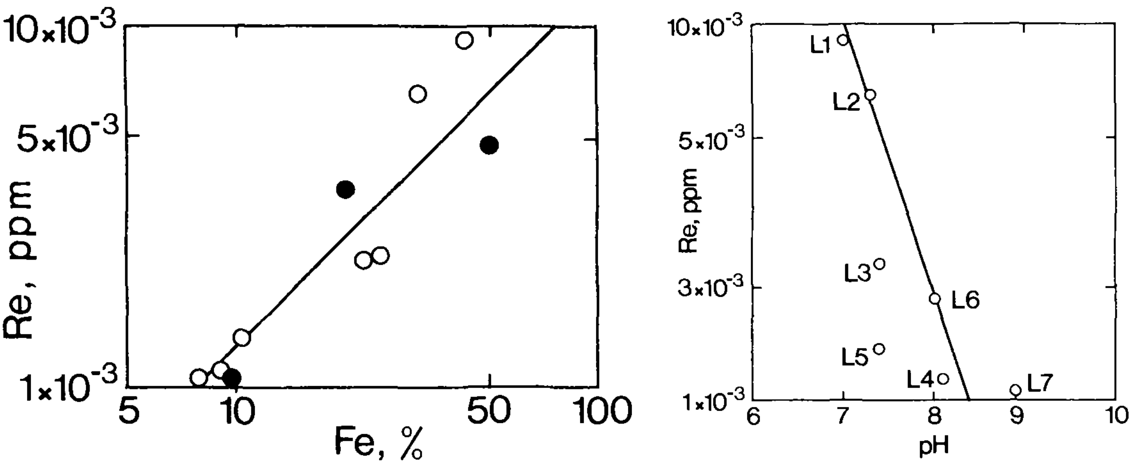
Results of determinations of rhenium and tungsten are presented in Table I.

In both the Guatemalan-L and the New Caledonian-BNC profiles there is up to a nearly tenfold concentration of rhenium in upper sections in comparison with the content of the element in the initial serpentinite. At first sight this may appear to be a rather surprising observation, because the perrhenate ion ReO$_4^-$ is stable in both acidic and alkaline solutions, and, on the basis of considerations of ionic potential (Keller, 1957; Gordon and Tracey, 1952), Re$^{\mathrm{VII}}$ [Re^{7+}, $r = 0{\cdot}56$ Å (Ahrens, 1952) $Z/r = 12{\cdot}5$] would be expected to be a leached moiety, and hence depleted in laterites.

Formation of organorhenium complexes must be taken into consideration as a possibly important factor influencing the distribution of rhenium. However, our work suggests that the major cause of the concentration of the element in the A and B horizons is sorption of ReO$_4^-$ through anion exchange reaction. The anion ReO$_4^-$, being large and having only a single negative charge, has a low (−ve) enthalpy of hydration, and it is readily sorbed by synthetic anion exchangers (Kraus and Nelson, 1959; Diamond and Whitney, 1966) —cf. ClO$_4^-$—perrhenates and perchlorates are usually isomorphous.

There is a notable geochemical coherence between rhenium and iron in each of the three profiles, especially L and BIP (fig. 1), and it seems reasonable to presume that anion exchange of aqueous ReO$_4^-$ with OH$^-$ groups in iron(III) oxohydroxides has occurred. If this is the case, sorption of rhenium would be expected to be diminished with increase in pH of circulating waters. Such a trend is illustrated in fig. 2. (In each lateritic occurrence the volume of rain water is great, and the decomposition products of organic matter are probably limited, as may be caused in a warm climate by the microflora consuming the residues of the macroflora. It follows that it is probably justifiable to assume that the pH of the weathering system ranges between that of rainwater and the leaching pH of the lateritic minerals.)

Further evidence in support of the anion exchange concentration thesis has been obtained from experiments with ^{186}Re of high specific activity in the form of ReO$_4^-$. It was found that sorption of the radiotracer by ore samples from solutions at equilibrium pH could be roughly collated with sorption by synthetic goethite from solutions of corresponding pH. However, the experiments were complicated by peptization and



FIGS. 1 and 2: FIG. 1 (*left*). Geochemical coherence between rhenium and iron in lateritic deposits. ○ = L profile. ● = BIP profile. FIG. 2 (*right*). Relation between rhenium content and reaction pH of the weathering profile L.

by changes of composition of solid phase occurring over certain pH variations; moreover, an apparent buffering effect was noted.

As weathering proceeds it is generally accepted that ultimately a downward movement of the elements results. Clearly our data indicate that Re is barely mobile in terms of migration from the ferruginous horizons. The greater depth at which the maximum concentration of rhenium is found in the New Caledonian deposit *vis-à-vis* the Guatemalan profile is compatible with the extensive evidence that the former occurrence has resulted from more pronounced weathering than the latter (Ahmad and Morris, 1978).

Rhenium shows definite chalcophile character. Particularly it concentrates in molybdenite, and the apparently richest mineral of rhenium, dzhezkazganite, according to Polyakova (1965) consists of a solid solution of ReS_2 and MoS_2. However, the sulphide content of the type of laterite with which we are concerned is likely to be low, and it does not appear to have an important influence on the distribution of rhenium in the profiles.

On the grounds of periodicity Mendeleev proposed the name *dvi-manganese* (Sanskrit, dvi, two) for rhenium, before the element was discovered. However, although manganese is concentrated in the lateritic profiles, our results demonstrate a closer correlation between the distribution of Re and Fe than between Re and Mn.

There is some uncertainty as to the form in which tungsten is significantly carried in aqueous solution geochemically, although under natural conditions the oxidation state is unlikely to be less than +6 (Krauskopf, 1970). Transport as the simple ion WO_4^{2-} in small amounts is possible in slightly acidic solutions. In silica-containing solutions the element may be rendered mobile as a heteropoly-acid, such as $H_8Si(W_2O_7)_6$; yet there is no relation between the distribution of tungsten and silicon in the laterites—W is somewhat concentrated, while Si is depleted. Tungsten in the profiles is associated with hydrous iron and manganese oxides, and Dekate (1967) has pointed out that the high concentration in ferruginous sandstones of India (av. 4·3 p.p.m. W) may be correlated with the ease of sorption of tungsten by iron(III) and manganese oxides. Dekate has also noted the concentration of tungsten in the B horizon of Indian soils, and Holman and Webb (1957) have reported appreciable enrichment over unmineralized rock in thick tropical soils in Uganda.

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Nuclear Science Centre, School of Chemistry
Brunel University, Uxbridge UB8 3PH

A. GHARIB
D. F. C. MORRIS

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A note on occurrences of nickeliferous and cupriferous mackinawite

TWO occurrences of mackinawite $Fe_{1-x}S$, one nickeliferous, the other cupriferous, examined by the writer so well illustrate the wide variability that may exist in the paragenesis of a single mineral as to warrant brief description.

Nickeliferous mackinawite was identified in the ores and enclosing country rocks of the Scotia nickel sulphide deposit, Western Australia (Ostwald, 1973). The mineral occurs in two associations: as irregular myrmekitic intergrowths with pentlandite of the ore, especially where the ore has undergone incipient supergene alteration; and as elongate 'stringers' and laminae (50 μm to 0·5 mm wide) in strongly deformed serpentinite layers within and adjacent to the ore body.

The mackinawite is optically spectacular, with bireflection from pale blue-grey to a dull golden-yellow. Anisotropism is very strong with well-defined colours, especially blues, and white. The bireflection is accompanied by a variation in $R\%$ (589 nm) from 22 to 45% (approx.). This range is sufficiently different from that of the optically similar mineral valleriite ($R = 14\text{-}22\%$) for optical distinction of the two minerals to be carried out. VHN determinations on the Scotia mineral (at 25 g load) yielded a range of values of 51-82, with a mean of 61 for ten determinations.

Electron probe microanalysis determinations (average of five chemically similar grains) indicated Fe 54·9%, Ni 8·8%, Co 0·4%, Cu 0·1%, S 35·8%, and calculations indicated a metal/sulphur ratio of 1·02 and a formula $(Fe_{0\cdot86}Ni_{0\cdot13}(Co+Cu)_{0\cdot01})_{\Sigma1\cdot02}S$.

Thus Scotia mackinawite is essentially FeS with part of the Fe replaced by Ni and very minor amounts of Co and Cu. In terms of its metal/sulphur ratio, the derived formula is within the range of values (0·994 1·026) determined by Springer (1968) for this mineral.

The *cupriferous mackinawite* was identified somewhat tentatively in a thin layer of black pyritic mud at a depth of some half metre beneath a water seepage situated at a conglomeratic sand (upper) and shale (lower) contact in a suburb of Newcastle, New South Wales. Attention was drawn to the layer during excavation by the presence of an iridescent coating on the layer (probably due to rapid oxidation of iron minerals in the layer). pH determinations on fresh exposures indicated 6·0 and the occurrence suggested that the mineral was the product of a reducing environment.

Microscopic examination of the dried mud showed the presence of abundant spheres of framboidal pyrite, detrital grains of quartz,