to fit more than two lines to the observed data. The attempts however proved unsuccessful.

It is known that iron in minerals of the type being investigated exists, in general, in the divalent and the trivalent charge states. It is also known that iron goes to two non-equivalent sites, M_1 and M_2, both of which have non-cubic site symmetry. Since in the present studies we have observed only two lines in the Mössbauer spectrum it is concluded that iron exists either in the Fe^{2+} or in the Fe^{3+} state. From the isomer shift value (1.2660 ± 0.0046 mm/sec with respect to stainless steel) it is inferred that iron is in the divalent state. In addition the difference in the quadrupole splitting values due to M_1 and M_2 sites reported by earlier workers being significantly large (≈ 0.3 mm/sec), the Mössbauer spectrometer in the present investigations would have distinguished Fe^{2+} at the two sites by recording two quadrupole doublets. The appearance of only one quadrupole doublet in the observed Mössbauer spectrum indicates the existence of Fe^{2+} only at one of the two sites. A comparison of the observed quadrupole splitting (2.2030 ± 0.0113 mm/sec) with those reported earlier (Bancroft, 1967; Evans, 1967) in the literature suggests that Fe^{2+} exists only at the M_2 sites. A slight asymmetry in the intensity of the two lines and the large line widths observed may be due to the presence of an extremely small amount of iron at the M_1 site.

As the Fe^{2+} is largely present in the M_2 site it is inferred that ordering was nearly complete due to slow crystallization during metamorphism.

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Distribution of lanthanum, europium, germanium, tin, phosphorus, and sulphur in nickeliferous lateritic profiles

GEOCHEMICAL distribution of several elements through three lateritic profiles on serpentinized peridotite has been ascertained by Ahmad and Morris (1978) and Gharib and Morris (1978). The deposits are in Guatemala, New Caledonia, and Indonesia; they are worked for Ni and could prove to be important sources of other elements, e.g. noble metals, Co, and Cr. In each case there is marked depletion of Si and Mg and sedentary concentration of iron (III) oxides and hydroxides. This is a typical result of the extensive weathering of ultrabasic rock under the tropical conditions where drainage is good (Krauskopf, 1967).

The present paper deals with the geochemistry of La, Eu, Ge, Sn, P, and S in the profiles. A description of most of the samples reported on here is given in the earlier article, Ahmad and Morris (1978).

Analytical methods

Lanthanum and europium. Instrumental neutron activation analysis (INAA) was used for the determination of these two elements. The 1.596 MeV gamma ray of ^{140}La and the 0.963 MeV γ-ray of $^{152}Eu^{m_1}$ were measured with a Ge(Li) semiconductor spectrometer. A comparison standard similar in composition to that described by Ahmad and Morris (1977), but doped with known additions of Specpure La(III) and Eu(III), was prepared. Samples of powdered laterite (0.4 g) were irradiated in the nuclear reactor HERALD together with similar weights of control. An irradiation was usually of 2 hours' duration in a thermal flux of 1.6×10^{12} neutrons $cm^{-2}\ s^{-1}$.

Counting was conveniently commenced about 24 hours after the end of irradiation. Repeat measurements were made over a period of 3 days to establish half-lives and confirm identification.

Germanium and tin. These two elements were determined by radiochemical neutron activation analysis (RNAA). Germanium was also estimated by the well-known spectrophotometric method of Schneider and Sandell (1954)—see Sandell (1959). Details are given elsewhere (Gharib and Morris, 1980).

Phosphorus. This element was determined both by RNAA and by spectrophotometry. The former method (Brunfelt and Steinnes, 1968; Henderson, 1967) provided higher sensitivity and appeared to be more appropriate for the analysis of samples containing low levels of phosphorus. It is based on the nuclear reaction $^{31}P(n,\gamma)^{32}P$ and β^--counting of ^{32}P (half-life 14.28d). Corrections for interference from the nuclear reactions (i) $^{32}S(n,p)^{32}P$ and (ii) $^{35}Cl(n,\alpha)^{32}P$ which occur with the fast component ($\approx 1\%$) of the neutron flux were made where necessary. The colorimetric procedure utilized the molybdovanadophosphoric acid complex (Marczenko, 1976; Jeffery, 1970; Maxwell, 1968); this was extracted into methyl *iso*-butyl ketone at pH ≈ 0.3 (Heslop and Ramsay, 1969). Absorbance measurements were made at 440 nm.

Neutron-activation analysis of phosphorus in the international standard basalt ('diabase') W-1 showed 552 ± 7 ppm; this corresponds to 0.126% P_2O_5, which may be compared with the figure 0.14% recommended by Flanagan (1973).

Sulphur. Estimations of (a) total sulphur and (b) acid-soluble 'sulphate' sulphur (Maxwell, 1968) were made by the barium sulphate-turbidimetric method described by Patterson and Pappenhagen (Boltz and Howell, 1978). Total sulphur found in W-1 was 118 ± 7 ppm; this may be compared with the value 123 ppm S, recommended by Flanagan (1973). Despite the consistency, it must be appreciated that there are well-known uncertainties in the turbidimetric method for quantitative estimation of sulphur.

Results

Analytical results are summarized in Table I. The series of samples L21–L26 are from a section at a lateral distance of 60 m from that which contained specimens L1–L7.

Discussion

Lanthanum and europium. The figures in Table I show that both La and Eu are enriched in each of the profiles. However, there is a notable difference in the distribution of these elements in the Guatemalan and New Caledonian deposits. In the former bodies La and Eu are most concentrated in A and B horizons, whereas in the profile BNC the major concentration of the two elements occurs at a greater depth. These observations confirm the conclusion revealed earlier that the New Caledonian profile has resulted from more extensive weathering than the Guatemalan one (Ahmad and Morris, 1978). On the basis of simple hydrolytic precipitation one would expect lanthanum (III) and europium (III) to be congregated towards the base of the region rich in iron (III) oxides and hydroxides,* and this is the case with the profile BNC. From considering the Pauling crystal radii of La^{3+} (r = 0.115 nm), Eu^{3+} (0.103), and Fe^{3+} 0.064), one would not expect extensive coprecipitation of the lanthanoid elements with iron (III) by isomorphous replacement. The correlation coefficients (ρ) for the BNC results for La–Fe (0.20) and for Eu–Fe (0.73) bear this out. On the other hand, there is a much greater mutual relationship between the distribution of the two lanthanoids and iron in the Guatemalan sections (ρ: L1–L7, La–Fe 0.88, Eu–Fe 0.80; L21–L26, La–Fe 0.81, Eu–Fe 0.91). In this deposit there is high correlation between the distribution of the two rare earth elements and phosphorus [ρ: L1–L7, La–P 0.94, Eu–P 0.85; L21–L26, La–P 0.85, Eu–P 0.98] and this is also noted in the BIP samples [La–P 0.79, Eu–P 0.99] but not with the BNC profile [La–P 0.40, Eu–P 0.14]. Rare earth phosphates are very insoluble compounds and it follows that lanthanum (III) and europium (III) may be concentrated at the upper levels of the Guatemalan deposit as phosphate. Oxalate is another precipitant for the lanthanoid group and the possibility arises that certain organic acids derived from decayed vegetation could also lead to the holding of La^{3+} and Eu^{3+} in A and B horizons. The similarity of distribution of lanthanum and europium in the different profiles indicates that formation of the lower oxidation state europium (II) is of little significance.

Germanium and tin. In peridotite the average concentration of Ge appears to be ≈ 0.9 ppm (Onishi, 1956; Burkov and Podporina, 1965; Hörmann, 1970; Flanagan, 1973). An average for Sn of about 0.5 ppm may be derived from the results of other workers (Onishi and Sandell, 1957; Turekian and Wedepohl, 1961; Brooks *et al.*, 1960; Hamaguchi *et al.*, 1964). It follows that there is some concentration of both germanium and tin in the lateritic profiles, and there appears to be little sign of mobility of the two elements resulting from the weathering process. This is not unexpected in the case of Sn, because it is well known that detrital cassiterite is highly resistant to weathering. On the other hand, it has been suggested that as germanium dioxide is more soluble in water (0.447 g per 100 cm^3 at 25 °C) than silica, germanium should be leached preferentially from rocks during weathering (Burton *et al.*, 1959). Our results and those of Zeissink (1971) do not support this hypothesis.

Phosphorus. The average amount of phosphorus in peridotite has been quoted as 0.05% P_2O_5 (Koritnig, 1978), but there does not appear to be

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* Precipitation pH values for hydrous oxides and hydroxides: La^{3+} 8.2; Eu^{3+} 7; Fe^{3+} 2.

TABLE I. *Trace elements in nickeliferous lateritic profiles as a function of depth (figures in ppm)*

Profile	Sample No.	Depth (m)	Description	La INAA	Eu INAA	Ge		Sn RNAA	P		S	
						RNAA	col.		RNAA	col.	tot.	(sol.)
Guatemala Lake Izabel region	L1	1.5–2	Surficial laterite	44	0.73	1.2	1.1	1.1	128	†	83	(14)
	L2	2.5–3	Plastic laterite	49	1.0	2.1	2.5	1.7	86	83	25	(21)
	L3	3.5–4	Saprolite	24	0.19	3.2	3.4	0.9	63	70	20	(*)
	L4	5.25–5.75	Boulders in saprolite zone	0.9	0.02	1.9	2.0	1.7	10	11	< 10	(*)
	L5	8–8.5	Weathered rock	0.03	*	2.1	2.3	1.1	4	5	*	(*)
	L6	8–8.5	Fines of weathered rock	*	*	1.4	1.6	1.5	20	22	*	(*)
	L7	10.25–10.75	Rock	*	*	0.7	0.7	1.5	4	6	*	(*)
	L21	0.75–2.00	Surficial laterite	36	2.3				154	141	52	(*)
	L22	2.00–2.75	Saprolite	51	1.5				101	94	24	(*)
	L23	3.5–4.5	Boulders in saprolite zone	8.1	0.21				4	6	53	(*)
	L24	4.75–5.75	Fines in weathered rock	1.1	0.05				27	28	54	(*)
	L25	4.75–5.75	Weathered rock	0.01	*				5	6	25	(*)
	L26	7.75–9.00	Rock	*	*				3	4	*	(*)
New Caledonia Lat. 22° 17′ S Long. 166° 58′ E	BNC1	0–2	Ferricrete	0.2	0.09	4.8	5.4	2.5	52	50	348	(140)
	BNC2	2–7	Limonite	0.05	0.19	4.5	5.3	1.4	39	36	316	(148)
	BNC3	7–11	Limonite	1.8	0.29	3.0	3.3	1.4	36	31	293	(29)
	BNC4	11–13	Limonite	1.6	0.24	3.0	3.3	1.4	40	34	249	(18)
	BNC5	13–14	Limonite and asbolite	22	0.39	4.5	4.4	2.3	23	16	166	(< 10)
	BNC6	14–17	Limonite and asbolite	15	0.22	3.1	2.0	1.7	16	14	51	(*)
	BNC7	17–20	Saprolite	0.8	0.02	1.4	1.3	2.1	3	5	< 10	(*)
Sulawesi Indonesia	BIP1	11–13	Limonite and asbolite	18	0.90	1.5	1.1	1.7	26	26	229	(14)
Lat. 4° 10′ S	BIP2	13–17	Saprolite	18	0.40	1.6	1.7	1.3	12	15	98	(< 10)
Long. 121° 37′ E	BIP3	18–19	Saprolite and quartz box work	3.5	0.01	1.2	1.6	1.2	5	8	38	(*)

All figures are the average of at least two determinations.

An asterisk indicates that the element is present in amounts less than the sensitivity (La, Eu < 0.01, S < 10 ppm).

col. = colorimetric analysis. tot. = total. (sol.) = soluble.

† Incomplete dissolution of sample attained.

much information concerning the concentration in serpentinite. Results shown in Table I indicate a decrease of phosphorus content with depth in the lateritic profiles. This effect can be explained on the basis of adsorption by the soils. In each profile there is an inverse relationship between phosphorus content and the leaching pH of the samples (fig. 1). This may correspond to anion exchange of phosphate ions in solution with minerals containing hydroxide groups. Rather similar behaviour has also been noted by Scheffer and Schachtschabel (1970) for adsorption of phosphate on Nipe clay (predominantly kaolinite) and Sharky clay (predominantly montmorillonite).

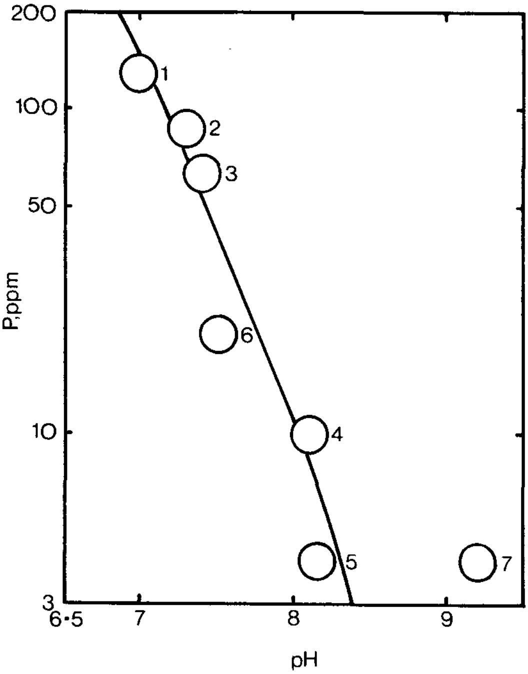

FIG. 1. Relation between phosphorus content and reaction pH of the weathering profile L1-L7.

The possibility that the higher phosphorus values in the top zones of the profiles may be related to the organic matter component should be considered. Yet it has been shown that phosphorus (V) is held in solution as phosphate by humus-bearing waters and is widely transported by such solutions (Swain, 1963). Some phosphorus may be held in A and B horizons as lanthanoid phosphate—*vide supra*.

Sulphur. Widely variable levels of this element have been found in serpentinite. For example, Turekian and Wedepohl (1961) report 9500–14000 ppm S in serpentinized ultramafic rocks from the Nickel Belt, Manitoba, Canada, and Zeissink (1971) finds 234 and 92 ppm respectively in the fresh serpentinite at the base of two nickeliferous lateritic profiles in Australia. Our studies of the slightly weathered peridotite-serpentine L7 and L26 indicate < 10 ppm S, and there is enrichment of sulphur in the higher levels of the profiles. It is regrettable that our measurements of total sulphur and acid-soluble 'sulphate' sulphur do not enable us to elucidate the chemical nature of its existence in the laterites.

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Artificial colouration of fluorite by electron bombardment

THE artificial colouration of fluorite by irradiation or electron bombardment has long been known (Blount and Sequira, 1919; Gobel, 1930; Przibram, 1954; Feltham and Ghosh, 1968; MacKenzie and Green, 1971; and Galwey *et al.*, 1979). This colouration has had something of a curiosity interest and has been discussed in connection with the natural purple colour of Blue John. However, if a simple inexpensive method can be found to turn fluorite a distinctive colour, then this can be used as a staining technique. With this in mind, uncapped, polished thin sections mounted in epoxy resin were irradiated in a diffractometer. The specimens were positioned normal to the X-ray beam; Cu-$K\alpha$ radiation was used with no divergence slit. After 1 hour at 40 kV and 20 mA a pale blue colouration developed. Several hours of treatment intensified the colour but, unfortunately, the whole irradiated area blackened. The diffractometer was used because of its wide availability, but the method is of limited use because insufficient intensity of colour is produced and this fades completely within a few hours.

A second method was tried involving a cathodo-luminescence chamber. The sections used in the diffractometer experiment were repolished and placed in the electron beam produced from a cold aluminium cathode to which 30 kV was supplied with a beam current of 800 μA. After 1 hour an intense, purple surface colouration developed with no blackening of the fluorite. Thin sections of colourless, blue, green, yellow, and purple transparent fluorite crystals all produced the same purple colouration after 1 hour's treatment. The intensity of colour developed on the specimens over an identical exposure time was different. The over-all colour differed, not only between specimens but also within individual crystals, some of which showed delicate colour zoning (fig. 1). One feature of the purple colour is that it is polarized. Thin sections rotated in plane polarized light show a distinctive change in colour from mauve to blue. The colour fades over a period of weeks. Detailed microscopy is best undertaken using a conventional petrological microscope, in preference to the microscope which bears the cathodo-luminescence chamber, since the latter is restricted to low-power objectives with long working distances.

The electron beam in the cathodo-luminescence chamber which produces the semi-permanent purple colour in fluorite also excites the fluorite to emit a strong blue luminescent light. This luminescent light fades over a few hours' exposure, which is either due to masking of the luminescence as the surface purple colouration develops, or because the activator(s) in the fluorite which causes the luminescence is slowly quenched by the electron beam. A comparison between the features shown by the semi-permanent purple colouration and those displayed in luminescent light reveals only one difference; the luminescent light is not strongly polarized.

The utility of this technique as a means of identifying fluorite depends on its specificity. In a recent review, Nickel (1978) records the luminescence properties of over fifty minerals, including the blue luminescence of fluorite (Mariano and Ring, 1975) but no mention of semi-permanent colouration is made. Przibram (1954) records yellow and blue semi-permanent colouration of halite when subjected to X-radiation. The author also investigated halite which behaves in a similar manner to fluorite