GEOCHEMICAL VARIATIONS IN SOLIMÕES FORMATION SEDIMENTS (ACRE BASIN, WESTERN AMAZONIA).

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SUMMARY

Major mineral, major element and minor element compositions are documented for a suite of drill core sediment samples representing a ~350m profile through the Solimões Formation sediments (Western Amazonia). Major element compositions are quantified using a chemical index of alteration (CIA) in order to assess the degree of weathering. Significant variations in CIA values throughout the profile, as well as abrupt changes between overlying sections, suggest that during the generation and deposition of these sediments there were rapid changes in the ambient tectonic setting.

INTRODUCTION

Documented here is the first detailed geochemical study of sediments from the Acre Basin. These sediments are considered to belong to the Solimões Formation (Schobbenhaus **et al**., 1984; Rego, 1930) and were obtained during a drilling program in Western Amazônia carried out by the Departamento Nacional de Produção Mineral (DNPM) in the early 1970's. According to Schobbenhaus **et al**., the Solimões Formation sediments cover extensive areas of Acre and Amazonas States. The strata are typically made up of clay, silt and fine sand. Calcareous concretions and gypsum veins are common, as are lenses of carbonaceous material. Recent work by Campbell **et al**. (1985) indicates that the Solimões Formation and overlying sediments also extend over much of the Western Amazon foreland basin lying within the borders of Peru and Bolivia. The ages of entrained biological material (Frailey, 1986; Kronberg **et al**., 1988) are consistent with the deposition of the upper sediments within the past 45,000 a.

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The intention of this study was to obtain geochemical information on a sediment profile through Solimões Formation sediments and to compare these data with those from a similar study of near surface (upper 10 m) sediments collected along the Upper Purus River in the vicinity of Boca do Acre (Benchimol **et al.**, 1987; Kronberg **et al.**, 1989).

EXPERIMENTAL

Sample Description

The drill core (1AS-9-AM) selected for sampling is one of a series of cores taken during a drilling program carried out by DNPM in the early 1970's, to determine coal (lignite) reserves in the Acre Basin. The drill core samples are from the southernmost drilling location (Rio Itaquai, Figure 1). Also included in this study are 2 rocks collected during field work along the upper Purus River (1984, 1985), which may represent basement rocks from the Iquitos Arch. The drill core samples analysed in this study represent a ~350m sediment profile (Figure 2) logged into 23 sections. Except for the top 3m, the sediments are considered to belong to the Solimões Formation. The drill core represents a sequence of interbedded sand, silt, clay, calcareous clay and layers of carbonaceous material (lignite) typical of the Solimões Formation.

Sample Analysis

The major mineral and major element composition of each sample were determined using x-ray diffraction and x-ray fluorescence respectively (Tables 1, 2a). The concentrations of some minor elements (Cr, Rb, Sr, Y, Zr, Nb, Ba) were also measured by x-ray fluorescence (Table 2b). In addition 4 samples (2, 17, 19, 20; Table 2c), selected to represent the range of chemical variation, were analysed by inductively coupled plasma mass spectrometry (Riddle **et al.**, 1988) to obtain rare earth element (REE) concentrations.

Mineralogy

The major minerals present (Table 1) are quartz and kaolinite with minor to trace amounts of mica, complex clays, feldspars, calcite and gypsum. In the carbonaceous samples (6, 9A, 11, 14, 16), unidentified peaks were attributed to crystalline organic phases. The rock samples were described using conventional petrographical techniques. Both samples (R2P84, R2P85) contain ~50% hornblende, ~45% plagioclase, ~5% pyroxene, and small amounts of chlorite and trace minerals. Plagioclase (An 48-andesine) forms laths 0.1 to 0.5 mm long which display "Albite-Karlsbad" twinning and interlocking borders. Hornblende (xenoblastic to subidioblastic) forms the matrix around the plagioclase laths, and individual grains (up to 0.5 mm) are pleochroic (Z = yellowish green, Y = brownnish green, X = brownish yellow). Unidentified opaque minerals, titanite, and zircon are commonly found as inclusions in hornblende. Clinopyroxene (xenoblastic; irregulary shaped) is present mostly in the cores of hornblende crystals as greenish crystal grains (0.1-0.2 mm long) and is tentatively identified as augite. Chlorite is observed along cleavage planes and fractures. Other minerals include interstitial quartz (with undulatory extinction), zoisite and apatite. In R2P84 there are thin microshear zones (0.06-0.1 mm thick) along which sercite has developed. The difference between these rocks is that in R2P84, igneous textures are preserved, while in R2P85, the original textures have been obliterated by deformation processes. Both rocks are considered to be of igneous (subophitic/ophitic textures) origin and have undergone amphibolitic facies metamorphism. The chemical compostion (e.g., low potassium contents, Table 2a) and REE signatures (Table 2c, Figure 3) would suggest that the original rocks were oceanic basalts.

Major Element Compositions

In the non-carbonaceous samples, the major element contents (Table 2a) show substantial variation (Na_2O, 0.1-0.8%; MgO, 0.1-2%; Al_2O_3, 9-23%; SiO_2, 50-77%; P_2O_5, 0.05-1%; K_2O, 0.5-3%; CaO, 0.1-5%; TiO_2, 0.6-1%; Fe_2O_3, 2-15%; MnO, 0.01-0.4%. These variations were quantified using a "chemical index of alteration", CIA, which is an assessment of the extent to which these materials have been weathered (Nesbitt & Young, 1982). The CIA is based on a feldspar weathering model (Kronberg & Nesbitt, 1981) and is calculated using the following ratio of oxide concentrations expressed in moles:

$$CIA = \frac{Al_2O_3}{Al_2O_3 + CaO^* + Na_2O + K_2O} \times 100\%,$$

where CaO^* represents calcium associated with silicate phases only. CIA values range from ~50 for average upper crust, to ~100 for the most highly weathered continental materials (e.g., Kaolin, bauxites). The assumption is that feldspar-derived components in sediments with similar geological histories would have similar CIA values.

The variation in CIA for the drill core sediments is shown in Figure 2. For comparison, the line at CIA = 81 represents the value for modern suspended sediments (Kronberg **et al**., 1986) discharged by the major Andean tributaries (e.g., Maranon River). Also included for reference are the range of CIA values (81-89, "hatched area") representing the range of CIA values found in near surface (upper 10m) sediments collected along the Upper Purus River (Amazonas State) in a concomitant study (Kronberg **et al**., 1989).

Minor and Trace Elements

In general, minor and trace element concentrations (Table 2 b,c) are within a factor of 2 of their crustal abundances (Cr, 122; Rb, 78; Sr, 384; Y, 31; Zr, 162; Nb, 20; Ba, 390; La, 34; Ce, 66; Pr, 9; Nd, 40; Sm, 7; Eu, 2; Gd, 6; Tb, 1; Er, 3.5; Tm, 0.5; Yb, 3.1). The exceptions are some relatively high concentration levels of Ba, attributed to Ba concentration in calcite and gypsum. Depleted rare earth element levels relative to chondrite values (Wakita **et al**., 1971; Figure 3) were found in the samples of basement rock. REE concentrations for sediment samples were normalized to North American Shale Composite, NASC (Haskin **et al**., 1968; Figure 3). Also included for comparison are NASC normalized values of REE concentrations in average deep-sea fan sediments (Nesbitt **et al**., 1988).

DISCUSSION

The most significant feature of the drill core samples investigated here is the variation in their mineral and chemical compositions. The variations in the mineral and chemical composition of alumino-silicate phases (Tables 1, 2a) are reflected in the range of CIA values (72-93) for the drill core samples analysed in this study (Figure 2). There appears to be no correlation between CIA values and sediment grain size.

Furthermore, the range in CIA values is significantly greater than found (CIA, 78-86; average CIA = 82) in a similar study of Upper Pleistocene Amazon deep-sea fan sediments (Kronberg **et al.**, 1986). In the latter study, the CIA values were shown to be very similar to those of suspended sediments derived from the modern mountainous basin (CIA= 81) and to the suspended muds discharged at the mouth of the modern Amazon River (CIA= 83). Other work (Gibbs, 1967; Meade **et al.**, 1985) has also shown that over 80% of Amazon River suspended sediments discharged to the Atlantic Ocean are derived from the mountainous basins. Thus, it is considered that the chemistry of the Amazon River suspended sediments is controlled mainly by intense chemical weathering in the mountainous source regions and that these processes have been operating since at least the Upper Pleistocene. This argument suggests that some samples in our study (Figure 2) with CIA values in the range of ~78-86 may represent sediments generated in Andean regions.

The variations in CIA values for the drill core samples are also significantly greater than for those of the near surface sediments from the Upper River (Kronberg **et al.**, 1988). The CIA values for the latter samples fall mainly in the range found for Andean derived sediments. Age determinations of biological materials entrained in these sediments indicates deposition during the late Pleistocene and early Holocene (11,000 - 45,000 a BP). These sediments presently are included in the Solimões Formation but a study (Souza Filho & Frailey, in preparation) suggests that they are a separate unit the identity of which is yet uncertain.

The general trend of the CIA values of the drill core samples is to oscillate between values corresponding to materials less chemically weathered than the Upper Pleistocene and modern Andean derived sediments, and values which correspond to extremely weathered materials. Materials characterized as extremely weathered (CIA > 90) are common in deeply weathered shield terrains of Amazonia (Kronberg **et al.**, 1979). Also the lowland tributaries (e.g., Xingu River) draining intensely leached shield terrains carry sediments dominated by kaolinite and gibbsite, and these sediments have very high CIA values (e.g., CIA = 99 for the Xingu River).

Oscillations in degree of weathering as seen in the Solimões Formation are interpreted as an indication of tectonic control of deposition in the Acre Subbasin. Resumption of tectonic activity would have flooded the subbasin with sediments and covered them before they were extensively weathered. During periods of tectonic quiescence, sediment weathering would have been extreme. This model of intermittent tectonism supports conclusions reached by Frailey **et al.** (1988) concerning the depositional environment for sediments exposed near Rio Branco (Acre State, Western Amazônia).

Geological considerations would indicate 2 major sediment sources. From the west, sediments would be generated by the Andean uplift, and there would also be contributions from shield terrains which form the northern, eastern and southern boundaries of the Acre Basin (Miura, 1972). The most proximal source for shield derived sediments in the drill core samples studied here would be the Iquitos Arch (Miura, 1972; RADAMBRASIL, 1978), which is considered to represent uplifted basement rocks and appears to link the Brasilian and Guyana shields. Basement rocks exposed near Boca do Acre may be one of the few surface expressions of the Iquitos Arch. Two amphibolitic rocks collected during field work (1984, 1985) along the Upper Purus River near Boca do Acre are included in this study as possible representatives of Iquitos Arch (?) basement rocks. The fact that these rocks have undergone virtually no weathering leads to the suggestion that sediment contributions from shield terrains may have included relatively fresh materials from more proximal sources such as the Iquitos Arch as well as more intensely chemically weathered sediments from more distal shield sources. In this context samples 7 and 19 (low CIA values) could represent sediments derived mainly from proximal basement rocks, while samples 2 and 20 (high CIA values) could represent sediments from intensely chemically weathered shield terrains. This suggestion is corroborated by the mineral compositions of samples 7 and 19, which contain significant amounts of feldspar and complex clay minerals. In samples 2 and 20, quartz and kaolin minerals are dominant.

This idea is further explored using a triangular weathering diagram (Figure 4) to compare the compositions of the sediments and rocks studied here with those of weathered shield rocks (Kronberg **et al**., 1979), modern Amazon River (Martin & Meybeck, 1979) and Upper Pleistocene Amazon deep-sea fan sediments (Kronberg **et al**., 1986), and average crust (Fairbridge, 1972). Also plotted are key minerals: feldspars, which dominate the upper crust; chlorite, a common alteration product of mafic rocks; and kaolin and gibbsite, the products of intense and extreme weathering respectively (Kronberg & Nesbitt, 1981). The range of chemical and mineral compositions of the drill core sediment samples appears to be more diverse than that indicated by using CIA values only. For example, sample 20, with CIA value 93, plots much closer to the "kaolin-gibbsite" apex than does sample 2, with a similar CIA value (90). However, sample 2 contains complex clay minerals, while in sample 20 only quartz and kaolinite were detected (Table 1). Also, sample 2 has higher Mg and Fe contents (Table 2a) than does sample 20. Similar arguments can be applied to samples 7 and 19, both with lower CIA values, but slightly different chemical compositions. Thus geochemical data may provide key information in distinguishing sources for these sediments, as well as in assessing the degree of mixing of materials from different source regions.

The REE signatures (Figure 3) of selected sediment samples are compared with those of Amazon deep-sea fan sediment. Relative to NASC, the signatures are generally similar to those of deep-sea fan sediments, which display positive Eu anomalies and are depleted in heavy rare earths (HRE) (Nesbitt **et al**., 1989). Exceptions are sample, which is slightly depleted in light rare earths (LRE), and sample 19, which is enriched in HRE relative to NASC. None of the samples from this study shows a positive Eu anomaly. These differences in signature may be attributed to differences in source regions. The amphibolitic rocks have signatures typical of tholeitic basalts and this is in accordance with the petrographical and chemical information.

The only chronological information for the drill core sediment samples is an age of 13,390 a BP for a calcareous shell fragment entrained in sample 9 (~130m below surface). This would indicate that these sediments were being deposited within the same time frame as those documented by Frailey **et al.**, 1988 and Kronberg **et al.**, 1989). The abrupt changes in mineral and chemical compositions between overlying sections suggests a chaotic depositional environment. That this environment was probably under tectonic control is reflected in the varying degrees of weathering seen at different levels.

CONCLUSIONS

The most striking feature of the Solimões Formation and overlying sediments in the profile studied here is the range in chemical and mineral composition and the abrupt changes in degree of weathering between overlying sections. This is considered evidence for a chaotic depositional environment, influenced by repeated pulses of tectonic activity. Geochemical information has been shown to be useful in quantifying variations in composition. Integration of geochemical, sedimentological and geochronological studies could contribute substantially to our understanding of the biogeological history of Western Amazônia.

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RESUMO

Os principais minerais, composições dos principais elementos e elementos secundários estão documentados para uma série de amostras de testemunhos sedimentários representando um perfil de 350 m através dos sedimentos de Formação Solimões (Amazônia Ocidental). As composições dos principais elementos estão quantificadas usando o índice químico de alteração (CIA) de modo a assegurar o grau de intemperismo. Variações signifi

cantes nos valores do CIA através do perfil, como também as mudanças abruptas entre seções sobrepostas sugerem que durante a geração e deposição destes sedimentos houve mudanças rápidas no cenário do ambiente tectônico.

Fig. 1. Sketch map showing drill core location.

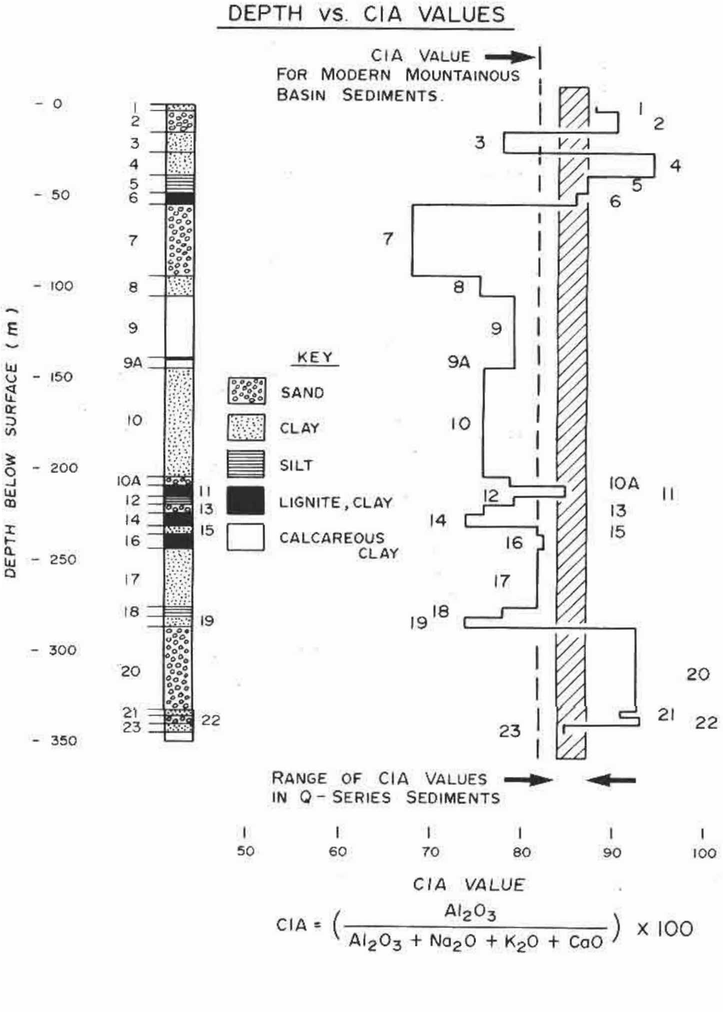

Fig. 2. Summary of Values of Chemical Index of Alteration (CIA, see text) with Drill Core Depth. Numbers to the left of core legend correspond to sample numbers as do the numbers beside the line showing variations in CIA. Low CIA values (<80) may correspond to a depositional environment under the influence of tectonic activity and higher ones (>80) to a tectonically quiescent depositional environment (see text).

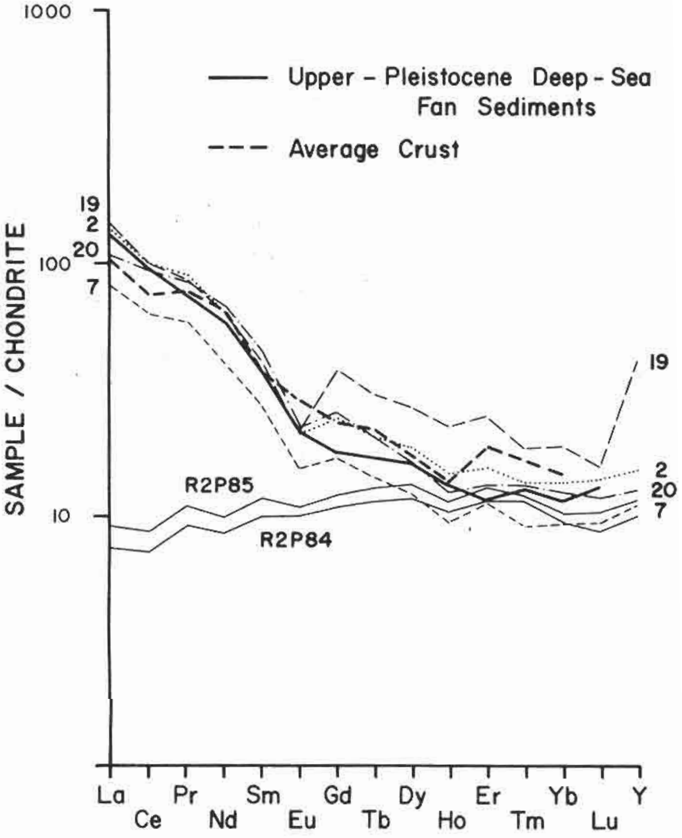

Fig. 3. Rare earth element patterns. Concentrations of rock samples (R2 P84, R2 P85) are normalized to corresponding chondrite values and those of sediment samples (2, 7, 19, 20) are normalized to corresponding North American Shale Composite (NASC) concentrations.

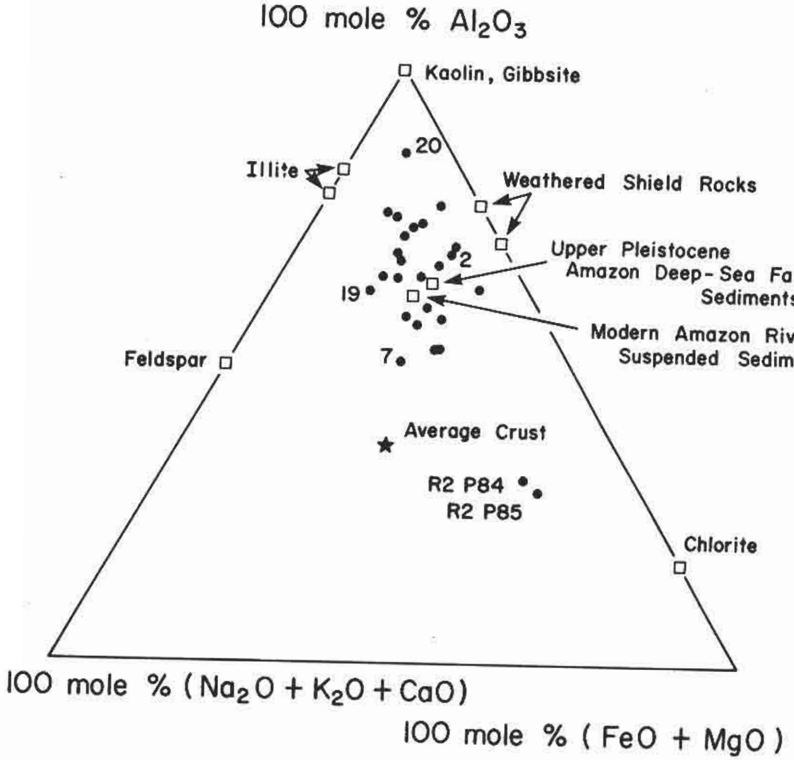

Fig. 4. Whethering diagram showing range of mineral and chemical compositions. Four sediment samples (2, 7, 19, 20) are discussed in text.

Table 1. FRANCO Series.

			MINERALOGY				
Numbers	**Quartz**	**Feldspar**	**Kaolinite**	**Mica**	**Complex Clays**	**Calcite**	**Gypsum**
1	M		M	t	t		
2	M		M		t	m	t
3	M	t	m		t	m	t
4	M	t	M		t		m
5	M		M		m		
*6	M	t	M				
7	M	m	m		m	M	
8	M	m	M		m	m	
9	M	t	m		t	m	t
*9A	M	t	m				m
10	M	t	M	t	t		
10A	M	t	M	m	m		
*11	M	t	M	t			t
12	M	t	M	m	t		
13	M		m	m			
*14	m	t		t			t
15	M	t	M	m	t		
*16	M	t	M		t		t
17	M		M	m			
18	M	t	M	m	t		t
19	M	m	m	m	m		
20	M		M				
21	M		M	m			
22	M		M	t			
23	M		M	m	m		

M = Major; m = Minor; t = Trace.

(*) In samples with high carbon contents, some peaks could not be identified, but were tentitatively attributed to crystalline organic phases.

Table 2. FRANCO Series

a) MAJOR ELEMENT OXIDE CONCENTRATIONS (WEIGHT %)

Sample	**Na_2O**	**M_gO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**Fe_2O_3**	**MnO**	**LOI**
1	0.11	0.59	13.2	70.2	0.10	1.34	0,28	0.92	4.23	0.22	8.2
2	0.10	0.95	18.7	50.2	0.11	1.60	2.71	0.77	11.4	0.38	13.7
3	0.41	1.83	13.8	56.4	0.98	2.26	4.89	0.75	5.81	0.25	11.5
4	0.30	0.70	19.3	64.5	0.05	1.20	0.79	0.99	2.34	0.02	9.8
5	0.42	1.20	20.6	58.1	0.06	1.65	0.78	0.87	3.53	0.02	12.8
6	0.32	1.38	17.6	40.4	0.08	1.57	0.66	0.73	6.55	0.03	30.5
7	0.83	1.39	10.6	65.9	0.27	2.05	4.34	0.67	4.29	0.07	8.6
8	0.82	1.41	13.0	67.2	0.17	1.80	2.07	0.60	4.17	0.06	8.6
9	0.74	1.92	15.7	58.2	0.19	2.36	2.82	0.83	5.32	0.10	11.2
9A	0.50	1.41	14.3	46.6	0.10	1.69	2.54	0.69	6.94	0.05	25.2
10	0.70	0.79	13.9	69.6	0.11	2.00	0.47	0.86	3.97	0.05	7.5
10A	0.61	1.05	18.6	63.3	0.10	2.61	0.37	1.19	3.88	0.03	8.1
11	0.45	0.91	17.6	56.9	0.06	1.56	0.50	0.87	3.55	0.01	17.6
12	0.74	0.98	16.9	62.6	0.05	2.18	0.67	0.94	6.10	0.09	8.8
13	0.36	0.72	8.7	70.5	0.09	1.47	0.56	0.59	9.06	0.12	7.8
14	0.35	0.29	4.4	9.0	0.04	0.34	1.51	0.27	5.04	0.02	79.1
15	0.55	1.08	19.3	60.4	0.10	2.37	0.43	0.99	5.06	0.05	9.5
16	0.50	0.78	18.0	40.0	0.05	1.94	0.47	0.65	7.65	0.01	29.5
17	0.39	0.93	19.6	57.9	0.09	2.74	0.36	1.03	7.07	0.04	9.4
18	0.64	0.89	14.6	63.5	0.30	1.91	0.90	0.87	6.72	0.07	8.6
19	0.67	0.45	11.7	70.5	0.05	1.72	0.55	0.86	4.28	0.01	8.5
20	0.12	0.11	12.3	77.3	0.05	0.50	0.09	1.17	2.42	0.03	5.4
21	0.14	0.43	17.3	55.6	0.13	1.15	0.19	1.01	14.7	0.06	8.8
22	0.13	0.34	18.4	59.9	0.19	0.97	0.23	1.18	9.89	0.02	8.7
23	0.57	0.84	23.0	55.9	0.07	2.00	0.50	0.92	5.39	0.01	11.0
R2P84	1.92	7.32	13.6	51.8	0.07	0.33	11.5	0.87	10.9	0.17	1.2
R2P85	2.07	8.63	13.7	49.3	0.08	0.29	11.5	0.96	11.6	0.17	1.0

b) MINOR ELEMENT CONCENTRATIONS ($\mu g\ g^{-1}$)

Sample	**Cr**	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Ba**
1	60	90	50	40	430	30	540
2	80	120	100	40	150	30	520
3	60	110	190	80	220	20	530
4	99	101	152	27	262	27	547
5	90	120	190	50	200	20	630
6	80	160	160	30	110	10	470
7	50	80	120	40	330	20	360
8	59	21	161	52	199	21	495
9	77	141	190	42	181	13	555
9A	70	120	180	20	150	20	470
10	80	130	120	50	290	40	550
10A	90	170	130	50	250	30	650
11	80	130	160	30	240	30	510
12	88	116	117	44	262	31	593
13	60	80	80	30	310	40	520

continuation (**Table 2 B**)

Sample	Cr	Rb	Sr	Y	Zr	Nb	Ba
14	60	30	210	20	50	10	450
15	90	160	140	50	230	30	680
16	80	140	150	20	110	20	550
17	110	180	200	30	160	40	1110
18	110	120	320	30	240	20	4540
19	80	110	110	100	370	30	500
20	80	40	80	60	540	30	330
21	160	<10	170	<10	260	40	490
22	170	70	210	30	350	40	450
23	150	190	230	40	170	20	680
R2P84	300	20	80	10	40	20	120
R2P85	300	10	70	10	40	10	120

c) RARE EARTH ELEMENT CONCENTRATIONS (µg g^{-1})

Element	2	7	19	20	R2P84	R2P85
Y	26.0	18.9	69.5	21.6	19.7	17.3
La	43.4	26.0	46.2	35.9	2.98	2.41
Ce	85.6	54.5	86.6	81.0	7.60	6.36
Pr	10.6	6.88	10.7	10.2	1.31	1.08
Nd	38.1	25.1	39.1	40.0	6.12	5.35
Sm	7.52	5.16	7.79	8.35	2.20	1.89
Eu	1.48	1.08	1.60	1.58	0.77	0.71
Gd	6.00	4.28	9.61	6.47	3.04	2.74
Tb	0.92	0.65	1.36	0.92	0.58	0.51
Dy	5.44	3.59	7.79	4.82	3.91	3.40
Ho	1.08	0.71	1.75	0.92	0.83	0.77
Er	3.03	2.12	4.77	2.63	2.51	2.26
Tm	0.43	0.28	0.58	0.41	0.37	0.35
Yb	2.80	2.01	3.28	2.61	2.16	1.94
Lu	0.46	0.31	0.52	0.39	0.34	0.29

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