Rare earth element geochemistry and Rb-Sr geochronology of Archaean stromatolitic cherts of the Dharwar craton, south India

R SRINIVASAN, G V C PANTULU and K GOPALAN

National Geophysical Research Institute, Uppal Road, Hyderabad 500 007, India

Stromatolites associated with cherty dolomites of the Vanivilaspura Formation of the Archaean Dharwar Supergroup show a morphology indicative of the deposition of the latter in a intertidal to subtidal environment. The cherts are moderately high in their Al/Al + Fe ratios but depleted in Fe_2O_3 and also most trace elements. Unlike most other Archaean cherts, the Vanivilaspur cherts exhibit significant negative Ce anomaly, which is interpreted to have resulted from contemporary manganese deposition. The Rb/Sr ratios in the cherts show a sufficient spread to define a linear correlation line in the Rb-Sr evolution diagram corresponding to an age of 2512 ± 159 Ma and initial Sr ratio of 0.7128 ± 0.0012 (2σ). While this age is strikingly close to that of regional metamorphism in the Dharwar craton, the initial ratio is distinctly higher than that of the associated volcanics. Acid leaching experiments on the cherts suggest that they may have been isotopically equilibrated on a mm to cm scale about 500 Ma later than the time of regional metamorphism.

1. Introduction

Cherts in general show low abundances of rare earth and many trace elements (Wildeman and Haskin 1973; Shimizu and Masuda 1977). In modern oceans, a variation in the abundance of rare earth elements in cherts with a change in tectonic environment of their deposition has been reported (Murray *et al* 1990; 1992). The relation of rare earth element systematics in Archaean cherts with their depositional environment is still not adequately studied. However, it has been observed that they do not show negative cerium anomalies indicating that the Archaean sea water from which they were precipitated was reducing unlike the Phanerozoic sea water. The general rarity in Archaean sequences of manganese deposits which are effective scavengers of Ce^{+4} corroborates such a conclusion. Negative cerium anomaly in sea water is considered to be the result of microbial oxidation followed by preferential scavenging of Ce^{+4} (Moffet 1990). Stromatolites in the Archaean are known to have been built by cyanobacteria capable of photosynthesis. This implies that stromatolitic cherts could record evidence of oxygenated microenvironment of Archaean seas. Stromatolitic cherts and dolomites which show facies gradation into manganese formation in the > 2.6 Ga Dharwar sequence (Taylor *et al* 1988) present a rather uncommon Archaean sedimentary association which can help verify this concept. We report a trace and REE geochemical study of stromatolitic cherts from the Dharwar sequence.

Isotopic age dating of pre-Cenozoic cherts has not received much attention. Petrographic and mineralogical studies of cherts reveal significant amounts of different minerals such as clays, carbonates, and phosphates (Blatt *et al* 1980). Shibata and Mizutani (1982) showed that it is possible to determine the age as well as duration of diagenesis of cherts using Rb-Sr systematics. Hurley *et al* (1972) and Weis and Wasserburg (1987b) have demonstrated the usefulness of the Rb-Sr method in dating cherts from the Onverwacht Group (3.5 Ga), South Africa. Encouraged by the work of Weis and Wasserburg on dating the metamorphosed Archaean cherts, we have carried

Keywords. Archaean; stromatolite; chert; Rb-Sr geochronology; Dharwar craton.

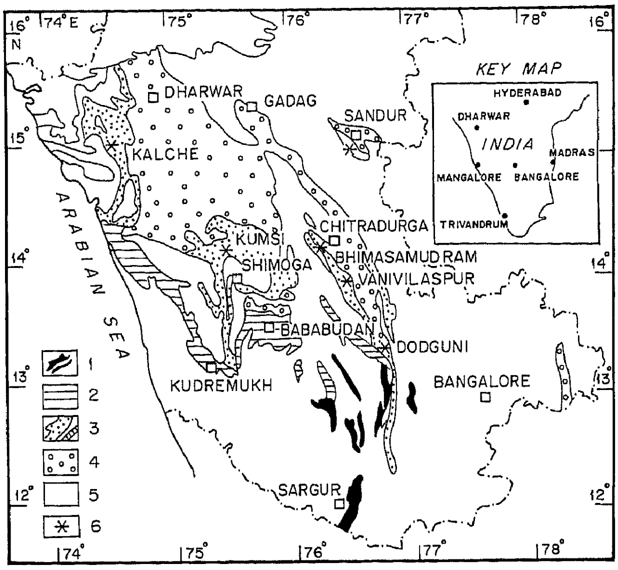

Figure 1. Generalised geological map of the Dharwar craton showing: **1**) older schist belts, **2**) Bababudan Group **3**) Vanivilas Formation of Chitradurga Group; **4**) Ingaldhal and Hiriyur Formations of Chitradurga Group; **5**) undifferentiated gneisses, granulites and granites. Asterix points to the areas where stromatolitic cherty dolomites occur. The stromatolitic cherts studied in this work are from Vanivilaspur, the type area for the Vanivilas Formation of the Chitradurga Group.

out Rb-Sr analyses of stromatolitic cherts from the Archaean Dharwar sequence with a view to date them. The stromatolites of the Dharwar sequence show a wide morphological diversity and complexity similar to many middle Proterozoic forms (Srinivasan *et al* 1989). The Rb-Sr dating of these cherts can therefore set a strict lower limit to the time of their deposition.

2. Geological setting

The Archaean Dharwar sequence of south India has been divided into the lower Bababudan and the upper Chitradurga Groups, distributed as shown in figure 1. The Chitradurga Group has been subdivided into the Vanivilas Formation, the Ingaldhal Volcanics and the Hiriyur Formation (Swami Nath and Ramakrishnan 1981). The Vanivilas Formation consists of greenschist facies metamorphosed conglomerate, arkose, quartz arenite, pelite, banded manganese formation gradational with stromatolitic chert, dolomite, limestone and banded iron formation. This association has been interpreted to reflect deposition in a shallow marine shelf environment (Srinivasan and Ojakangas 1986). The overlying Ingaldhal volcanics and the Chitradurga granite intruding them set a minimum age for the Vanivilas Formation at 2.6 Ga (cf. Taylor *et al* 1988; Bhaskara Rao *et al* 1992, Nutman *et al* 1996).

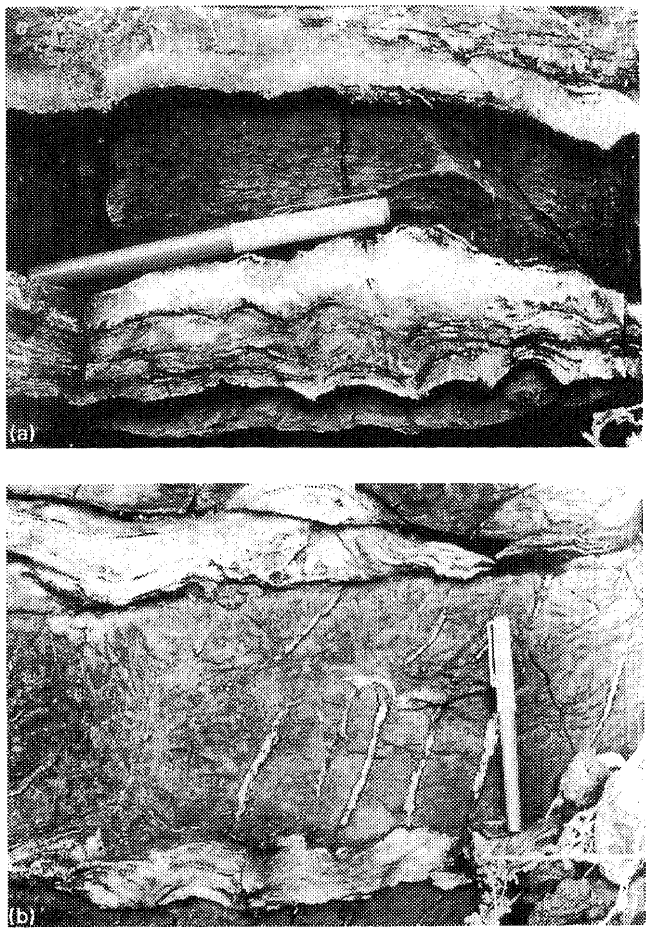

Figure 2(a and b). *Stratifera* and *Nuclella* type stromatolites in cherty dolomites of Vanivilaspur. Dark and light grey portions are dolomite and the more whitish portions are chert. Such stromatolites indicate subtidal environment of deposition. Pen for scale 15 cm long.

3. Field and petrographic relations

The cherts occur as discontinuous lenses, bands and interlayers in dolomite. Both chert and dolomite exhibit stromatolitic structures at some places. Stromatolites with the morphology of *Stratifera* and *Nuclella* (figure 2) have been observed in the type area near Vanivilaspur where samples were collected for this study (figure 1). Elsewhere in the same stratigraphic horizon columnar stromatolites have been observed. These have been interpreted to have developed in intertidal to subtidal environment (Srinivasan *et al* 1989, 1990). The chert bands are four to six centimetres thick and alternate with dolomite beds varying in thickness from four to fifty centimetres. The chert is light to dark grey in colour, finely laminated, with each layer as thin as ~ 0.5 mm. In thin sections the chert shows microcrystalline quartz which at places alternates with layers comprising fine to coarse grained megaquartz. Variation in crystallanity imparts a laminated appearance to the rock in addition to minor variations in composition.

The fine grained dark grey laminae show a higher concentration of clayey (argillaceous) and carbonaceous matter. Small amounts of dolomite occurs disseminated in the rock. These impurities may reach about 10% in the rock. Association with terrigenous sedimentary rocks as well as their dark grey to black colour show that these cherts resemble bedded cherts deposited along continental margins (Jones and Murchey 1986).

4. Analytical techniques

About 4–5 kg of each chert sample was coarsely crushed and chipped to remove the megascopically recognizable carbonate component. About 1 kg of the crushed sample was then reduced in a jaw crusher to −5 mm size chips. The sample chips were sonicated in distilled water, air dried and finely powdered in a tungsten carbide mill to −200 mesh. Homogenized powders of ~200 gm of each sample were used for chemical and isotopic analyses.

Major element analysis of a few representative samples was carried out by atomic absorption spectrophotometry. For the determination of trace and rare earth elements, samples were digested in a mixture of hydrofluoric, nitric and perchloric acids and made up to 0.1% solutions with indium added as an internal monitor. Analyses were carried out on a plasma source mass spectrometer (VG-PlasmaQuad PQ-1) as per the procedure given by Balaram *et al* (1992).

For Rb-Sr isotopic analysis 400 to 600 mg of each sample were dissolved in 1 : 3 $HNO_3 + HF$ mixture. Complete dissolution was not achieved in some cases. However, the insoluble residue was found to be carbonaceous and free of minerals containing Rb and Sr. Sample solutions were spiked with ^{87}Rb and ^{84}Sr tracers and centrifuged before ion exchange separation of Rb and Sr. Typical total process blanks were about 0.5 and 2.5 ng for Rb and Sr, respectively, which are negligible compared to the amount of total Rb and Sr handled. Three samples (MKV-7, MKV-17 and MKV) were also separately leached for 30 minutes in closed FEP vials under ultrasonication in cold 1N HCl. The insoluble residue (R) was rinsed in water, dried and weighed before $HF + HNO_3$ dissolution. The leach (L) and residue (R) were spiked with Rb-Sr spikes before ion exchange separation of their Rb and Sr. Rb and Sr fractions were loaded on single Ta filaments for isotopic analysis on a VG-354 mass spectrometer in single collector peak jumping mode.

5. Results

The major and trace including REE analyses of the stromatolitic cherts of Vanivilaspur are given in tables 1, 2 and 3 respectively. Except two carbonate rich samples (MKV and MKV7), they are rich in SiO_2(> 95%), depleted in Fe_2O_3 and moderately high in Al/Al + Fe ratio. The Si/Si + Al + Fe is close to one (figure 3). The CaO and MgO are low except in the carbonate rich samples. All are low in phosphorous. As for trace elements the Vanivilaspur cherts are low in trace elements except for cobalt. The very high cobalt is most likely due to contamination from grinding samples in a tungsten carbide mill (cf. Sreenivas *et al* 1994). Unlike many other Archaean chemogenic sedimentary rocks of the Dharwar sequence (see Naqvi *et al* 1986), the cherts are depleted in chromium (range 5 to 15 ppm) and also nickel. However, two samples have relatively high nickel (70 and 90 ppm). All samples are depleted in zirconium (0.2 to 1.6 ppm). The Rb/Sr ratio varies from 0.028 to 0.473. Six out of eleven samples have this ratio greater than 0.1 indicating significant enrichment of Rb in these cherts relative to sea water.

The Vanivilaspur cherts like most of the cherts elsewhere (Wildemen and Haskin 1973) are depleted in their REE content (ΣREE max ~ 5 ppm). In the (REE-Ce×10)-Al-Fe plot (figure 4) after Steinberg *et al* (1983), they plot close to the Al corner in the field of cherts deposited along continental margins (terrigenous environment). Chondrite normalized REE patterns show that the various REEs are enriched by a factor of 0.1 to 8 times that of Chondrite

Table 1. *Major element composition of the Archaean stromatolitic cherts of Vanivilaspur Formation in Chitradurga schist belt (in wt%).*

Sample	MKV	MKV2	MKV7	MKV17	MKV17T	MKV25T
SiO_2	81.50	99.30	81.51	96.32	99.30	96.48
Al_2O_3	1.90	0.50	1.20	1.10	0.70	2.90
CaO	6.64	0.99	6.19	1.15	0.92	1.12
MgO	1.50	0.54	2.20	1.29	0.25	0.29
Na_2O	0.05	0.05	0.06	0.05	0.07	0.02
K_2O	0.04	0.07	0.06	0.07	0.09	0.07
Fe_2O_3	0.63	0.86	0.43	0.31	0.16	0.12
P_2O_5	0.01	0.04	0.06	0.03	0.01	0.01
LOI	nd	nd	nd	nd	nd	nd
Total	92.27	102.35	91.71	100.32	101.50	101.01

Table 2. *Trace element composition of Archaean stromatolitic cherts of Vanivilaspur (in ppm).*

Sample	MKV	MKVT	MKV1	MKV2	MKV2A	MKV7	KKV13T	MKV17	MKV17T	MKV25T
Sc	0.57	0.60	0.33	0.49	0.81	0.51	1.11	0.37	0.66	0.49
V	0.49	0.52	0.41	0.48	0.95	0.37	2.46	0.64	0.36	0.42
Cr	8.98	8.66	12.72	13.14	5.87					
Co	247.96	214.38	244.73	279.47	33.57	221.51	99.20	314.40	250.95	218.73
Ni	8.57	5.87	7.39	8.20	71.30	18.73	92.58	12.50	5.12	7.65
Cu	0.41	0.45	0.27	0.27	0.51	0.31	0.74	0.42	0.25	0.46
Zn	10.69	9.36	7.76	10.63	13.62	8.17	22.12	10.13	9.29	22.35
Ga	0.32	0.41	0.51	0.54	0.45	0.20	0.06	0.34	0.62	0.32
Rb	0.50	0.32	0.90	0.72	1.15	0.54	3.08	0.14	0.64	0.65
Sr	4.13	1.20	1.90	2.66	19.31	6.60	31.15	5.00	1.59	1.87
Y	0.20	0.15	0.07	0.07	0.63	0.08	2.18	0.12	0.13	0.06
Zr	0.80	0.20	0.60	0.37	0.79	0.41	1.64	0.55	0.38	0.47
Nb	0.24	0.02	0.04	0.07	0.10	0.05	0.18	0.07	0.06	0.02
Ba	1.19	3.05	4.24	8.41	14.10					

Table 3. *Rare earth element, Hf and Te composition of Archaean stromatolitic Vanivilaspur cherts (in ppm).*

	MKV	MKVT	MKV1	MKV2	MKV2A	MKV7	MKV13T	MKV17	MKV17T	MKV25T
La	0.50	0.49	0.58	0.34	1.39	0.55	2.22	0.55	0.43	1.96
Ce	0.09	0.16	0.10	0.08	1.12	0.28	2.56	0.21	0.08	0.12
Pr	0.02	0.04	0.04	0.04	0.11	0.02	0.27	0.02	0.02	0.02
Nd	0.14	0.28	0.28	0.07	0.56	0.42	1.12	0.14	0.07	0.14
Sm	0.08	0.19	0.15	0.11	0.19	0.15	0.23	0.11	0.19	0.08
Eu	0.03	0.02	0.01	0.02	0.02	0.03	0.09	0.07	0.01	0.01
Gd	0.17	0.03	0.20	0.13	0.17	0.10	0.33	0.10	0.10	0.03
Yb	0.21	0.10	0.15	0.05	0.26	0.10	0.36	0.15	0.04	0.15
Lu	0.01	0.01	0.02	0.04	0.01	0.01	0.03	0.01	0.02	0.01
Hf	0.04	0.10	0.05	0.05	0.05	0.15	0.20	0.10	0.04	0.10
Ta	0.09	0.04	0.06	0.06	0.17	0.07	0.31	0.07	0.05	0.06

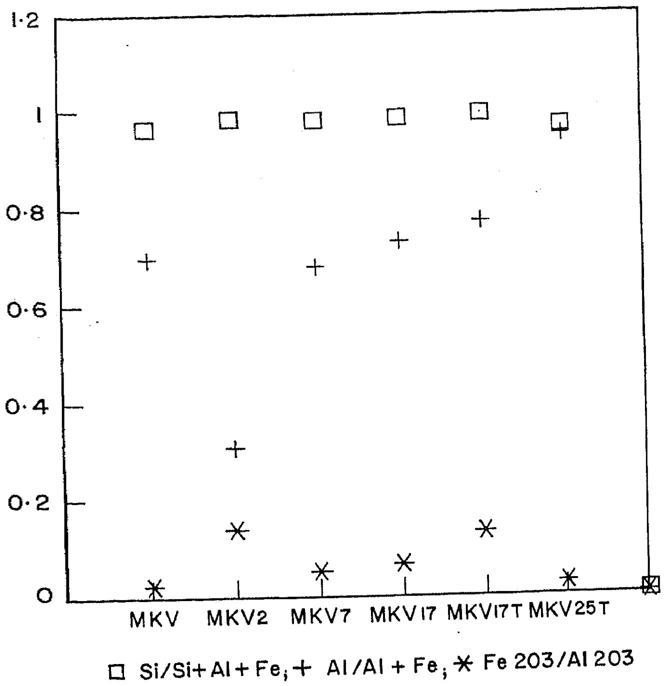

Figure 3. Some significant major element ratios of the Vanivilaspur cherts showing their continental margin affinity.

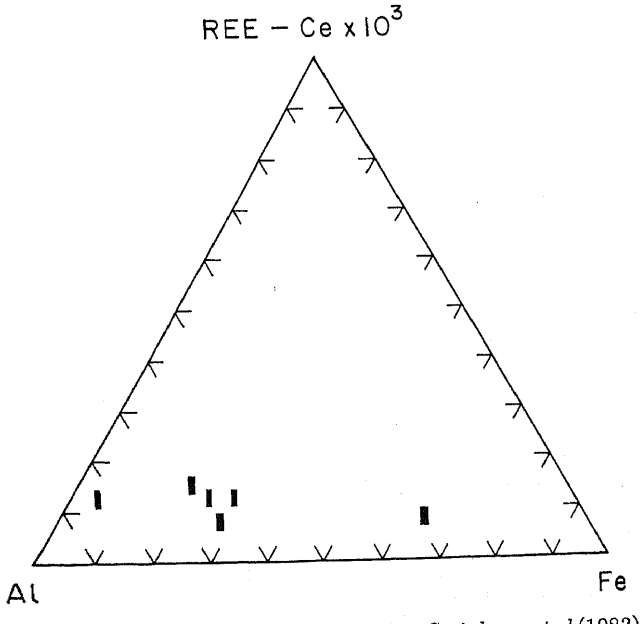

Figure 4. REE-CeX10^3-Al-Fe plot after Steinberg *et al* (1983) for the Vanivilaspur cherts showing their continental margin affinity.

(figure 5a). $(La/Sm)_N$ varies from 1.42 to 15.42. Chondrite, NASC as well as PAAS normalized REE patterns show a consistent negative cerium anomaly (figures 5a, b, and c) but not consistent Eu anomaly.

The Rb, Sr concentrations and Sr isotopic compositions of six different bulk chert samples (designated B) of the Vanivilaspur Formation and leaches and residues (designated L and R, respectively) of three of these samples are given in table 4. Major element data (table 1) show that at least two of the samples (MKV and MKV7) have high (~ 10%) carbonate content. The Rb/Sr ratio of bulk samples ranges from 0.082 to 0.403, while their $^{87}Sr/^{86}Sr$ ratio from 0.72265 to 0.75450. These data, as plotted in the Rb-Sr evolution diagram of figure 6, conform to a nearly linear array. Since the carbonate rich samples (MKV and MKV7 and possibly MKV17) have higher Sr contents and lower Sr isotopic ratios, the possibility that this correlation line is just a mixing line essentially between carbonate and silicate components of the chert samples needs to be assessed. The fact that MKV is lower both in Sr content and Sr isotopic ratio relative to MKV17 and the widely different Rb/Sr ratios of the three residues argue against such a possibility. So the linear correlation is plausibly the result of *in situ* Rb decay in isolated systems with a common Sr initial composition. Since the deviation of the data points from the best fit straight line exceeds their analytical errors as evident from the high MSWD (~ 50), the samples seem to have deviated slightly from isochron conditions. Interpreted as an approximate isochron (errorchron), it corresponds to an age of 2512 ± 159 Ma and initial Sr ratio of 0.7128 ± 0.0012 (2σ errors).

Leaching experiments were done on three samples with a high carbonate content in an attempt to separate this component from the silicate component (clays) in them. The results are quite regular. In all the three cases, the leaches (L) contain a large proportion of the bulk Sr of the samples, while the Rb appears to be well fixed in the residues (> 95%). Whereas the major element analysis of the MKV17 shows it to be low in carbonate relative to MKV and MKV7, its leachable fraction is comparable to that of the latter. If the leachable fraction is mainly carbonate, MKV17 is also carbonate rich, which is also corroborated by the similarity of the Sr content in the three samples. Also, the Rb and Sr concentrations of the residue and leach of MKV and MKV7 yeild their calculated bulk (CB) values in very good agreement with their direct bulk analyses. In MKV17, the agreement is good only for the Rb but not Sr (7.89 ppm and 5.21 ppm, respectively). The cause of this discrepancy is not clear. But we believe it to be due to inhomogeneous distribution of carbonate in the powdered sample of MKV17, as we have taken approximately the same amount of the powdered sample for major element analysis and Rb and Sr analyses of the bulk and acid fractionated portions.

The spread of the Rb-Sr data is greatly enhanced by the leaching process, the most dramatic change being the high $^{87}Sr/^{86}Sr$ ratio of 1.0003 in the residue relative to 0.72265 in the bulk of the MKV7. In the absence of any significant differential leaching of Rb and Sr, the isotopic correlation between leach, residue and bulk of each sample should be strictly linear. This is indeed seen from the Sr evolution diagrams for

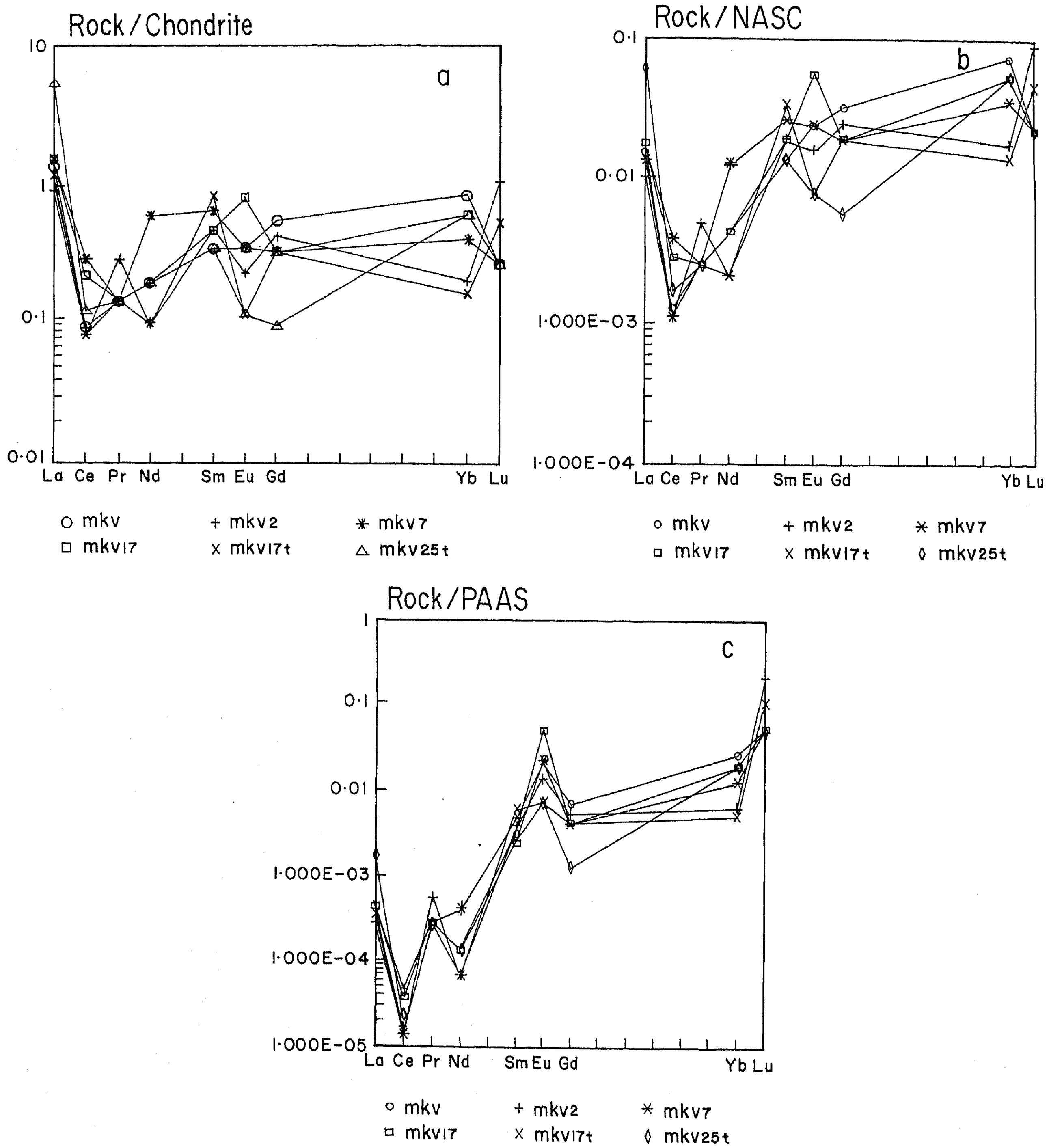

Figure 5(a, b and c). Chondrite, NASC and PAAS normalized REE patterns for Vanivilaspur cherts showing distinct negative Ce anomaly.

the three leaching experiments (figures 7a, b and c) including that for MKV17 with the Sr discrepancy between bulk and calculated bulk results. If these correlation lines are deemed to be also wholerock-mineral isochrons, they correspond to the following ages and initial Sr ratios; MKV 1870 ± 16 Ma, 0.7151 ± 1; MKV17 2038 ± 34 Ma, 0.7189 ± 1 and MKV7 2153 ± 150 Ma, 0.7143 ± 3. While the three ages are approximately concordant at about 2000 Ma, the three initial ratios are not only distinct but also show a systematic increase with the Rb/Sr ratio in the corresponding bulk sample.

6. Discussion

Biogenic and abiogenic silica precipitated from sea water diagenetically replaces a variety of rock types to give rise to cherts (Hesse 1988, 1989; Knauth 1992). Aitchison and Flood (1990) observed that biogenic

Table 4. *Rb-Sr isotopic analysis results and composition of stromatolitic cherts of Vanivilaspur.*

Sample	Weight mg	Rb ppm	Sr ppm	$^{87}Rb/^{86}Sr$ [1] (atomic)	$^{87}Sr/^{86}Sr$ [2] (atomic)
MKV(B)	407.2	0.50	4.13	0.351	0.72450 ± 3
(L)	39.8	1.12	53.91	0.062	0.71678 ± 6
(R)	577.3	0.49	0.66	2.15	0.77310 ± 6
(CB)*	617.1	0.53	4.10		
MKV17(B)	255.0	1.37	5.21	0.762	0.74181 ± 4
(L)	32.1	4.09	117.50	0.101	0.72181 ± 4
(R)	475.5	1.3	0.49	7.86	0.94642 ± 6
(CB)	507.6	1.48	7.89		
MKV7(B)	307.5	0.54	6.6	0.237	0.72265 ± 12
(L)	74.0	0.61	52.07	0.034	0.71527 ± 3
(R)	533.9	0.52	0.16	9.58	1.00030 ± 7
(CB)	607.9	0.53	6.48		
MKV2(B)	315.8	0.72	2.66	0.785	0.73964 ± 3
MKV25T(B)	253.6	0.65	1.87	1.014	0.75203 ± 34
MKV17T(B)	396.4	0.64	1.59	1.163	0.75450 ± 4

B – Bulk; **L** – Leach; **R** – Residue; **CB** – Calculated Bulk.
* Values obtained by mass balance calculations.
[1] 2σ error less than 1%.
[2] Errors are 2σ of the mean.

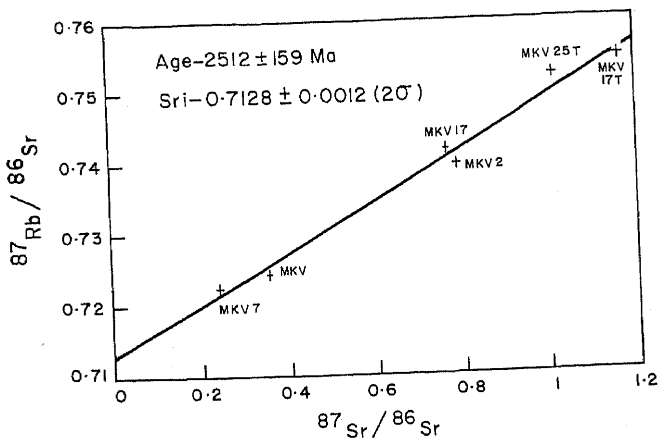

Figure 6. Rb-Sr isotope correlation line for Vanivilaspur stromatolitic cherts.

silica have high Si/Si + Al + Fe ratio close to 1. Murray *et al* (1990) noted that cherts deposited in a terrigenous environment carry more Al_2O_3 and are depleted in Fe_2O_3 as compared to the deep sea cherts. The Vanivilaspur stromatolitic cherts inferred to have been deposited in intertidal to subtidal zones exhibit these characteristics. The abundance of various trace and rare earth elements in cherts apparently depends upon rock types that have been replaced by silica and the quantum of impurities that have survived such replacement processes. Cherts resulting from replacement of volcanic or volcaniclastic rocks may have much higher trace and rare earth element abundances relative to those that result from limestones and dolomites which are themselves depleted in these elements. The wide range in trace and REE abundances seen, for example, in the Onverwacht cherts formed most probably by replacement of a wide variety of volcanic and sedimentary rocks supports this contention (Knauth and Lowe 1978; Weis and Wasserburg 1987b). The extremely low abundances of trace elements in the Vanivilaspur cherts is consistent with their origin through replacement of carbonate rocks which were depleted in the trace and REE constituents.

Weis and Wasserburg (1987a and b) have noted that biogenic silica is enriched in Rb. The Rb/Sr ratios in Vanivilaspur cherts show significant enrichment of Rb relative to sea water, and are comparable to many Phanerozoic cherts with Rb/Sr ratios ranging from 0.1 to 0.8.

Low abundances of REE in the stromatolitic Vanivilaspur cherts are similar to those of cherts deposited at continental margins (cf. Shimizu and Masuda 1977; Murray *et al* 1990, 1991, 1992). This depletion has been attributed by Murray *et al* to one or more of the following causes: (**a**) whole-rock SiO_2 dilution; (**b**) decreasing aluminosilicate abundances; (**c**) high rates of sedimentation limiting absorption from the sea. The LREE enriched nature of the cherts indicated by $(La/Sm)_N = 1.4$ to 15.4 and $(La/Yb)_N = 1.4$ to 7.9 is in accord with the derivation of the Dharwar sediments from a continental source (Srinivasan and Ojakangas 1986). While these ratios are similar to those of Archaean cherts elsewhere, the negative cerium anomaly seen in Vanivilaspur cherts is uncommon. Cherts deposited in the continental margins of the Phanerozoic oceans also do not show cerium anomaly (see Shimizu and Masuda 1977; Murray *et al* 1990, 1992). As pointed out in the

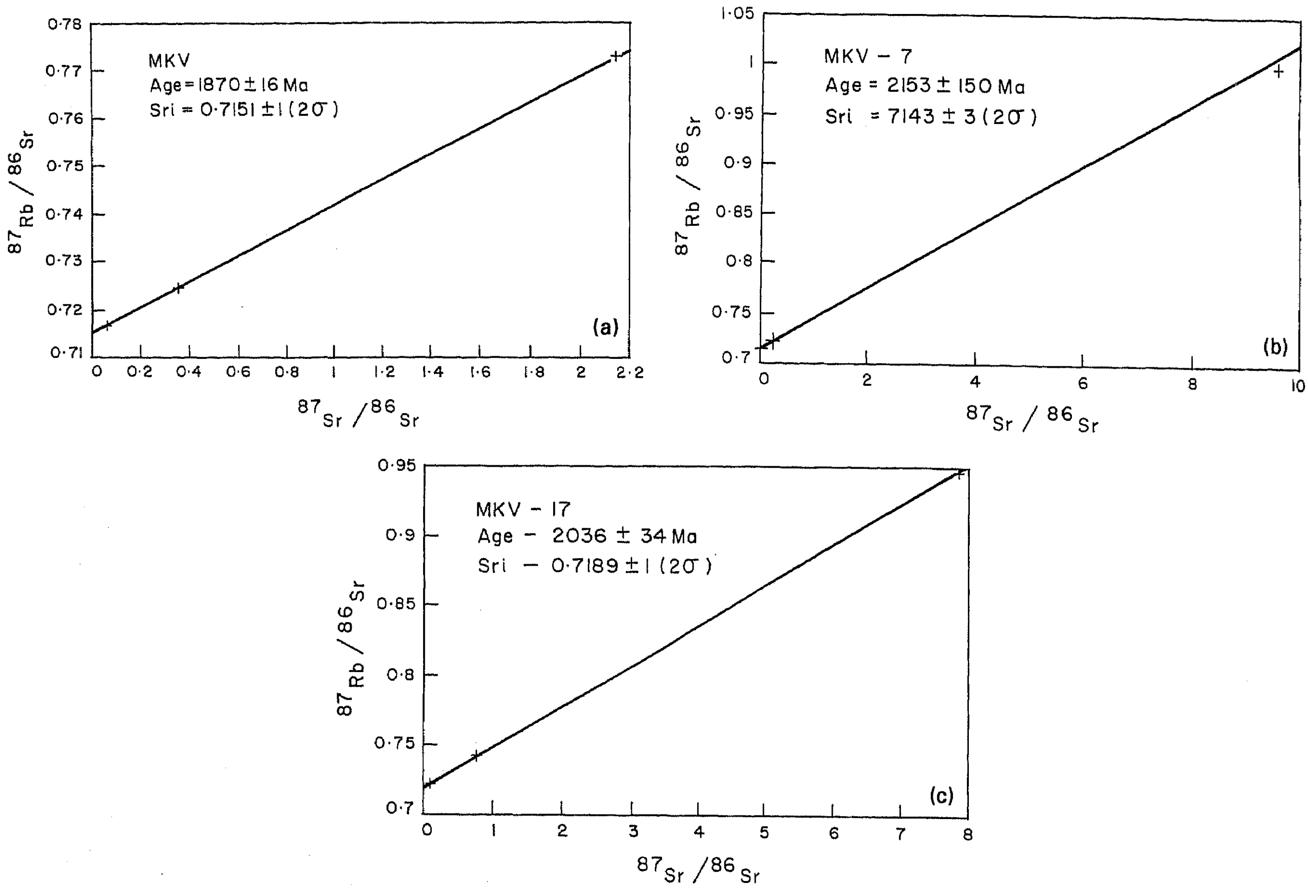

Figure 7(a, b and c). Rb-Sr isotopic correlation lines for leach and residues of Vanivilaspur cherts.

introduction, negative cerium anomaly in the present day seas arises from microbial oxidation followed by preferential scavenging of Ce^{+4} by manganese (Moffet 1990). The Arhaean stromatolites are considered to have been built by cyanobacteria. Fossil cyanobacteria have been noted in Dharwar ferrugenous cherts (Venkatachala *et al* 1990). Assuming that such cyanobacteria formed the Vanivilaspur stromatolites, the oxidation in the immediate environment of the Dharwar seas could have precipitated manganese together with Ce^{+4} to cause the observed negative Ce anomaly in the sea water from which the Vanivilaspur cherts precipitated. It may be pertinent to note that the stromatolitic cherty dolomite, sampled for this study is within a few metres from a manganese mine. Thus the observed negative Ce anomaly represents a depositional setting peculiar to the Archaean Dharwar province where manganese precipitation was prevalent.

The present Rb-Sr isotopic data on the bulk samples are consistent with their isolated evolution for close to 2500 Ma from a common initial Sr composition of 0.7129. While this age is strikingly close to the age of the regional low grade metamorphism at about 2600 Ma of the associated volcanic rocks, the initial Sr ratio is distinctly higher than that of the latter at 0.7013 to 0.7038 (Bhaskar Rao *et al* 1992). The quality of the correlation in our data is not as good as that in the case of the low carbonate ($\sim$ 1%) cherts from the Onverwacht Group, South Africa reported by Weis and Wasserburg (1987b). This is surprising as the latter set of samples come from a much thicker section of the Onverwacht Group than our samples collected within a few meters of each other. It is also to be noted that Weis and Wasserburg analysed bulk samples powdered from chips of not more than 50 g each, while we homogenized rock samples weighing a few kilograms. The most likely cause of the poor fit of our samples to a well defined line is that they became slightly open systems due to secondary events much later than 2500 Ma. This is indicated by the distinctly younger age of $\sim$ 2000 Ma defined by the whole rock-residue-leach isochron from the three leaching experiments. As pointed out earlier the initial Sr ratio defined by each of these internal isochrons is distinctly higher than 0.7129 of the whole rocks. The fact that the three initial ratios differ and correlate with the bulk Rb/Sr ratios suggests that the individual whole rocks were isotopically equilibrated on a mm to cm scale about 2000 Ma ago, nearly 500 Ma after the homogenization of the Sr isotopes on a much larger scale (whole rocks) 2500 Ma ago. Bhaskar Rao *et al* (1992) have also documented Sr isotopic equilibration on a mineral scale about

2000 Ma ago from the Rb-Sr systematics of mineral phases in the Chitradurga Granite. The time of deposition of the Dharwar Supergroup sediments is still debated, but is not less than 2600 Ma, this being the Rb-Sr and Pb-Pb age of the intrusive Chitradurga granite. The Sm-Nd age reported recently for the Ingaldhal volcanic rocks of the Chitradurga Group at 2747 ± 15 Ma (Anil Kumar *et al* 1996) fixes a minimum age for the Vanivilaspur cherts underlying them. The correlation line for the Vanivilas chert samples is therefore interpreted as reflecting the age of rehomogenization of Sr isotopes in the deposited sediments. This implies that 2500 Ma is a minimum age for the stromatolites associated with cherts in the Vanivilaspur Formation.

References

Aitchison J C and Flood P G 1990 Geochemical constraints on the depositional setting of Palaeozoic cherts from the New England orogen, NSW, Eastern Australia; *Marine Geol.* **94** 79–95

Anil Kumar, Bhaskar Rao Y J, Sivaraman T V and Gopalan K 1996 Sm-Nd ages of Archean metavolcanics of the Dharwar craton, south India; *Precambrian Res.* **80** 206–216

Balaram V, Manikyamba C, Ramesh S L and Anjiah K V 1992 Rare earth and trace element determination in iron formation reference samples by ICP-MS; *Atomic Spectroscopy* **13** 19–25

Bhaskar Rao Y J, Sivararaman T V, Pantulu G V C, Gopalan K and Naqvi S M 1992 Rb-Sr ages of late Archaean metavolcanics and granites of Dharwar craton, south India and evidence for early Proterozoic thermotectonic events; *Precambrian Res.* **59** 145–170

Blatt H, Middleton G and Murray R 1980 Origin of sedimentary rocks; 2nd ed; Prentice Hall pp 782

Hesse R 1988 Origin of chert: Diagenesis of biogenic siliceous sediments; *Geoscience Canada* **15** 171–192

Hesse R 1989 Silica Diagenesis: Origin of Inorganic and Replacement Cherts; *Earth-Science Reviews* **26** 253–284

Hurley P M, Pinson W H Jr., Nagy B, Teska T M 1972 Ancient age for the Middle Marker Horizon, Onverwacht Group, Swaziland Sequence, South Africa; *Earth Planet. Sci. Lett.* **14** 360–366

Jones D L and Murchy B 1986 Geological significance of Palaeozoic and Mesozoic radiolarian chert; *Ann. Rev. Earth and Planet. Sci.* **14** 455–492

Knauth L P 1992 Origin and diagenesis of chert: An isotopic perspective, In *Isotopic signatures and sedimentary rocks* (eds.) N Clauer and Chaudhuri (Berlin: Springer Verlag) 23–152

Knauth L P and Lowe D R 1978 Oxygen isotopic geochemistry of cherts from the Onverwacht Group (3.4 billion years), Transvaal, South Africa with implications for secular variations in the isotopic compositions of cherts; *J. Geol.* **41** 209–272

Moffet J W 1990 Microbially mediated cerium oxidation in sea water; *Nature* **345** 421–423

Murray R W, Marilyn R, Buchholtz Ten Brink M R, Jones D L, Gerlach D C and Russ G P III 1990 Rare earth elements as indicators of different marine depositional environments in chert and shale; *Geology* **18** 268–271

Murray R W, Buchholtz Ten Brink M R, Gerlach D C, Russ G P III and Jones D L 1991 Rare earth, major and trace elements in chert from the Fransiscan Complex and Monterey Group, California: Assessing REE sources for fine grained marine sediments; *Geochim. Cosmochim. Acta.* **55** 1875–1895

Murray R W, Buccholtz Ten Brink M R, Gerlach D C and Russ G P III 1992 Rare earth, major and trace element composition of Monterey and DSDP chert and associated host sediments: Assessing the influence of chemical fractionation during diagenesis; *Geochim. Cosmochim. Acta.* **56** 2657–2671

Naqvi S M, Govil P K and Rogers J J W 1981 Chemical sedimentation in the Archaean–Early Proterozoic greenschist belts of the Dharwar craton, India; In *Archaean Geology*, (eds) J E Glover and D I Groves Spl. Publ. 7 Geological Soc. Australia. Inc pp. 245–254

Nutmann A P, Chadwick B, Krishna Rao B and Vasudev V N 1996 SHRIMP U/Pb zircon ages of acid volcanic rocks in the Chitradurga and Sandur Groups and granites adjacent to the Sandur schist belt, Kanataka; *J. Geol. Soc. India* **47** 153–164

Shibata and Mizutani 1982 Isotopic ages of Jurassic siliceous shale and Triassic bedded chert in Unuma, Central Japan; *Geochem. J.* **16** 213–223

Shimizu H and Masuda A 1977 Cerium in chert as an indicator of marine environment of its formation; *Nature* **266** 346–348

Sreenivas B, Balaram V and Srinivasan R 1994 Trace and rare earth element contamination during routine preparation of sample powders for geochemical studies; *Indian J. Geol.* **66** 296–304

Srinivasan R and Ojakangas R W 1986 Sedimentology of the quartz pebble conglomerates and quartzites of the Bababudan Group, Dharwar craton, South India: Evidence for early crustal stability; *J. Geol.* **94** 199–214

Srinivasan R, Shukla M, Naqvi S M, Yadav V K, Venkatachala B S, Uday Raj B and Subba Rao D V 1989 Archaean stromatolites from the Chitradurga schist belt, Dharwar craton, south India; *Precambrian Res.* **43** 239–250

Srinivasan R, Naqvi S M and Vasantha Kumar 1990 Archaean shelf facies and stromatolite proliferation in the Dharwar Supergroup, North Kanara District, Karnataka; *J. Geol. Soc. India* **35** 203–212

Steinberg M, Bonnot-Courtois C and Tlig S 1983 Geochemical contribution to the understanding of the bedded chert: In *Siliceous deposits of the Pacific region*, (eds) A Ijima, J R Hein and Siever R Developments in Sedimentology 36 (Amsterdam: Elsevier) pp 193–210

Swami Nath J and Ramakrishna M 1981 Early Precambrian Supracrustals of southern Karnataka; *Geol. Surv. India Mem.* **112** pp 350

Taylor H P, Chadwick B and Friend C R L 1988 New age data on the geological evolution of southern India; *J. Geol. Soc. India* **31** 155–157

Venkatachala B S, Shukla M, Sharma M, Naqvi S M, Srinivasan R and Uday Raj B 1990 Archaean microbiota from the Donimalai Formation, Dharwar Supergroup, India; *Precambrian Res.* **47** 27–34

Weis D and Wasserburg G J 1987a Rb-Sr and Sm-Nd systematics of cherts and other siliceous deposits; *Geochim. Cosmochim. Acta* **51** 959–972

Weis D and Wasserburg G J 1987b Rb-Sr and Sm-Nd isotope geochemistry and chronology of cherts from the Onverwacht Group (3.5 AE), South Africa; *Geochim. Cosmochim. Acta.* **51** 973–984

Wildeman T R and Haskin L A 1973 Rare earths in Precambrian sediments; *Geochim. Cosmochim. Acta.* **37** 413–439