[AMERICAN JOURNAL OF SCIENCE, VOL. 303, APRIL, 2003, P. 319–351]

CONSTRAINTS ON CONTINENTAL GROWTH MODELS FROM Nb/U RATIOS IN THE 3.5 Ga BARBERTON AND OTHER ARCHAEAN BASALT-KOMATIITE SUITES

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ABSTRACT. The average Nb/U ratio of modern mid-ocean ridge and oceanic island basalts (MORBs and OIBs) is 47 compared with 34 for the primitive mantle and this difference is attributed to the separation of the continental crust from the mantle. Variation in the Nb/U ratio in basalts of different ages can therefore be used to identify the time at which the bulk of the continental crust separated from the mantle. This study reports Nb/U ratios for a suite of 3.5 Ga basalts and komatiites from the Barberton Mountain Land in South Africa, the oldest well-preserved, basalt-komatiite suite, and compares the results with published Nb/U ratios for other Archaean basalt-komatiite suites.

The average Nb/U of the Barberton basalts and komatiites is 43, which is essentially the same as the average of all of the other Archaean basalt-komatiite suites (42). These values can be used to calculate the total amount of continental crust extracted from the mantle source region of these magmas as a percentage of the amount extracted from the modern mantle. The values obtained are 75 percent for the source region to the Barberton basalts and 70 percent for the average source region of all of the Archaean basalt-komatiite suites considered in this study. The lack of systematic variation in Nb/U through the Archaean precludes the possibility that the late Archaean was a period of rapid growth of continental crust. The rate of growth of the continental crust can be further constrained by the observation that Nb/U in the modern MORB and OIB sources are the same. This requires that the net rate of increase in the mass of the continental crust was negligible over the last 1.5 billion years. Finally, Nd and Hf model ages of Earth's oldest sediments, and the rarity of zircons older than 4.0 Ga in these rocks, indicate that little continental crust formed between 4.5 to 4.0 Ga. Taken together these constraints suggest that 4.5 to 4.0 Ga was a period of slow growth for the continental crust and that it was followed by a period of rapid growth between 4.0 and 3.0 Ga, with approximately 70 percent of the continental crust having formed by the end of that period. Crustal growth was again slow between 2.5 and 0 Ga and may have reached a steady state, with no net increase in the mass of continental crust during that period. If the average age of the preserved continental crust of 1.4 to 1.8 Ga, based on Nd model ages of modern sediments, is correct, much of the 70 percent of the continental crust that had formed by 3.0 Ga must have been destroyed by recycling through the mantle. The rate of recycling required is substantial but less than that envisaged by Armstrong (1968, 1991), especially between 4.5 and 4.0 Ga.

INTRODUCTION

There are two end-member models for the timing and rate of growth of the continental crust. The most accepted view is that the continental crust began to form at 4.0 Ga, the age of the Earth's oldest crust, and that it has been growing continuously and largely irreversibly since then (Moorbath, 1977; McLennan and Taylor, 1982; Fyfe, 1983; Reymer and Schubert, 1984). The present age distribution of the exposed continental crust appears to support this view. Old crust covers only a small fraction of the continents and the fraction covered by younger crust increases as the age of the crust decreases. In the other end-member model the continental crust is in a steady state and is being destroyed by recycling into the mantle at the same rate as it forms (Armstrong, 1968, 1991). According to this hypothesis the mass of continental crust that existed between 4.0 and 4.5 Ga was similar to today's, but all of this original material has been destroyed by recycling into the mantle (Armstrong, 1991).

Isotopic studies have been unable to distinguish between the steady state and continuous growth models for the formation of the continental crust. Nd model ages for modern sediments show that the average age of the continental crust is a relatively young 1.4 to 1.8 Ga (Jacobsen, 1988; Goldstein and Jacobsen, 1988), which suggests that most continental growth took place after 3.0 Ga, and appears to support the continuous growth hypothesis. Although Nd model ages may date the average time of formation of the present continental crust, they do not preclude the possibility that much of this material had previously been recycled through the mantle (Armstrong, 1981). On the other hand, the steady state hypothesis appears to be supported by Nd isotopic studies of samples of the Earth's oldest crust, which shows evidence of being derived from a mantle from which a significant volume of old continental crust had already been extracted (Bowring and others, 1989; Collerson and others, 1991; Bennett and others, 1993; Bowring and Housh, 1995). However, if an extensive reservoir of old continental crust is the complement to the positive ε_{Nd} values in these ancient rocks, little evidence for its existence has been found either in Nd model ages of the Earth's oldest sediments (Jacobsen and Dymek, 1987) or in the zircons extracted from them (Nutman, 2001). Furthermore, the reliability of the positive ε_{Nd} values for the oldest rocks has been questioned on the grounds that their Sm-Nd systematics may have been perturbed by alteration (Vervoort and others, 1996).

Using the Lu-Hf system, which is less susceptible to alteration, can minimize the problems associated with disturbance of the Sm-Nd systematics. Studies of Lu-Hf in old rocks, and especially zircons from early Archaean Greenland gneisses, confirm that the Earth's oldest crust was derived from a mantle that had already undergone a significant enrichment in its Lu/Hf (and by inference Sm/Nd) ratio by 3.8 Ga (Vervoort and others, 1996). Although Nd and Hf isotopes provide unequivocal evidence of a significant increase in the Sm/Nd and Lu/Hf ratios of at least parts of the Earth's mantle prior to 3.8 Ga, it is not clear whether this early fractionation event is due to the formation of the Earth's continental crust (for example, Bowring and others, 1989; McCulloch and Bennett, 1994), to the formation of a primitive basaltic crust (Chase and Patchett, 1988; Galer and Goldstein, 1991), or whether it is a remnant of fractionation of an early magma ocean, because all of these processes would increase the Sm/Nd and Lu/Hf ratios of the mantle residue.

An alternative approach is to use the Nb/U ratio in basalts of different ages to determine the timing of continental crust extraction. Hofmann and others (1986) have shown that U and Nb have similar partition coefficients during the partial melting process that produces OIBs and MORBs. As a consequence, the Nb/U ratio in these basalts is essentially the same as their mantle source region. However, during extraction of the continental crust, Nb is fractionated from U so that the Nb/U ratio of the continental crust is 9.7 (Rudnick and Fountain, 1995), compared with 34 for the primitive mantle (Sun and McDonough, 1989). Extraction of the continental crust from the mantle has raised the average Nb/U ratio of the upper mantle, as sampled by modern MORBs, from 34 to 47 (Hofmann and others, 1986). If the increase in this ratio is due to extraction of the continental crust, it should be possible to use Nb/U ratios in basalts of different ages to determine the fractionation of continental crust extracted from the mantle as a function of time.

Nb/U has two important advantages over Nd and Hf isotopes.

1. Nb is fractionated from U by the formation of continental crust and not by the formation of oceanic crust, so major shifts in the Nb/U ratio of the mantle provide unambiguous evidence of continental crustal extraction. In this re-

spect Nb/U contrasts with Sm/Nd and Lu/Hf ratios which can not discriminate between extraction of continental versus oceanic crust.

2. Nb/U, unlike the Sm-Nd and Lu-Hf isotopic systems, is not time dependent, which allows direct comparison between Nb/U in komatiite-basalt suites of different ages. As a consequence, Nb/U can be used to quantify the amount of continental crust extracted from the mantle at a given time as a percentage of the average amount extracted from the modern mantle.

Previous Work

Jochum and others (1991) were the first to recognize the potential of analyzing Nb/U ratios in basalts of differing ages to model the rate of growth of the continental crust. They analyzed komatiites and basalts from a number of locations but found an erratic variation in Nb/U ratios, which they attributed to U mobility in the altered Archaean and Proterozoic rocks used in their study. Nb/Th ratios were used as a proxy for Nb/U but uncertainty as to the extent of Nb/Th fractionation during partial melting, and differences in the Nb/Th of the modern OIB and MORB sources, limited the confidence that could be placed in the interpretation.

Sylvester and others (1997) adopted a different strategy. They analyzed 43 basalts and gabbros from a single 2.7 Ga formation from the Norseman-Wiluna greenstone belt of Western Australia for a range of trace elements including Nb, Th and U. By analyzing multiple samples from the same sills, they were able to show that U and Th were immobile in the samples they studied. They also found that Nb/U varied systematically with Nb/Th and that the data lay on a mixing line between Nb/U-Nb/Th ratios of 32, 8 and 47, 12 respectively. The implication of the high Nb/U, Nb/Th end member is that the fraction of continental crust removed from the mantle source of these basalts is similar to the fraction removed from the average modern upper mantle.

Although the Sylvester and others study showed that extensive continental crust had separated from the mantle source region of the Kambalda-Norseman basalts by 2.7 Ga, it cannot be used to distinguish between the steady state and continuous growth models for the origin of the continental crust. The analyzed basalts formed 1.3 Ga after the oldest preserved continental crust during a period, which is thought by many to be a time of rapid growth of the continental crust (Veizer and Jansen, 1979; McLennan and Taylor, 1982). The continuous growth hypothesis is therefore compatible with up to 70 percent of the present continental crust having formed by 2.7 Ga (McLennan and Taylor, 1982).

A better test of the two hypotheses is to analyze basalts with ages as close as possible to 4.0 Ga. The Armstrong (1991) steady state hypothesis for continental crustal growth requires the bulk of the crust to have separated from the mantle prior to 4.0 Ga and to have been continually recycled through the mantle. This hypothesis predicts that the regions of the early mantle from which continental crust has been extracted should have high Nb/U and Nb/Th ratios. It further predicts that these ratios should decrease with decreasing age as this depleted mantle mixes with primitive mantle from which no continental crust has been extracted and with recycled continental crust. Alternatively, if the continental crust separated gradually and continuously from the mantle over the history of the Earth, with minimal recycling through the mantle, the oldest basalts derived from the Earth's mantle should have chondritic or near chondritic Nb/U and Nb/Th ratios and these ratios should increase gradually through time.

The most suitable material for the Nb/U and Nb/Th ratios test of the continental growth hypotheses is the oldest known komatiite-basalt association that is free from intense deformation and/or high-grade metamorphism, the 3.5 Ga basalts and komatiites from the Barberton Mountain Land in South Africa (Armstrong and others, 1990). Fifteen basalts and basaltic komatiites and four komatiites were analyzed from the classic Komati River section of Barberton area in South Africa (Jahn and others, 1987). Nine of the Barberton basalt samples are from the Komati Formation and three are from each of the Theespruit and Sandspruit Formations. Crustal contamination in these samples is minimal. The Barberton data are supplemented by analyses of five spinifex-textured komatiites from the Norseman-Wiluna greenstone belt in the Yilgarn Craton and from Munro Township in the Abitibi greenstone belt, which were kindly provided by Dr. Shen-su Sun (Sun and Nesbitt, 1978). These data, together with Nb, Th, U analyses for other Archaean basalts and komatiites obtained from the literature, are used to evaluate models for the rate of early continental crust extraction.

ANALYTICAL METHODS

All of the basalt samples analyzed in this study were crushed in an alumina mill, melted to form glasses and analyzed by excimer laser ablation ICP-MS. The glasses were made by placing approximately one gram of powder in a covered graphite crucible and preheating at 800°C for 5 minutes to drive off water. The dried powder was then heated in a Kanthal furnace for 10 minutes at 1350°C in an argon atmosphere and quenched in Milli Q water. Failure to dry the sample prior to melting, or melting for too long or at too high a temperature, can lead to the formation of small metallic iron droplets, which will lower the siderophile element content of the glass but have no influence on the incompatible elements that are the subject of this study. Major elements were analyzed by XRF at the Australian National University using the method of Norrish and Hutton (1969) and Y, Zr, Nb, Hf, Ta, Th, U and the REE by ELA-ICP-MS. Their absolute concentrations were determined by ratioing against Ca, following procedures described by Eggins and others (1998). The NIST glass 612, which had previously been calibrated against a number of international standards, was used as a standard. Nb, U and Th were analyzed separately from the other trace elements to achieve maximum precision and their ratios determined by direct comparison with the standard to minimize the effect of mass bias drift during analyses. The data reported are the mean of 4 analyses using a spot size of 100 millimeters. Nb, Th and U concentrations for glasses made from the international standards BCR2 and BHVO were 12.8, 5.9, 1.59 and 19.6, 1.26, 0.42 respectively. Nb/Th and Nb/U ratios for the standards were 2.18 ± 0.02 and 8.08 ± 0.07 for BCR2 and 15.61 ± 0.11 and 46.79 ± 0.34 for BHVO.

The komatiites were analyzed by solution ICPMS following the method of Eggins and others (1997) in order to obtain maximum precision for elements, such as U, Th and Ta, that are present in komatiites at low concentrations. Sun and Nesbitt (1978) and Nesbitt and Sun (1976) report XRF major and trace element data for the same samples.

RESULTS

The major and trace element analyses for the Barberton basalts are listed in table 1 and sample locations and field descriptions in table 2. The analyzed samples are low to high MgO basalts and komatiitic basalts with MgO concentrations that vary between 8.5 and 13.2 wt.%. Iron concentrations are generally high and range between 8.6 and 14.9 wt.% total Fe as FeO, with all but two samples having over 10 wt.% FeO. SiO_2 contents are also generally high for these rock types and show considerable variation, ranging from a low of 48.8 to a high of 55.6 wt.%. Al_2O_3/TiO_2 ratios vary between 5.6 and 14.5, well below the chondritic ratio of 20, which suggest that much of the Al_2O_3 has been held back in the mantle source region by garnet during melting. Nb/U ratios vary between 34.4 and 66.7 and Nb/Th ratios between 8.1 and 17.1. The average Nb/U has been calculated by two methods, by averaging the measured Nb/U values and by dividing the average Nb concentration by the average U concentration. The former gives an average Nb/U of 43 and the latter 42. The average ratio method is

Table 1

Major and trace elements for basalts and komatiitic basalts from the Barberton

determined by XRF (wt%)															
Sample no.	97-383	97-384	97-385	97-386	97-387	97-389	97-390	97-391	97-392	97-405	97-406	97-407	97-408	97-410	97-411
SiO_2	53.24	55.00	50.72	52.66	54.47	48.82	50.83	55.56	53.83	51.59	49.54	52.89	51.46	51.04	54.46
TiO_2	0.79	0.80	0.76	0.51	0.74	0.89	0.82	0.72	0.62	1.48	1.38	0.75	1.03	1.21	0.81
Al_2O_3	8.49	9.38	9.45	7.42	10.11	10.38	11.80	10.19	7.49	8.31	10.64	9.98	9.18	10.15	8.63
FeO^t	10.39	10.01	11.71	8.62	10.62	11.61	11.26	10.79	10.17	14.88	13.26	10.84	12.84	12.52	11.86
MnO	0.17	0.19	0.20	0.14	0.19	0.20	0.18	0.18	0.20	0.21	0.24	0.18	0.29	0.22	0.21
MgO	11.34	10.05	10.54	13.19	8.52	12.72	10.10	8.00	11.98	10.89	9.11	10.98	10.32	9.03	10.08
CaO	9.75	9.37	11.07	9.74	9.06	10.21	9.29	9.79	11.48	10.11	11.71	10.36	10.52	11.18	11.06
Na_2O	3.14	3.63	2.23	2.60	3.82	2.19	2.86	3.68	2.55	0.28	2.13	2.26	1.47	2.15	2.16
K_2O	0.13	0.17	0.15	0.10	0.19	0.19	0.29	0.09	0.06	0.34	0.16	0.13	0.96	0.73	0.42
P_2O_5	0.07	0.08	0.07	0.05	0.09	0.11	0.09	0.08	0.06	0.12	0.13	0.07	0.08	0.11	0.07
SO_3	0.04	0.04	0.05	0.15	0.03	0.03	0.06	0.02	0.03	0.15	0.02	0.01	0.03	0.01	0.01
Cr_2O_3	0.17	0.09	0.10	0.16	0.10	0.19	0.11	0.09	0.21	0.09	0.24	0.12	0.15	0.09	0.12
V_2O_5	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.04	0.04	0.05	0.06	0.04	0.04	0.04	0.04
Total	97.76	98.85	97.09	95.38	97.98	97.59	97.74	99.23	98.72	98.50	98.62	98.61	98.37	98.48	99.93
mg#	66.05	64.15	61.60	73.17	58.85	66.13	61.52	56.93	67.74	56.61	55.05	64.36	58.89	56.25	60.24
CaO/Al_2O_3	1.15	1.00	1.17	1.31	0.90	0.98	0.78	0.96	1.53	1.22	1.10	1.04	1.15	1.10	1.28
Al_2O_3/TiO_2	10.7	11.7	12.43	14.55	13.66	11.66	14.4	14.2	12.1	5.6	7.7	13.3	8.9	8.4	10.7
determined by ICP (ppm)															
Y	18.39	19.32	21.62	12.83	23.76	13.44	20.69	19.42	18.96	19.89	31.93	18.13	24.63	31.37	20.97
Zr	56.96	63.89	60.51	33.35	75.17	36.38	68.25	65.95	54.55	89.49	115.99	54.20	94.37	109.69	63.25
Nb	2.990	3.390	3.190	1.550	4.740	2.400	4.170	3.930	2.980	8.710	5.450	2.090	6.050	7.950	2.910
La	3.220	4.479	4.777	1.299	8.010	2.453	4.479	4.357	4.372	8.906	6.510	2.139	9.679	13.046	4.826
Ce	8.853	10.706	12.172	3.775	16.534	6.638	11.540	11.557	11.011	24.229	17.235	7.557	24.613	29.855	11.427
Pr	1.335	1.466	1.733	0.581	2.143	0.984	1.611	1.657	1.633	3.591	2.552	0.967	3.392	4.139	1.696
Nd	6.520	6.932	8.366	2.876	9.478	4.749	7.373	7.712	7.759	16.984	12.451	4.803	15.375	18.340	8.167
Sm	2.172	2.151	2.577	1.028	2.617	1.454	2.207	2.197	2.263	4.344	4.002	1.698	3.973	4.587	2.472
Eu	0.731	0.591	1.272	0.418	0.799	0.619	0.719	0.724	0.828	1.644	1.564	0.609	1.306	1.448	0.909
Gd	2.823	2.861	3.292	1.608	3.283	1.938	2.809	2.809	2.853	4.432	5.149	2.489	4.368	5.164	3.206
Tb	0.489	0.502	0.558	0.300	0.577	0.336	0.503	0.485	0.490	0.707	0.877	0.453	0.722	0.847	0.551
Dy	3.070	3.165	3.456	1.956	3.663	2.154	3.266	3.093	3.098	4.096	5.395	2.977	4.375	5.208	3.468
Ho	0.652	0.684	0.732	0.440	0.788	0.462	0.703	0.675	0.665	0.808	1.114	0.643	0.900	1.088	0.734
Er	1.845	1.966	2.099	1.271	2.333	1.336	2.046	1.981	1.914	2.210	3.100	1.861	2.523	3.095	2.086
Tm	0.254	0.268	0.284	0.175	0.318	0.186	0.283	0.277	0.261	0.291	0.413	0.251	0.340	0.418	0.284
Yb	1.702	1.797	1.878	1.121	2.163	1.258	1.951	1.852	1.748	1.909	2.686	1.676	2.215	2.751	1.840
Lu	0.258	0.278	0.283	0.172	0.334	0.192	0.303	0.288	0.267	0.286	0.400	0.250	0.328	0.420	0.282
Hf	1.448	1.572	1.492	0.844	1.801	0.899	1.624	1.599	1.370	2.460	2.934	1.405	2.325	2.693	1.627
Ta	0.179	0.197	0.193	0.097	0.290	0.137	0.256	0.251	0.205	0.600	0.392	0.147	0.445	0.533	0.206
Th	0.300	0.330	0.320	0.160	0.520	0.140	0.420	0.380	0.290	0.700	0.670	0.190	0.730	0.710	0.320
U	0.076	0.080	0.082	0.038	0.123	0.036	0.103	0.098	0.068	0.165	0.151	0.042	0.176	0.175	0.074
Nb/U	39.34	42.38	38.90	40.79	38.54	66.67	40.49	40.10	43.82	52.79	36.09	49.76	34.38	45.43	39.32
Nb/Th	9.97	10.27	9.97	9.69	9.12	17.14	9.93	10.34	10.28	12.44	8.13	11.00	8.29	11.20	9.09
Th/U	3.95	4.13	3.90	4.21	4.23	3.89	4.08	3.88	4.26	4.24	4.44	4.52	4.15	4.06	4.32

preferred because it is directly comparable to the average Nb/U values available for modern OIBs and MORBs. The sampling proportions of nine Komati Formation samples to three from each of the Theespruit and Sandspruit Formations is approximately in proportion to their outcrop areas. However, the outcrop area of the formations is poorly known. Th/U ratios vary between 3.88 and 4.44 and average 4.2 ± 0.2, which compares well with a value of 4.1 ± 0.3 determined from Pb isotopes (Brevart and others, 1986).

The incompatible trace elements variations in the basalts are shown on a primitive mantle normalized diagram in figure 1 (Sun and McDonough, 1989). The light REE (LREE) are generally enriched relative to the heavy REE (HREE) but the magnitude of the enrichment is variable, and all but one sample has a pronounced negative Ti anomaly. HREE depletion and negative Ti anomalies are consistent with residual garnet in the mantle source region.

The komatiite trace element data, together with selected major element information, are listed in table 3. MgO contents vary between 18.95 and 32.16 wt.% and Mg#

TABLE 2

Sample location, field description and formation

Sample No.	Location	Field Description	Formation
97-383	25°58'15"S, 30°50'15"E	komatiitic basalt	Komati
97-384	40m SSW of 383	komatiitic basalt	Komati
97-385	25m SSW of 384	komatiitic basalt	Komati
97-386	25°58'08"S, 30°50'19"E	komatiitic basalt	Komati
97-387	25°59'30"S, 30°51'10"E	komatiitic basalt	Komati
97-389	60m S of 387	komatiitic basalt	Komati
97-390	25°59'33"S, 30°51'58"E	komatiitic basalt	Komati
97-391	80m S of 390	komatiitic basalt	Komati
97-392	25°59'32"S, 30°51'56"E	komatiitic basalt	Komati
97-405	25°59'54"S, 30°49'38"E	komatiitic basalt	Theespruit
97-406	26°00'09"S, 30°50'01"E	weakly sheared amphibolite	Theespruit
97-407	26°00'00"S, 30°50'03"E	weakly sheared amphibolite	Theespruit
97-408	26°02'30"S, 30°48'04"E	amphibolite	Sandspruit
97-410	26°04'48"S, 30°04'48"E	amphibolite	Sandspruit
97-411	26°04'47"S, 30°51'08"E	amphibolite	Sandspruit

between 78.3 and 87.5. Three of the Barberton komatiites are Al-depleted, with Al_2O_3/TiO_2 ratios that lie between 10.5 and 11.0. The remaining samples, including 49J from the Barberton, have normal Al contents. Nb/U ratios vary between 24 and 69, Nb/Th ratios between 3.7 and 26 and Th/U ratios between 3.0 and 6.4.

Figure 2 shows primitive mantle normalized incompatible trace element diagrams for the komatiites. The Al-depleted Barberton komatiites are depleted in the HREE and in U and Th relative to Nb, Ta and La. They also have small negative Ti anomalies. The normal Al komatiite, 49J, has a flatter pattern but still shows depletion of U and Th relative to Nb, Ta and La. Three of the four Yilgarn komatiites show similar LREE depletion and have small negative Ti anomalies. The fourth sample, 331/531 from Marshall Pool, has higher incompatible element concentration than the other Yilgarn samples, a Th/U ratio of 5.6 and a Nb/Th ratio of 6. The Th/U ratio of this sample is above any reasonable value for the mantle and its Nb/Th is below the value of 8.0 expected for the primitive mantle. This sample has either been contaminated by continental crust or its Th and U systematics have been disturbed by alteration. It will not be considered further. The sample from Munro Township, 422/95, is strongly depleted in the LREEs and has a pronounced positive Nb-Ta anomaly.

Silica Mobility

The high silica content of many of the Barberton basalts merits comment. The silica content of basalts, derived from normal mantle, is buffered by olivine and orthopyroxene and decreases as the pressure of melting increases. The lowest pressure melting of the mantle occurs at mid-ocean ridges where the magmas produced typically have SiO_2 of less than 50 percent. Bearing in mind that the low Al_2O_3/TiO_2 ratios of the Barberton basalts implies that they formed in the presence of garnet, and therefore at moderate pressure, a SiO_2 content of greater than 50 percent in these rocks is unlikely to be representative of the primary magma. One possibility is that the high SiO_2 basalts are produced by extreme fractional crystallization of a komatiite but there is no correlation between SiO_2 and MgO or between SiO_2 and any of the

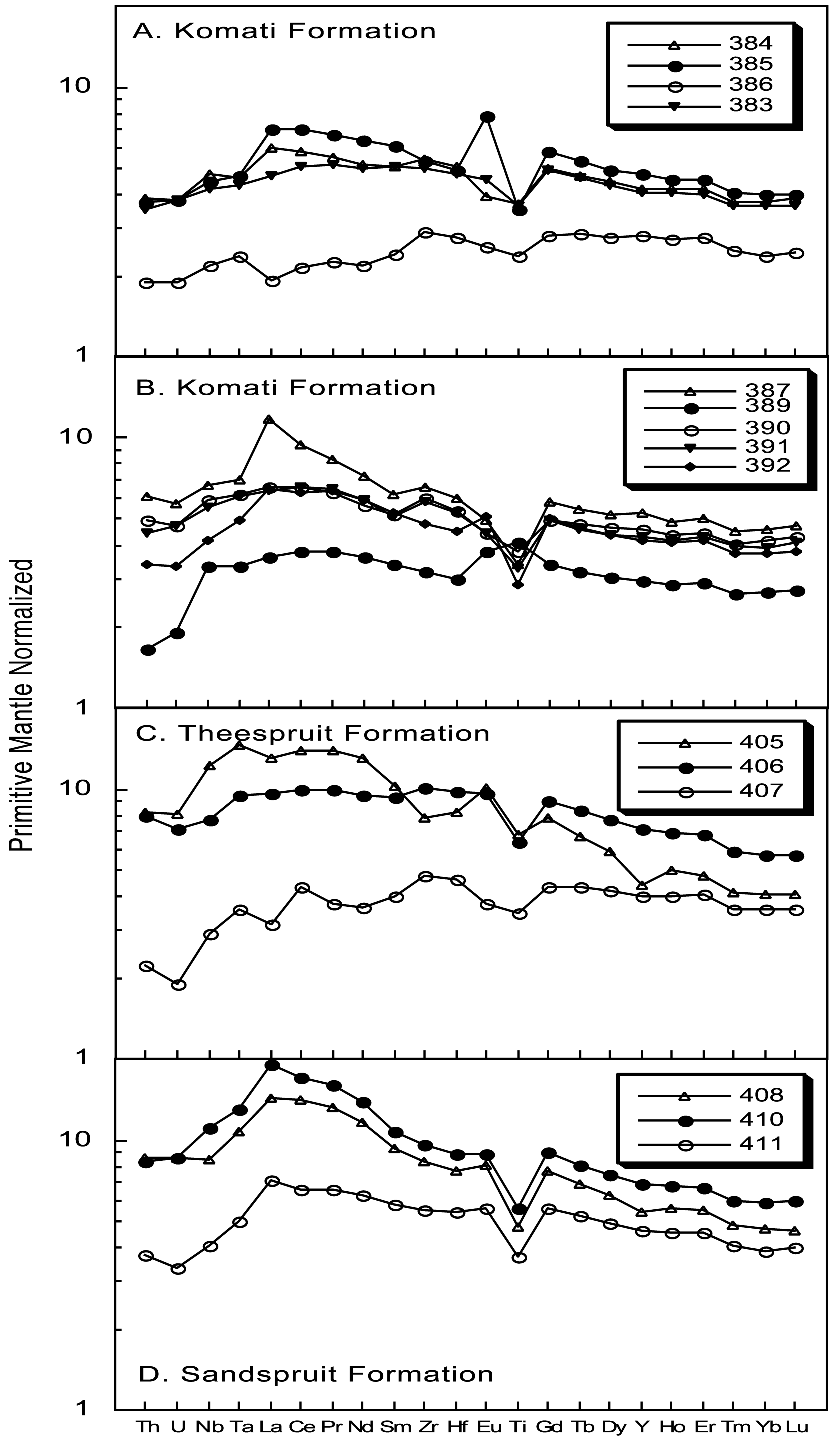

Fig. 1. Mantle normalized incompatible element plots for basaltic komatiite samples from the Komati River section of the Barberton Mountain Land. Note that the light REE do not vary systematically with adjacent trace elements as the abundance of the incompatible elements increases. A and B: Komati Formation, C: Theespruit Formation, and D: Sandspruit Formation. Mantle normalizing values from Sun and McDonough (1989).

TABLE 3

Trace in ppm and selected major elements for spinifex textured komatiites from the Barberton and Yilgarn cratons, and Munro Township

Major element data from Nesbitt and Sun (1976)

	Barberton	Barberton	Barberton	Barberton	Yakabindie	Mt Burgess	Marshall Pool	Scotia	Munro
	49J	331/81	331/777a	331/783	331/347	331/144/42	331/531	SD4/193	422/95
determined by XRF (wt%)									
SiO_2	45.23	47.95	48.41	46.71	45.42	45.58	48.66	44.95	45.85
TiO_2	0.20	0.42	0.41	0.42	0.27	0.30	0.50	0.28	0.35
MgO	32.16	25.29	26.26	26.69	31.46	29.11	18.95	31.94	23.45
mg#	86.1	82.2	83.7	82.1	87.0	85.2	78.3	87.5	81.9
CaO/Al_2O_3	1.45	1.60	1.69	1.65	1.00	0.97	0.96	0.97	1.05
Al_2O_3/TiO_2	18.2	11.0	10.6	10.5	20.7	21.0	18.3	20.7	23.7
determined by ICP-MS (ppm)									
Y	4.280	9.080	9.400	9.690	6.710	7.330	10.600	6.830	9.940
Zr	9.210	26.40	24.85	23.90	14.0[a]	16.3[a]	26.25	15.5[a]	17.68
Nb	0.577	2.290	1.730	1.730	0.507	0.810	1.043	0.520	0.692
La	0.649	1.971	1.850	1.880	0.554	0.650	1.083	0.540	0.403
Ce	1.619	5.710	5.245	5.390	1.642	1.975	3.310	1.685	1.283
Pr	0.257	0.830	0.810	0.847	0.291	0.333	0.579	0.303	0.242
Nd	1.226	4.090	3.910	4.186	1.643	1.863	3.105	1.651	1.480
Sm	0.402	1.227	1.177	1.259	0.602	0.679	1.087	0.618	0.693
Eu	0.147	0.404	0.386	0.389	0.243	0.276	0.393	0.268	0.292
Gd	0.541	1.446	1.463	1.467	0.890	0.957	1.447	0.883	1.179
Tb	0.102	0.260	0.261	0.267	0.167	0.182	0.272	0.168	0.233
Dy	0.648	1.568	1.576	1.580	1.059	1.143	1.710	1.074	1.572
Ho	0.145	0.323	0.333	0.340	0.233	0.254	0.374	0.237	0.351
Er	0.421	0.928	0.936	0.968	0.688	0.742	1.086	0.688	1.039
Yb	0.397	0.820	0.815	0.867	0.640	0.688	0.989	0.631	0.971
Lu	0.062	0.124	0.124	0.132	0.101	0.107	0.147	0.097	0.150
Hf	0.245	0.707	0.666	0.687	nr	nr	0.736	nr	0.538
Ta	0.043	0.137	0.110	0.116	0.038	0.044	0.069	0.046	0.034
Th	0.049	0.217	0.173	0.179	0.042	0.056	0.173	0.051	0.027
U	0.015	0.054	0.038	0.045	0.012	0.015	0.031	0.013	0.010
Nb/U	38.47	42.41	45.53	38.44	42.25	54.00	33.65	40.00	69.20
Nb/Th	11.76	10.55	10.01	9.66	12.07	14.48	6.03	10.20	25.63
Th/U	3.27	4.02	4.55	3.98	3.50	3.73	5.58	3.92	2.70

*determined by XRF
nr = not reported

incompatible elements as might be expected if this were the case. Crustal contamination can also be ruled out because a minimum of 20 percent contamination is required to raise the SiO_2 content of a magma from 50 to 55 percent. This level of contamination is inconsistent with the Nb/U evidence. It is concluded that the most likely explanation for the high SiO_2 content of the Barberton basalts is that the excess SiO_2 was introduced during alteration. The absence of a clear correlation between SiO_2 and any other major or trace element in these rocks supports this view.

Primitive Mantle Normalized Trace Element Plots

Figure 1 is a primitive mantle normalized plot for a selected group of incompatible trace elements that are normally regarded as immobile during alteration. The

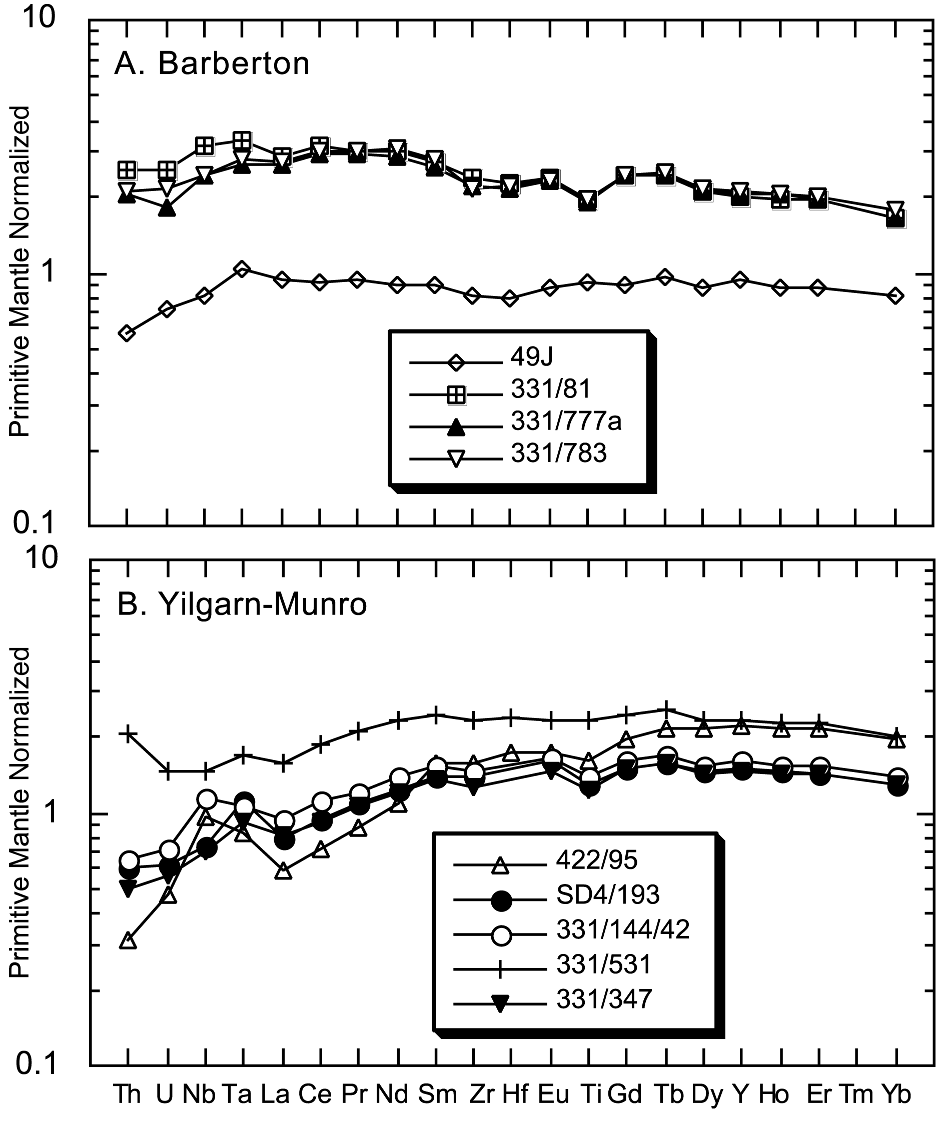

Fig. 2. Mantle normalized incompatible element plots for komatiite samples from the Komati River section of the Barberton Mountain Land, the Yilgarn Craton and Munro Township. Mantle normalizing values from Sun and McDonough (1989).

slope of the patterns indicates that most samples have primitive mantle normalized LREE/HREE ratios that are greater than one, but some have flat REE patterns and two have primitive mantle normalized LREE concentrations that are slightly below the HREE. The HREE concentrations decrease with increasing MgO, as would be expected for a suite of basalts that are related to each other by fraction crystallization, or by different degrees of partial melting of the same mantle source. However, the data do not lie on well-defined olivine control lines, as is the case for some komatiite-basalt suites (Arndt, 1986). A conspicuous feature of the data is that the LREE, from La to Sm, behave erratically and do not correlate with variations in adjacent incompatible elements. This can be demonstrated by omitting the LREE from the diagram (fig. 3). The ratios of the other "immobile", incompatible trace elements, as indicated by the slopes of the patterns, vary systematically, indicating that they have not been affected by the process that has affected the LREE (fig. 3). The overall shape of the pattern can be characterized by the $(Zr/Lu)_n$ or $(Hf/Lu)_n$ ratio, representing the slope of the right hand half of the diagram, and the $(Nb/Zr)_n$ or $(Ta/Hf)_n$ ratio representing the slope of the left hand side. The $(Zr/Lu)_n$ ratio shows little variation and is always between 1 and 2. This consistent depletion in the HREE, relative to Zr and Hf, supports the interpretation, based on the Al_2O_3/TiO_2 ratios of the basalts, that the magma formed in equilibrium with garnet. The $(Nb/Zr)_n$ ratio shows slightly more variability than the $(Zr/Lu)_n$ ratio and may be slightly less than or greater than one. This range is probably controlled by a combination of variations in the $(Nb/Zr)_n$ ratio of the mantle source region (variable extraction of continental crust?) and variations in the amount of garnet in the residual mantle. A notable exception is 405 which has a $(Nb/Zr)_n$ ratio that is distinctly greater than the other samples.

There are two possible explanations for the differences in the behavior of the LREE and adjacent elements on the mantle normalized trace element plot. The first is that variations are due to variable amounts of garnet remaining in the mantle residue after melting. This hypothesis is supported by the samples from the Theespruit and Sandspruit formations. Four of the samples, 405, 406, 408 and 410, have low Al_2O_3/TiO_2 and high LREE, whereas the remaining two samples have higher Al_2O_3/TiO_2 and lower LREE, suggesting that residual garnet is controlling LREE fractionation. However, 387 from the Komati Formation is likewise enriched in LREE but does not have an unusually high Al_2O_3/TiO_2, so there is an exception to this relationship. The second possibility, that should also be considered, is that some of the variation in LREE enrichment was produced by LREE mobility during sea floor alteration, metamorphism or weathering.

Although Sylvester and others (1997) have shown that U was not mobile in the samples they studied from the Norseman-Wiluna greenstone belt, this conclusion does not necessarily apply to the Barberton samples analyzed in this study. Puchtel and others (1998a, 1999), for example, have argued that U is mobile in the Sumozero-Kenozero and Kostomuksha greenstone belts of the Baltic Shield. These samples are characterized by highly variable Th/U. However, in the Barberton there is a strong correlation between Nb/U and Nb/Th (fig. 4), similar to the one documented by Sylvester and others (1997), and variations in Th/U are small. Uranium can only have been mobile in the Barberton samples if Th was also mobile such that the Th/U ratio remained constant over a wide range of Nb/U ratios and this is unlikely. It is therefore assumed that U was not mobile in the Barberton samples.

One of the Barberton samples, the normal Al komatiite 49J, has a measured Th/U ratio of 3.27 and lies well above the correlation line (see fig. 4). It is not clear whether this ratio has been changed by alteration, whether Al-depleted and normal Al komatiites come from source regions with different Th/U ratios, or whether the difference is due to an increase in Th/U ratio of the Al-depleted komatiites during partial melting.

The reliability of the Nb, Th, U systematics for the komatiites analyzed in this study is more difficult to evaluate because there are insufficient data, for individual regions, to use the Nb/Th against Nb/U plots to test for Th-U mobility. An alternative approach is to compare the measured Th/U ratio of the komatiites and basalts with the Th/U ratio determined by Pb isotopes. The Th/U ratio for the Barberton, Yilgarn and Munro komatiites, determined in this way are, 4.1 ± 0.3, 3.86 ± 0.21 and 2.86 to 2.96 respectively (Roddick, 1984; Dupré and others, 1984; Brevart and others, 1986). These values agree favorably with the measured Th/U ratios of the Barberton Al-depleted

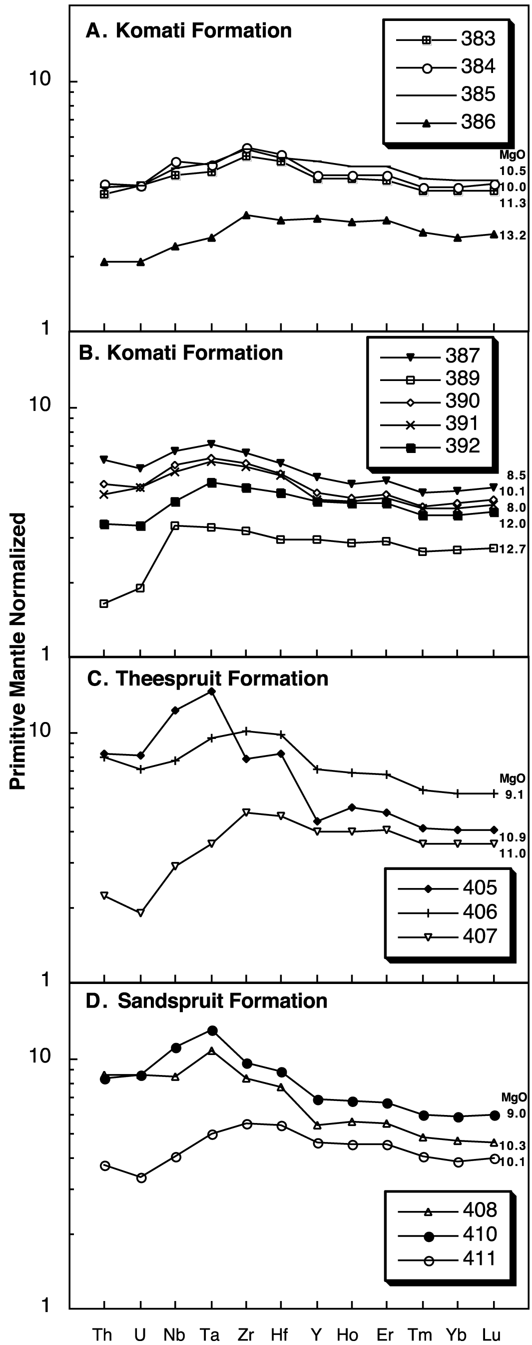

Fig. 3. Mantle normalized incompatible element plots, with the light REE omitted, for basalt and basaltic komatiite samples from the Komati River section of the Barberton Mountain Land. Note that, with the exception of sample 405, the trace element patterns tend to remain parallel as the abundance of the elements increase. A and B, Komati Formation; C, Theespruit Formation; and D, Sandspruit Formation. Mantle normalizing values from Sun and McDonough (1989).

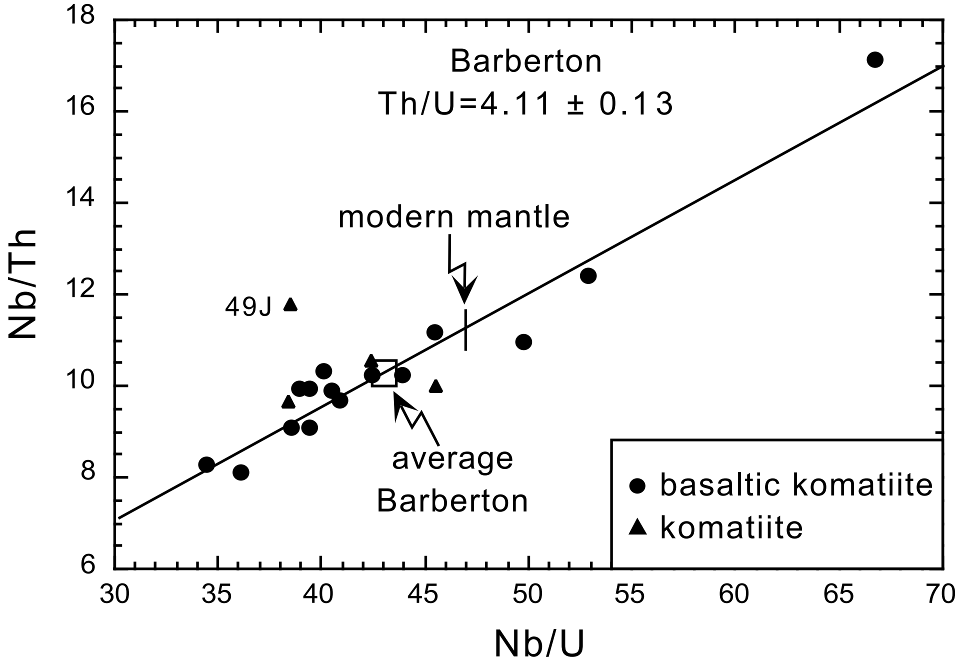

Fig. 4. A plot of Nb/Th against Nb/U for samples from the Komati River section of the Barberton Mountain Land. The open square gives the average Nb/U-Nb/Th for the komatiites and basaltic komatiites and the arrow the average Nb/U for the modern OIB and MORB sources.

komatiites, the Munro Komatiite, and the Yilgarn komatiites with the exception of the discarded Marshall Pool sample (table 3).

Nb, Th AND U DATA FOR OTHER ARCHAEAN BASALTS AND KOMATIITES

Other extensive data sets of Nb, Th, U analyses for Archaean basalt-komatiite association are: (1) the 2.9 to 3.0 Ga Lumby Lake and Steep Rock greenstone belts of the Western Superior Province (Tomlinson and others, 1999), (2) the 2.9 Ga Sumozero-Kenozero greenstone belt of the SE Baltic Shield (Puchtel and others, 1999), (3) the 2.8 Ga Kostomuksha greenstone belt, NW Baltic Shield (Puchtel and others, 1998a), (4) the 2.7 Ga Val d'Or-Stoughton-Roquemare, Tisdale and Munro Townships areas of the Abitibi greenstone belt (Fan and Kerrich, 1997; Kerrich and others, 1999), and (5) the 2.7 Ga Kambalda-Norseman area of the Norseman-Wiluna greenstone belt (Sylvester and others, 1997). The results from these studies, together with data from the komatiites analysed for this study and a suite of basalts from the 2.0 Ga Onega plateau in the Baltic Shield, are plotted in figure 5.

The Kambalda-Norseman basalts and three komatiite samples from the broader Norseman-Wiluna greenstone belt, lie on a mixing line that extends from slightly below the primitive mantle Nb/U ratio of 34 to a ratio of 47. The average Th/U ratio of this suite is 3.86 ± 0.2 which agrees with a value of 3.83 ± 0.13 obtained from Pb isotopes (Roddick, 1984).

Most of the Lumby Lake-Steep Rock samples have Nb/U and Nb/Th ratios that lie near or above the primitive mantle value. The highest Nb/U ratio of the Lumby Lake-Steep Rock samples is 55 and the highest Nb/Th ratio is 13.8. Some of the samples show evidence of crustal contamination in their trace element patterns (Tomlinson and others, 1999). For example, a Type-5 Lumby Lake basalt, not plotted

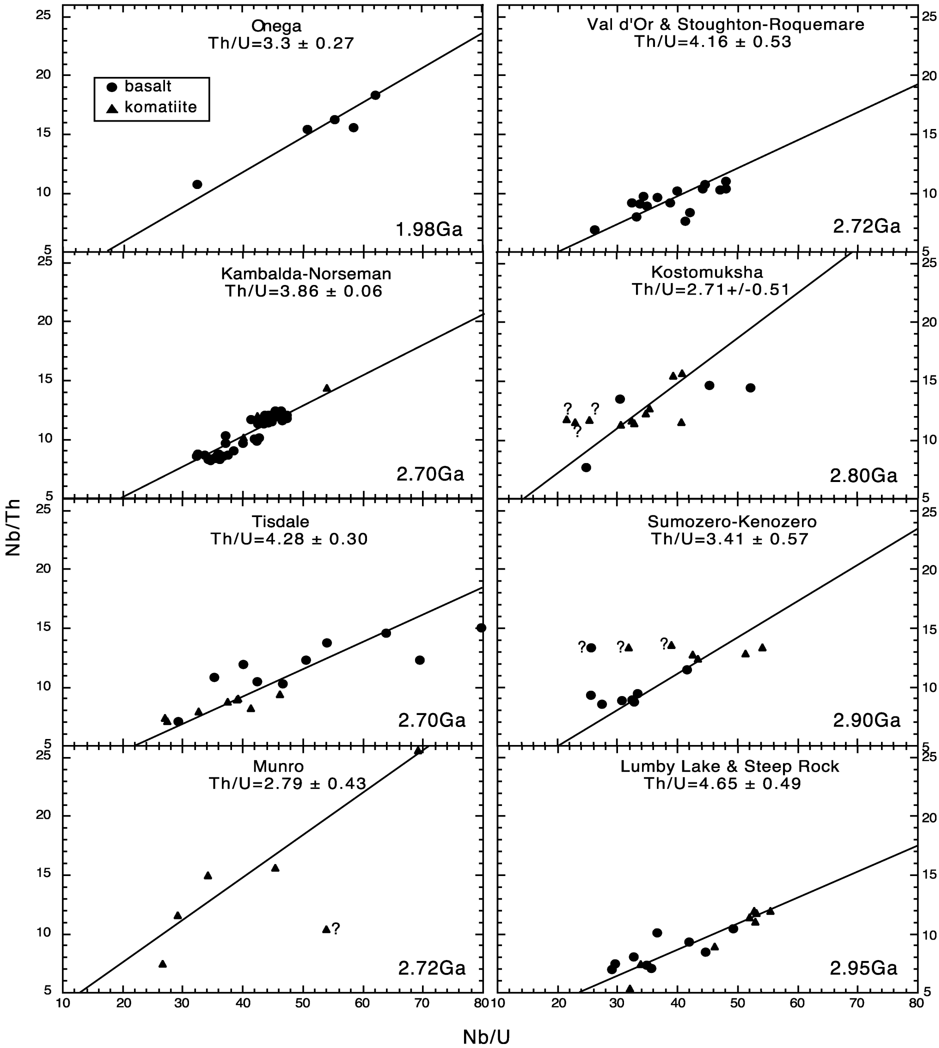

Fig. 5. Plots of Nb/Th against Nb/U for samples from Onega, Kambalda-Norseman, Tisdale and Munro Townships, Val d'Or and Stoughton-Roquemare, Kostomuksha, Sumozero-Kenozero and Lumby Lake-Steep Rock. Data from Sylvester and others (1997), Fan and Kerrich (1997), Puchtel and others (1998a, 1998b, 1999), Tomlinson and others (1999), and Kerrich and others (1999).

on figure 5, has a Nb/U ratio of 11.2, a Nb/Th ratio of 2.6, and a pronounced negative Nb-Ta anomaly in its trace element pattern. The trend seen in the Nb/Th-Nb/U plot, which extends from high values back towards the primitive mantle composition and beyond, is probably largely due to variable amounts of continental crust being incorporated into the basalts and komatiites. Samples with Nb/U below 30 are assumed to have been contaminated by continental crust. They have been rejected when calculating the average Nb/U for the Lumby Lake-Steep Rock suite and for all of the other suites included in this study, to minimize the influence of crustal contamination. Thirty was chosen as the cut off value because it lies at the lower end of the range of estimates for Nb/U in the primitive mantle (Hofmann and others, 1986; Sun and McDonough, 1989). Three Lumby Lake-Steep Rock samples were rejected on this basis. The data also show a scatter in Th/U ratios that are well in excess of the scatter seen in the Barberton and Kambalda-Norseman data. This could be a source characteristic, or be due to U mobility, or to the difficulty of analyzing U at low concentrations. Samples with Th/U above 5 were rejected as being disturbed and unlikely to represent their mantle source region.

Puchtel and others (1998a, 1999) have made detailed geochemical studies of two komatiite-basalt suites from the Baltic Shield, the Kostomuksha and Sumozero-Kenozero greenstone belts, which they interpret to be obducted oceanic plateau. The 2.8 Ga Kostomuksha greenstone belt has a range of Nb/U from 22.5 to 52.1 and a Th/U of 2.71 ± 0.51, slightly lower than the value of 3.01 ± 0.19 calculated from Pb isotopes (Puchtel and others, 1998a). Four of fifteen samples from the Kostomuksha greenstones have measured Nb/U below 30. These low Nb/U values imply that the samples are contaminated by continental crust, which is inconsistent with the obducted oceanic crust hypothesis for the suite. Puchtel and others (1998a) have shown that La, Th and other incompatible elements in the Kostomuksha greenstones lie on an olivine control line, whereas U does not. They attribute this difference to U mobility and this interpretation is consistent with the large variation in the measured Th/U values for the suite. Puchtel and others (1998a) calculated the pre-alteration U concentration, U*, from the measured Th and Th/U calculated from Pb isotopes, making the assumption that the Th/U was the same in all samples prior to alteration. If Nb/U is calculated in this way the number of sub-30 Nb/U is reduced from 4 to 1. The Puchtel and others (1998a) method has been used in this study to determine Nb/U for suites that have published Pb isotope data to minimize the possible effects of U mobility. Note that because the average value of the measured Th/U is similar to the value calculated from Pb isotopes for most suites, it makes little difference whether the measured Nb/U or Nb/U* is used to calculate the average Nb/U for the suites.

Nb/U for the 2.9 Ga Sumozero-Kenozero greenstone belt lie between 26 and 54 and the average Th/U value is 3.41 ± 0.57, which compares with a Th/U of 3.41 ± 0.51 calculated from Pb isotopes (Puchtel and others, 1999). Three of fourteen samples have Nb/U below 30. Uranium again does not lie on an olivine control line, which suggests that U may again be mobile (Puchtel and others, 1999). The number of sub-30 samples reduces to one if Nb/U* is used in preference to measured Nb/U, supporting the use of the Puchtel and others (1998a) method.

The data from Tisdale, Val d'Or-Stoughton-Roquemaure and Munro Townships are similar to those from Lumby Lake and Steep Rocks. The Tisdale points extend from the primitive mantle composition to a maximum Nb/U ratio of 79 and a Nb/Th ratio of 15 and the Val d'Or-Stoughton-Roquemaure suite to a Nb/U of 48 and a Nb/Th of 11. The Munro data extend to a maximum measured Nb/U ratio of 69 and a Nb/Th ratio of 26. Two Munro samples with Th/U ratios above 5 have been omitted from figure 5. The scatter about the Th/U correlation line is again greater for the Tisdale, Val d'Or-Stoughton-Roquemaure and Munro Township data than for the Barberton and Kambalda-Norseman data, which suggests that U may have been mobile in these suites. Nb/U* has therefore been used in preference to measured value to calculate the average Nb/U for the Munro suite, but this is not possible for the Tisdale and Val d'Or-Stoughton-Roquemaure because no Pb isotopic data are available for these suites. Two samples, one with low Nb/U* and one with high Th/U, were rejected from the average Nb/U calculations for both the Munro and Val d'Or-Stoughton-Roquemaure suites. Three Tisdale samples, two with Th/U above 5 and one with a sub-30 Nb/U, were also rejected.

Four samples of lavas and the average value of a sill from the Suisaarian suite of the 2.0 Ga Onega Plateau, in the Baltic Shield, have also been included in this study as representative of the early Proterozoic mantle. Niobium/U* for these samples range between 32.3 and 62.1 and the average Th/U is 3.46, which compares with 3.4 calculated from Pb isotopes (Puchtel and others, 1998b). Six samples from the Zaonega suite, five of which have Nb/U* below 30, were rejected as being contaminated by continental crust (Puchtel and others, 1998b).

DISCUSSION

Fractionation of Th from U During Partial Melting

An important assumption of this study is that Nb/U, Nb/Th and Th/U are not significantly fractionated during partial melting. Hofmann and others (1986) have argued that, because $D_{Nb} \sim D_U$, Nb/U is not fractionated during partial melting. However, if $D_{Th} \neq D_U$, Th/U may be fractionated during partial melting and, if it is and Nb/U is not, Nb/Th must also be fractionated during melting.

The best evidence for Th/U fractionation during partial melting to produce basalt comes from uranium series disequilibrium studies of basalts. These studies show that both MORBs and OIBs have activity ratios r that lie between 1 and 1.4. Initially this was interpreted to indicate that the Th/U of the melt was r times higher than the Th/U of the mantle source region (Allègre and Condomines, 1982). However dynamic melting models have shown that the Th/U fraction must always be less than r by an amount that is dependent on the rate of upwelling of the mantle and the geometry of the melt zone (McKenzie, 1985; Williams and Gill, 1989). The constraints imposed by the uranium series disequilibrium studies are (1) that $D_{Th} > D_u$ and (2) that the magnitude of Th/U fractionation during melting is less than r.

If the degree of partial melting (F) is high, so that $F >> D_{Th}$ and D_U, all of the highly incompatible elements are concentrated in the melt and the Th/U of the melt is approximately equal to the Th/U ratio of the mantle source. This conclusion is true for all melting models (Williams and Gill, 1989). If $D_{Th} < D_U$, the Th/U of the basalt must be greater than the Th/U of the mantle source region and the Th/U of the residue must always be less. From mass balance considerations, the increase in the Th/U of the melt can be very small at high degrees of partial melting, but the decrease in the Th/U ratio of the residue can be substantial, depending on F and the difference between D_{Th} and D_U.

The assumption that the Th/U ratio of a melt is the same as its mantle source region may not be valid for Al-depleted komatiites, which are interpreted to form in the transition zone and to have abundant garnet in their residue (Sun and Nesbitt, 1978). Garnet is the mantle mineral with the highest partition coefficient for Th and U (Salters and Longhi, 1999). If abundant garnet remains in the residue the assumption that $F >> D_{Th}$ and D_U may no longer be valid. As a consequence, the Th/U ratio of an Al-depleted komatiite may be significantly higher than its source region. Fortunately they are readily distinguished from other komatiites by their high CaO/Al_2O_3 and low Al_2O_3/TiO_2 (Sun and Nesbitt, 1978).

The Barberton normal Al komatiite, 49J, has a Th/U ratio of 3.3 which is lower than the value of 4.2 for the Al-depleted komatiites and basalts. One possible explanation for this difference is that the Th/U ratio of the source region for both types of magma is 3.3 and the higher Th/U ratio of the Al-depleted komatiites is due to the presence of residual garnet in the source region. However, the limited range of Th/U ratios of the Barberton komatiites and basalts, over the wide range of partial melting required to produce komatiites and basalts, make it unlikely that substantial fractionation of Th from U occurred during melting.

The Nature of the High and Low Nb/U End-members

As is the case with the 2.7 Ga basalts from the Kambalda-Norseman area of Western Australia, the Barberton data lie on a mixing array between an end-member with Nb/U and Nb/Th ratios similar to the primitive mantle, and an end-member with high Nb/U and Nb/Th. The high Nb/U-Nb/Th end-member is mantle from which continental crust has been extracted. The nature of the low Nb/U-Nb/Th end-member is less certain. There are three possibilities: (1) it could be primitive mantle that has never melted to produce basaltic or continental crust, (2) it could represent a depleted mantle reservoir from which basaltic crust has been removed but not continental crust, or (3), the linear array could represent a suite of elevated Nb/U basalts that are variably contaminated by continental crust. Distinguishing between these possibilities is important.

If the array was produced by mixing between a primitive mantle and mantle with elevated Nb/U, the data would provide evidence that extraction of the continental crust produced a highly heterogeneous mantle that persisted from at least 3.5 Ga to 2.7 Ga. If this interpretation is correct, only part of the mantle sampled by the Barberton and Kambalda-Norseman basalts had elevated Nb/U, which implies that only part of the mantle source region for these basalts has had continental crust extracted from it. Alternatively, if the array is due to variable levels of crustal contamination, the measured Nb/U ratios are minimum values for the mantle source region. All of the samples could then be from an elevated Nb/U mantle from which some continental crust has been extracted, with much of the variability in Nb/U resulting from variations in the amount of crustal contamination. If continental crust extraction produced a mantle with a homogeneous Nb/U, the maximum Nb/U of a suite of basalts will provide the best estimate of the Nb/U in the mantle source region. However it is more likely that extraction of continental crust was heterogeneous, leaving behind a mantle with a variable Nb/U. The average Nb/U ratio of the uncontaminated basalts in this case is uncertain. It must be greater than the average of the measured values but less than the high Nb/U end-member. These conclusions also apply to the other suites shown in figure 5.

There is a simple test that can be used to discount the first possibility for the Kambalda-Norseman basalts. If the linear relationship seen in the Kambalda-Norseman data is due to a mixing between primitive and Nb/U enriched mantle, the mixing array is constrained to pass through the primitive mantle, which has chondritic values of Nb/U = 34 and $\varepsilon_{Nd} = 0$. Twelve of the Norsemen basalts analyzed by Sylvester and others (1997), and 16 gabbro samples from 3 sills at Kambalda (Carey, ms, 1994), were analyzed by Ghaderi (ms, 1998) for Nd isotopes. The ε_{Nd} value for the 12 Norseman basalts range between +1.3 and +3.2 and there is no indication of ε_{Nd} decreasing towards zero as the Nb/U ratio approaches the chondritic value. The three sills have chondritic Nb/U and Nb/Th ratios and ε_{Nd} values that range between 2.0 and 4.0 with a mean of 2.7 ± 0.5 for 16 analyses. The mantle source of the low Nb/U end-member of the Kambalda-Norseman basalts therefore can not be primitive mantle.

No Nd isotopic data are available for the Barberton samples analyzed in this study. It is therefore not possible to apply the tests used to identify the low Nb/U end-member in the Kambalda-Norseman basalts to the Barberton basalts. Hafnium isotope measurements of 9 Barberton komatiites and basalts, including 4 of the samples analysed for this study (385, 405, 406 and 407), yield ε_{Hf} values between +0.2 and +7.1 (Blichert-Toft and Arndt, 1999). If the high value of +7.1, which appears to be an outlier, is excluded the mean is 2.1 ± 1.0 (1σ). There is no evidence of a correlation between Nb/U and ε_{Hf} for samples for which both Hf and Nb/U data are available but the number of samples for which both measurements have been made is only 4. It therefore appears unlikely that the low Nb/U Barberton end-member is pristine mantle.

Sylvester and others (1997) were unable to distinguish between the second and third possibilities for the Kambalda-Norseman basalts. The problem is that if the high Nb/U end-member is produced by removing continental crust from the mantle, basalts that are contaminated with continental crust lie on a mixing array between continental crust and Nb/U enriched mantle, which passes through the primitive mantle. Furthermore, the amount of continental crustal contamination required to shift the Nb/U ratio of the Kambalda-Norseman basalts from the enriched end-member (Nb/U = 47) to the primitive end-member (Nb/U = 34) is only 1 percent, which has a negligible influence on Nd isotopes. As a consequence, it is difficult to distinguish between basalts produced from mantle that is heterogeneous because variable amounts of continental crust have been removed from its source, and basalts produced from a Nb/U enriched source that has been variably contaminated by a small amount of continental crust.

The likely extent of Nb/U variability in the Archaean mantle can be assessed from the variability in Nb/U modern oceanic basalts. Niobium/U in modern OIBs, with the exception of two samples from the Society Islands, range from 30 to 106 (Hofmann and others, 1986; Hemond and others, 1993; Eggins, unpublished data) and MORBs from 41 to 86 (Hofmann and others, 1986). In these cases the variation can not be due to contamination by continental crust and must be due to these basalts being derived from a heterogeneous mantle. It is therefore likely that most of the variation in Nb/U in the Barberton basalts is derived from a heterogeneous mantle. However, because contamination by continental crust is a common feature of Archaean basalts and komatiites from the Barberton region, Kambalda and elsewhere, the possibility of crustal contamination must also be considered. For example, the formation that overlies the basalts and komatiites that were analyzed by Sylvester and others (1997) at Kambalda shows unambiguous evidence of crustal contamination (Arndt and Jenner, 1986). Similarly, basalts from the top of Komatii Formation in the Barberton region, collected by A. Glikson, are contaminated by continental crust (IHC, unpublished data). It is therefore likely that some of the Barberton samples analysed for this study have undergone contamination by small amounts of continental crust. If some of the variation in the Nb/U ratios in the Barberton basalts is due to crustal contamination, the average Nb/U ratio of the source region must be greater than the average of the measured values. This conclusion is also true for other komatiite-basalt suites that have erupted onto continental crust.

Some of the variation in Nb/U seen in the Archaean komatiites and basalts may be due to recycling of sediment into the mantle (Armstrong, 1991). The excluded basalts from the Society Islands for example, which have sub-chondritic Nb/U of 20, sample EM2-type mantle that is thought to contain a sedimentary component. Their low Nb/U is consistent with this interpretation. However, only 2 of 69 OIBs and MORBs analyzed by Hofmann and others (1986) have sub-chondritic Nb/U values, suggesting that sedimentary recycling is not an important process in the modern OIB and MORB sources. In any case sedimentary material returned to the mantle by recycling should be considered to be part of the mantle and samples affected by this process should be averaged with other samples so that this process is taken into account.

RATE OF GROWTH OF THE ARCHAEAN CONTINENTAL CRUST

The most significant feature of the data is the elevated Nb/U and Nb/Th ratios in the 3.5 Ga Barberton basalts. The formation of an early mafic crust, or crystallization in a magma ocean, may fractionate Sm from Nd and Lu from Hf but these processes can not fractionate Nb from U. The high Nb/U in the Barberton basalts provide unambiguous evidence that that they have formed by melting mantle from which continental crust had already been extracted. Furthermore the relationship between Nb/U and the fraction of continental crust extracted from the mantle is not time dependent, allowing a direct comparison between Nb/U in basalts of different ages. This in turn allows the amount of continental crust extracted from mantle source regions to be quantified as a fraction of the amount extracted from the modern mantle. However before this can be done two questions must be addressed:

(1) which part of the Archaean mantle do komatiites and associated basalts sample, and
(2) how representative is the sampled material of the Archaean mantle?

Tectonic Setting of the Archaean Komatiite-basalt Association

Any inference drawn about the chemistry of the Archaean mantle from komatiites and basalts is critically dependent on the tectonic setting in which the komatiite-basalt association is thought to have formed. Modern basalts form in three tectonic settings in the modern mantle convection cycle: subduction zones, plumes and mid-ocean ridges, and the same was probably true for the Archaean. Subduction zone magmas originate from a mantle source region that was modified by metasomatic fluid derived from the down-going slab, and provide little information about the composition of the unmodified mantle. Plume magmas provide information about the boundary layer from which plumes originate, and MORBs sample the upper mantle. Distinguishing between these possibilities has obvious implications for how the Nb-Th-U data are interpreted.

The case for komatiites is clear. They are the highest temperature melts produced from the mantle, with liquidus temperatures that can exceed 1600°C (Green, 1975). Komatiites can only be produced by melting the hottest part of the mantle, that is, by melting mantle plumes (Jarvis and Campbell, 1983; Campbell and others, 1989).

The origin of basalts associated with komatiites, however, is less straightforward. The high Nb/U ratios and general trace element characteristics of the Barberton basalts analysed for this study preclude the possibility that they are island arc basalts, leaving plumes and mid-ocean ridges as the most likely alternatives. The relevant characteristics of the Barberton basalts are:

(1) They are inter-bedded with high temperature komatiites that are generally attributed to mantle plumes.
(2) They have high MgO (8.5 to 13.2 wt.% MgO) and low REE concentrations, indicating that they are high temperature basalts that formed at a high degree of partial melting.
(3) Their relatively HREE depletion and low Al_2O_3/TiO_2 ratio indicate the presence of abundant garnet in their source region, which is consistent with deep melting.

If the Archaean mantle was hotter than the modern mantle, Archaean MORBs might be expected to have started melting deeper in the mantle, possibly in the presence of residual garnet. It is therefore likely that Archaean MORBs would have higher maximum MgO contents than modern MORBs and it is plausible that they would show the HREE depletion and low Al_2O_3/TiO_2 ratios characteristic of the Barberton basalts. Icelandic picrites, which were produced when the Iceland plume rose beneath a mid ocean ridge, provide an indication of what to expect at an Archaean spreading center. Here anomalously hot mantle rose to shallow depths beneath a mid-ocean ridge and melted to produce picrites and basalts, as would have been the case for an Archaean spreading center if the Archaean mantle was hotter than the modern mantle. The Iceland picrites have flat HREE patterns and Al_2O_3/TiO_2 ratios that are close to or above the chondritic value (Hemond and others, 1993). Melting of hot Archaean mantle at a spreading center is unlikely to produce HREE depleted basalts with sub-chondritic Al_2O_3/TiO_2 ratios.

The closest modern equivalent of the Barberton basalts are the picrites from Baffin Bay which, like the Barberton basalts, are characterized by low Al_2O_3/TiO_2 ratios and HREE depletion (Lightfoot and others, 1997). They also formed by melting of the Iceland plume, but in this case, melting occurred beneath stable lithosphere. The difference between melting hot mantle in a plume rising beneath stable lithosphere versus melting at a spreading center is that in the former, the ascent of the hot mantle is arrested by the base of the lithosphere, which effectively provides a lid to the column of melting, whereas in the latter, the column of melting extends almost to the surface. Where the Iceland plume melts beneath stable lithosphere, all or most of the melting takes place at a depth below the spinel-garnet transition and the resulting melts show a clear garnet signature. Where the plume rises beneath a spreading center, melting extends to a much shallower depth, and because of the strong influence of pressure on melting, most of melting occurs above the spinel-garnet transition. As a consequence, the high-pressure melts that show the garnet signature are overwhelmed by low pressure melts that do not, so that the evidence for melting in the garnet field is lost. It is suggested that presence of a clear garnet signature in the Barberton basalts, together with their association with komatiites, make it likely that both the komatiites and the basalts are the product of an Archaean mantle plume that melted beneath stable lithosphere.

All of the basalts and komatiites found in the Steep Rock, Lumby Lake, Kostomukshu, Val d'Or-Stoughton-Roquemare and Tisdale areas include Al-depleted varieties (Fan and Kerrich, 1997; Tomlinson and others, 1999) so the arguments used to link the Barberton basalts to a mantle plume apply equally for these occurrences. The Norseman-Wiluna, Sumozero-Kenozero, Onega and the Munro basalts, however, do not include Al-depleted basalts (or komatiites). Nevertheless, the geochemical similarity between the basalts from these areas and the Al-depleted basalts, and the close association of all of these basalts with high temperature komatiites suggest that the normal Al basalts included in this study, are also the product of melting a mantle plume. In the discussion that follows it will be assumed that Archaean komatiite-basalt associations are the products of melting of Archaean mantle plumes.

How Representative of the Archaean Mantle is the Material Sampled by the Komatiite-basalt Association?

Before this question can be answered it is necessary to identify the source of mantle plumes. Plumes must originate from a thermal boundary layer within the mantle, either the core-mantle boundary or the boundary between the upper and lower mantles. Distinguishing between these possibilities has implications for the volume of mantle represented by the Archaean komatiite-basalt association. It is likely that modern plumes originate from the core-mantle boundary. There are a number of observations and arguments that support this view including:

(1) Seismic images that show slabs sinking through the 670 kilometer discontinuity (van der Hilst and others, 1991; van der Hilst, 1995; Widiyantoro and van der Hilst, 1996) and plumes rising from the core-mantle boundary (Helmberger and others, 1998; Russell and others, 1998).

(2) Displacement of the 670 kilometer discontinuity to a greater depth below Iceland is interpreted to be due to a column of anomalously hot mantle passing through the 670 kilometer discontinuity beneath Iceland (Shen and others, 1998).

(3) The inferred size of mantle plume heads required to produce continental flood basalts (Campbell and Griffiths, 1990).

(4) The fixed position of hotspots relative to each other (Gurnis and Davies, 1986).

(5) The estimated heat flux carried by all plumes is less than 10 percent of Earth's total heat budget, which is consistent with plumes originating from the core-mantle boundary but is inconsistent with plumes originating from an

upper mantle-lower mantle boundary, which would require at least 70 percent of the heat to be carried by plumes (Davies, 1988).

It is likely that Archaean plumes had the same boundary layer source as modern plumes, that is that they originated from the core-mantle boundary.

The nature of mantle convection.—Whether the mantle convects in one layer or two was, until recently, a hotly debated topic. The recognition that subducted slabs and rising plumes can pass through the 670 kilometer discontinuity, as discussed above, has ended that debate. It is now widely accepted that the mantle convects as a single layer. Furthermore, it will be shown that a layered mantle is inconsistent with the Nb/U values of modern OIBs and MORBs. In the discussion that follows it will be assumed that the mantle convects in a single layer, with plumes originating from the core-mantle boundary.

What fraction of the Archaean mantle has elevated Nb/U?—Nb/U enriched mantle must have developed at the top of the mantle, below the regions where continental crust was forming. Some of this material was apparently carried to the core-mantle boundary where it collected to form the source material for Archaean plumes. That is, mantle with elevated Nb/U must have occurred at both the top and bottom of the 3.5 Ga mantle. A feature of the modern mantle is that although both the OIB and MORB sources are highly heterogeneous, their average values are the same (Hofmann and others, 1986). This requires that the Nb/U in the modern mantle was well stirred on a broad scale by mantle convection so that the average Nb/U in the source of plumes (bottom of the mantle) and MORB source (top of the mantle) are the same.

It is likely that the average Nb/U of the upper and lower mantle were also the same, or at least similar, by 3.0 Ga. Enhanced heat production in the early Earth must have led to a hotter, lower viscosity Archaean mantle and to a rate of mantle convection and stirring that was much greater than it is in the modern mantle. Heat production was approximately four and a half times as great at 4.5 Ga, and twice as great at the end of the Archaean, as it is today. The rate of mantle convection scales with the square of the rate of heat production (Davies, 2002). As a consequence mantle convection, and therefore stirring, was ~20x faster at 4.5 Ga and ~5x as fast at the end of the Archaean, as it is in the modern mantle. This is illustrated in figure 6, which shows the total percentage of stirring in the mantle as a function of time. Twenty percent of the total stirring occurred in the first 300 Myr of Earth's history, which is approximately equal to the amount of stirring that occurred in the last 2.0 Gyr, and 50 percent of the total stirring occurred in the first 1.2 Gyr. It is therefore likely, that by the end of the Archaean, the mantle was dominated by Nb/U enriched material and that average Nb/U of the upper mantle was similar to the average of the Archaean plume source (bottom of the mantle), as sampled by komatiites and their associated basalts. That is, it is probably safe to assume that the mantle was well mixed on a broad scale and that there is no systematic difference between the average Nb/U of the mantle sampled by komatiite-basalt suites and the average Nb/U of the remainder of the mantle. If there is a difference between the top and bottom of the mantle, the bottom, which is furthest from the region where continental crust is extracted, should have the lower Nb/U. As a consequence, assuming that the average Nb/U of plume basalts and komatiites is representative of the mantle as a whole, will lead to a conservative estimate of the amount of continental crust that has been extracted from the mantle.

The Fraction of Continental Crust Extracted from the Mantle

The simplest and least model-dependent way of interpreting the Nb/U data is to calculate the fraction of material, with the trace element composition of the bulk continental crust, which must be removed from the mantle to produce a given change in its Nb/U ratio. The mantle is considered to be made up of a series of finite elements, each with its own Nb/U ratio. The volume of each of these elements is defined as the

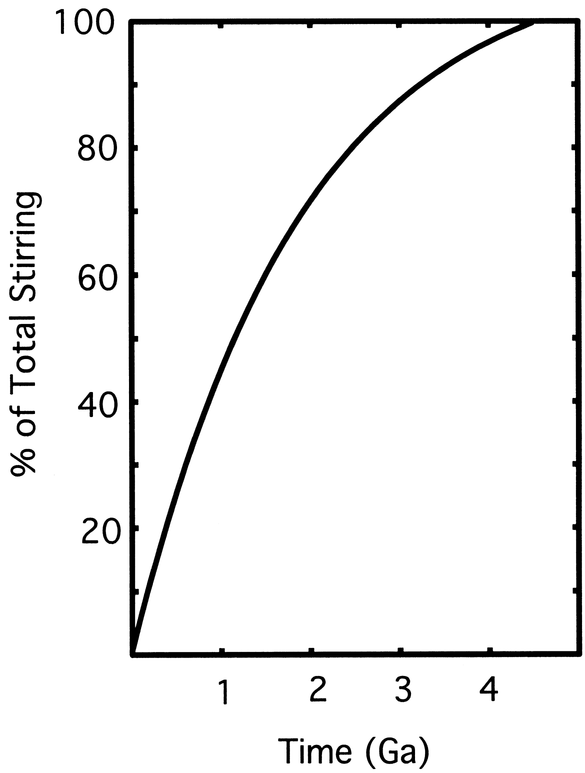

Fig. 6. The percentage of total stirring in the mantle as a function of time. Adapted from Davies (2002).

volume of mantle sampled by the individual volcanic flows that are analyzed for trace elements and/or radiogenic isotopes. The calculations are concerned only with the initial and final Nb/U ratios of the mantle and ignore the complexities of how the continental crust formed. The results, for the continental crust compositions of Taylor and McLennan (1985), Rudnick and Fountain (1995), and McLennan (2001) are shown in figure 7. The Taylor and McLennan (1985) composition requires the extraction of appreciably more continental crust to achieve a given change in the Nb/U ratio of the residual mantle than the composition of Rudnick and Fountain (1995), because the former has lower concentrations of Nb and U than the latter. The McLennan composition is between these extremes.

If the amount of continental crust extracted from the source of Archaean komatiites and basalts is expressed as a percentage of the amount of continental crust extracted from the average modern MORB and OIB sources, the results are similar regardless of which values are used for the continental crust (fig. 8). This is because the ratios of most incompatible elements, including Nb and U, are similar for all of the crustal compositions and because the curves are constrained to have the same Nb/U at 0 percent and 100 percent continental crust extraction. If the average Nb/U of the source region of the Barberton komatiites and basalts is 43, the average percentage of the continental crust removed from it is 75 percent of the amount removed from the modern OIB and MORB sources.

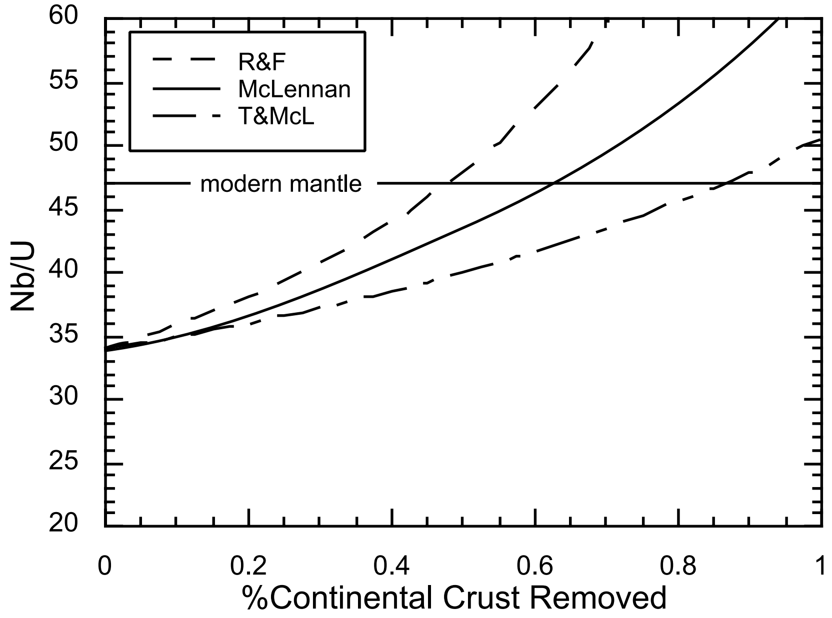

Fig. 7. Effect of extracting different percentages of continental crust from a finite volume of mantle on its Nb/U ratio. The concentrations of Nb, Th and U used for the continental crust are taken from Rudnick and Fountain (1995; Nb = 15, Th = 6.1, U = 1.54), McLennan (2001; Nb = 8, Th = 4.2, U = 1.1) and Taylor and McLennan (1985; Nb = 11, Th = 3.5, U = 0.91). The mantle Nb, Th and U values are from Sun and McDonough (1989; Nb = 0.713, Th = 0.0.85, U = 0.021).

Continental Crust Extraction Through Time

Figure 9 is a plot of Nb/U against time for the komatiites and associated basalts discussed in the previous section. Both the average and maximum values are plotted, on the assumption that some of the variation in Nb/U is due to crustal contamination. Samples with Nb/U below 30 have been omitted from the average because their sub-chondritic values are attributed to crustal contamination. Notice that average Nb/U varies between 38 and 49 and that there is little suggestion of a decrease in this ratio with increasing time. The percentage of continental crust extracted from the sources of the Archaean suites included in this study, expressed as a percentage of the crust extracted from the modern MORB and OIB source, is shown on the side of figure 9. It varies between 45 percent and 110 percent.

Average Amount of Continental Crust Extracted from the Archaean Mantle

It is not possible to determine the average Nb/U for the Archaean mantle from an individual suite because the average Nb/U of the individual Archaean komatiite-basalt suites is variable. This is also true for modern plumes suites. The average Nb/U of the Iceland and Reunion basalts are 64 and 41 respectively (Hemond and others, 1993; Albarède and others, 1997). It is only when the data from a large number of OIBs are averaged, from several sites, that a reproducible result is obtained. For example, the average Nb/U of 41 OIBs analyzed by Hofmann and others (1986) is 47, which compares with 47 for 101 OIBs analyzed by Eggins (unpublished data). The best way to assess the average Nb/U of the late Archaean mantle is to include all of the Nb/U data for late Archaean komatiite-basalt suites.

An average Nb/U has been calculated for one hundred and two analyses from the seven late Archaean basalt-komatiite suites included in this study, which range in age

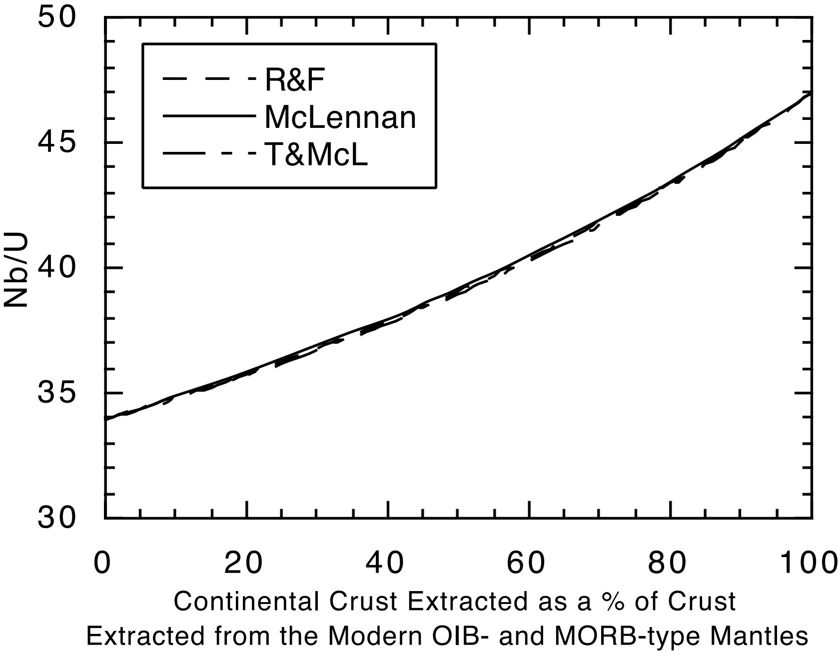

Fig. 8. Effect on the Nb/U ratio of the mantle of extracting different amounts of continental crust, expressed as a percentage of the amount extracted from the modern mantle. The concentration of Nb, Th and U of the continental crust and mantle are the same as for figure 6.

from 2.7 to 2.95 Ga, and have an average age of ~2.8 Ga. The average Nb/U value has been calculated in two ways; by averaging the average Nb/U for each of the suites and by taking a grand average of all of the Nb/U data. The former gives an average Nb/U of 41.9 ± 2.7 (1σ) and the latter 42.2 ± 1.4 (2σ standard error). The grand average method has been used because it is the method used to calculate the average for modern OIB and MORB sources and therefore forms a better basis for comparison with the modern mantle. No attempt has been made to weight the suites or individual analyses according to the volume of mantle they represent because the data required to do this are unavailable. However, because the number of data used to calculate the average is large, a correction of this type is unlikely to affect the result. Taking 42.2 ± 1.4 as the average Nb/U of the late Archaean mantle gives 70 ± 10 percent for the amount of continental crust extracted from the mantle as a percentage of the amount extracted from the modern mantle. This figure should be regarded as a minimum because basalts and komatiites that have erupted onto continental crust may have had their Nb/U reduced by crustal contamination. However two of the suites, Sumozero-Kenozero and Kostomuksha, are interpreted by Puchtel and others (1998a, 1999) to be obducted oceanic plateaus. If this interpretation is correct the basalts and komatiites from these suites cannot be contaminated by continental crust. Their average Nb/U* (38.2 and 38.6) lies at the low end of the range for the Archaean komatiite-basalt suites, which suggests that continental crust contamination may not have a major influence on the average Nb/U of the other suites, provided the precaution is taken of rejecting samples with Nb/U below 30.

The average Nb/U value of 43 for the Barberton suite is slightly above the average for the other Archaean samples. It suggests that extensive continental crust may have

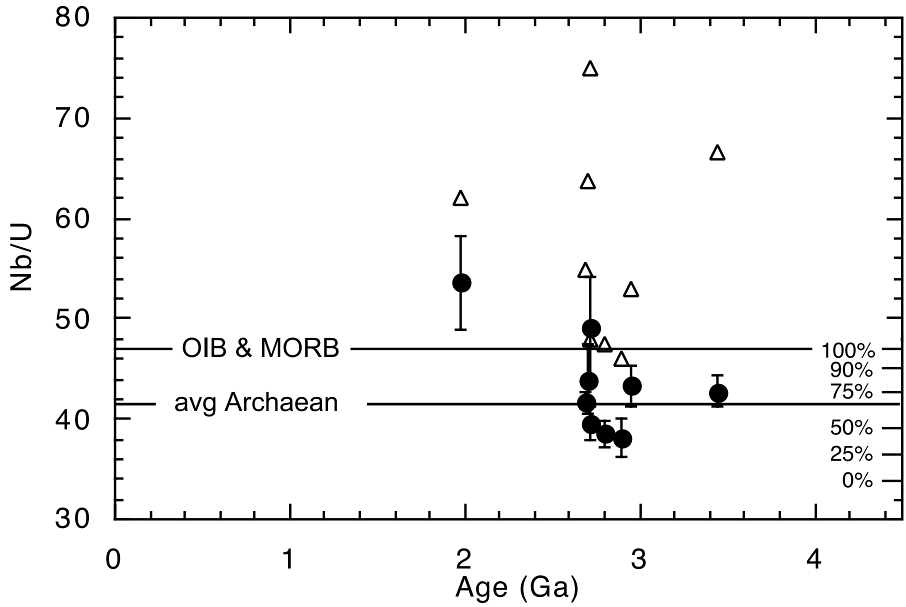

Fig. 9. Variations in Nb/U of basalt-komatiite suites through time. The circles give the average for each suite and the triangles the maximum value. Error bars are 1σ standard errors. Percentage crust extracted is expressed as a percentage of the amount extracted from the modern MORB and OIB sources. Note that the Onega point is based on only 5 samples. Barberton, data this study; Lumby Lake-Steep Rock, data from Tomlinson and others (1999); Sumozero-Kenozero, from Puchtel and others (1999); Kostomuksha, from Puchtel and others (1998a); Tisdale and Munro, from Fan and Kerrich (1997); Val d'Or-Stoughton-Roquemare, from Kerrich and others (1999); Kambalda-Norseman, from Sylvester and others (1997); and Onega, from Puchtel and others (1998b).

existed as far back as 3.5 Ga but it is difficult to be as confident on this point because samples of the 3.5 Ga mantle are confined to a single suite of komatiites and basalts.

Timing of the Increase in Nb/U in the Archaean Mantle

It should be remembered that the mantle sampled by Archaean plumes acquired its high Nb/U in the upper mantle. It takes time for material to sink from the upper mantle to the core-mantle boundary and to return in plumes to the top mantle where it can melt to form basalts and komatiites. Isotopic studies of OIBs suggest that the time-scale for this cycle is 1 to 2 billion years in the modern mantle (Chase, 1982). Heat production in the late Archaean mantle, between 2.7 and 3.0 Ga, was 2 to 2.2 times higher than it is today and this is expected to have resulted in mantle convection being 4 to 5 times faster (Davies, 2002). It is therefore likely that the mantle sampled by Archaean plumes developed its high Nb/U in the upper mantle 200 or 400 million years before it melted to produce komatiites and basalts. This pushes the timing of increase in the Nb/U of the mantle source region of the 2.8 Ga Archaean basalts and komatiites back to 3.1 Ga or even earlier. Similarly the increase in Nb/U seen in the 3.5 Ga Barberton samples probably occurred at or before 3.8 Ga.

SECULAR VARIATION IN THE Th/U RATIO OF THE MANTLE

Variations in Th/U in komatiites and basalts with time have been used to argue that the mantle maintained a Th/U close to its primitive mantle value of about 4.0 during the Archaean and early Proterozoic. It then underwent a period of accelerated decline at ~ 2.0 Ga, until it reached its modern value of ~ 2.3 in the upper mantle. The accelerated decline in the Th/U ratio is attributed to a change in the partial pressure of oxygen in the atmosphere at 2.0 Ga (McCulloch, 1993; Staudigel and others, 1995; Elliott and others, 1999; and Collerson and Kamber, 1999). According to this hypothesis the partial pressure of oxygen in the Archaean atmosphere was low so that U remained as immobile U^{4+} during weathering. At about 2.0 Ga the partial pressure of oxygen began to increase, as a consequence of changing biological activity, and U was converted from U^{4+} to mobile U^{6+} during weathering. Some of the U^{6+} found its way into sediments that were dragged back into the mantle at subduction zones. Because the Th and U content of the incompatible trace element depleted upper mantle is low, the addition of a small amount of U to the upper mantle was sufficient to accelerate the rate of decrease of its Th/U ratio from the Archaean value of ~ 4.0 to the modern value of 2.3.

There are two problems with this interpretation. The first is that previous compilations of Th/U have included both Al-depleted and normal Al komatiite-basalt suites. As already noted, the Al-depletion in komatiites and basalts is attributed to melting in the presence of garnet, which fractionates Th from U. Al-depleted komatiites and basalts commonly have Th/U above the primitive mantle value of 4.05. The Lumby Lake-Steep Rock komatiites, for example, which have an average Al_2O_3/TiO_2 of 9, have an average Th/U of 4.7, the Tisdale komatiites and basalts an average Al_2O_3/TiO_2 of 13.3 and a Th/U of 4.3 and the Barberton komatiites and basalts an average Al_2O_3/TiO_2 of 11.3 and a Th/U of 4.2. It therefore appears that Th/U in Al-depleted komatiite-basalt suites is controlled as much by the amount of garnet in the source region as by its Th/U. If Al-depleted samples are omitted from the compilation a very different picture emerges.

The second problem is that the Th/U of the modern mantle has generally been taken from MORB. If the arguments presented in this paper are correct, komatiite-basalt suites sample Archaean plumes, and the Th/U in Archaean komatiite-basalt suites should be compared with modern plume sources (OIBs) and not with MORBs.

Figure 10 is a plot of variations in Th/U with time for komatiite-basalt suites of various ages, with emphasis on the Archaean. All of the plotted suites, with the exception of the weakly Al-depleted Sumozero-Kenozero suite (average Al_2O_3/TiO_2 = 16) and the Lumby Lake basalts (Al_2O_3/TiO_2 = 15), are normal Al suites. The data points for these suites are marked by downward pointing arrows to indicate that they are maximum values. The Th/U values have been taken from both direct measurement and from values calculated from Pb isotopes. Where both types of data are available for the same suite the results invariably agree within error. The values calculated from Pb isotopes were plotted in preference to the measured values to minimize the risk of U mobility. The average Th/U of Archaean normal Al komatiites and basalts is 3.3 and they vary between a low of 2.9 for Munro Township and a high of 3.8 for Norseman-Wiluna. These values are well below the values of ~ 4.0 suggested by some previous authors but similar to modern OIBs, which typically range between 3.1 and 3.9 and average about 3.5. Many Archaean komatiite and basalts originate from mantle sources that are depleted in highly incompatible elements. It is not clear whether the Th/U of Archaean komatiite-basalt suites should be compared to all modern plume (OIB) picrites and basalts or only to plume magmas that originate from geochemically depleted mantle, such as Iceland and Gorgona, which have Th/U of 3.0 and 2.5 respectively. Whichever way the comparison is made there is no compelling evidence of a secular decrease in the Th/U of the mantle. It is clear that the Th/U ratio in the Archaean komatiite-basalt source is heterogeneous and that its departure from the primitive mantle value of 4.05 began well before the end of the Archaean. This departure could have started as early as 3.5 Ga but this inference is based on a single

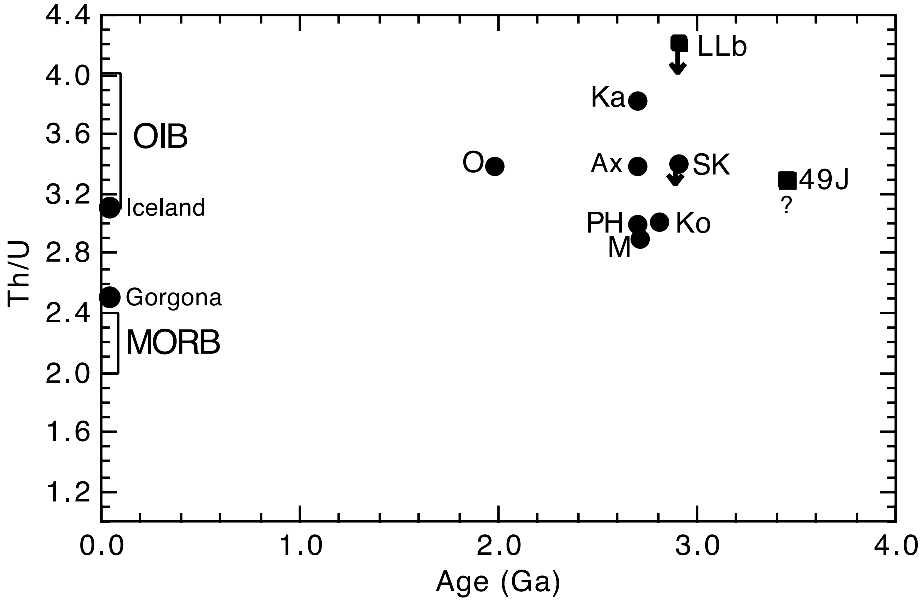

Fig. 10. Variations in Th/U in normal Al komatiite-basalt suites through time with emphasis on the Archaean. Th/U have been obtained from both direct measurement and from Pb isotopes. Values calculated from Pb isotopes are plotted as circles and those determined by direct measurement as squares. Note that the point marked 49J is for a single sample of normal Al komatiite from the Barberton. SK = Sumozero-Kenozero, data from Puchtel and others (1999); Ko = Kostomuksha from Puchtel and others (1998b); O = Onega from Puchtel and others (1998a); Ka = Kambalda-Norseman from Roddick (1984); and M = Munro, Ax = Alexo and PH = Pike Hill all from Dupré and others (1984).

sample of a normal Al komatiite, 49J from the Barberton, and should be treated with caution.

Nb/U in the Modern Mantle

Mass Balance Considerations

The effect on the Nb/U ratio of extracting different percentages of the continental crust from the mantle can be calculated from mass balance relationships, if the Nb and U concentrations in the mantle and continental crust are known, and if it is assumed that all of the major mantle reservoirs have similar Nb/U ratios. The latter assumption is justified by the observation that the Nb/U of the modern OIB and MORB sources are the same (Hofmann and others, 1986).

The effect on the Nb/U ratio of the mantle residue of extracting various fractions of continental crust from: (1) the upper mantle, and (2) the whole mantle, are shown in figure 11. The mantle Nb and U concentrations used in the calculations are those of Sun and McDonough (1989) and the continental crust values have been taken from McLennan (2001), Rudnick and Fountain (1995), and Taylor and McLennan (1985). If the continental crust formed entirely from the upper mantle, the Taylor and McLennan (1985) continental crust model requires extraction of only 48 percent of the modern continental crust from the upper mantle to raise its Nb/U to 47. If the more recent Nb-U values of McLennan (2001) are used, the percentage of continental crust that can be extracted from the upper mantle, without raising its Nb/U ratio above 47 falls to 35 percent, and to 27 percent if the value of Rudnick and Fountain (1995) are used. These calculations show that the Nb/U of the modern mantle is not

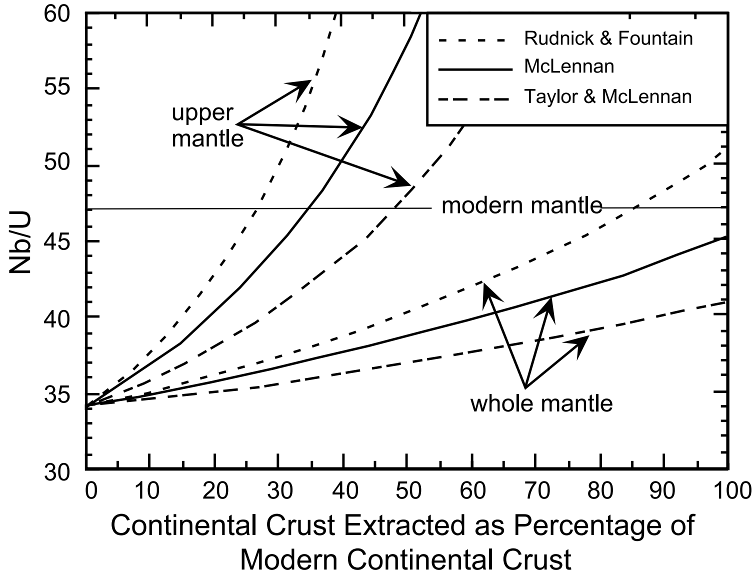

Fig. 11. The effect on the residual mantle Nb/U of extracting various fractions of continental crust from: (1) the upper mantle, and (2) the whole mantle for the continental crust Nb, Th and U concentrations of Rudnick and Fountain (1995), McLennan (2001) and Taylor and McLennan (1985). Note that the modern continental crust can not be extracted solely from the upper mantle without leaving behind a residue with an infinite or impossibly high Nb/U.

consistent with extraction of continental crust solely from the upper mantle (see also Hofmann and others, 1986).

Similar calculations for the whole mantle show that extraction of continental crust from the mantle raises its average Nb/U from 34 to 41 if the Nb and U concentrations of Taylor and McLennan (1985) are used for the continental crust, to 45 for the values of McLennan (2001), and to 51 for the values of Rudnick and Fountain (1995). That is, the value of 47 for the modern OIB and MORB sources lies between the values of 45 and 51 calculated from the most recent estimates of the Nb and U concentrations in the continental crust taken from McLennan (2001) and Rudnick and Fountain (1995), respectively. The calculations are therefore consistent with the continental crust being extracted from the whole mantle and inconsistent with it being extracted from the upper mantle. They provide further confirmation of the whole mantle convection hypothesis.

Constraints on Continental Crust Formation from Nb/U in Modern OIBs and MORBs

The observation by Hofmann and others (1986) that the average Nb/U ratios of the OIB and MORB sources are similar places an interesting constraint on the timing of the formation of the continental crust. If the change in the Nb/U ratio of the OIB source region is due to the extraction of the continental crust, it can only occur at the top of the upper mantle where the continental crust is forming. This requires the OIB source region to have acquired its high Nb/U ratio while it was near the top of the mantle, which implies that it is a sample of former upper mantle (Hofmann and White, 1982; Hofmann and others, 1986). As already noted, isotopic studies of OIBs suggest that the time taken for the OIB source to form in the upper mantle, to sink to the core-mantle boundary, and to return to the upper mantle in plumes, is about 1 to 2 Ga (Chase, 1982). The average Nb/U of the modern OIB source region must therefore be the same as the average of the 1 to 2 Ga upper mantle. The observation that the Nb/U ratio of the OIB and MORB sources are the same therefore implies that the net amount of continental crust that has separated from the upper mantle over the last 1 to 2 Ga is negligible.

Nb/U CONSTRAINTS ON CRUSTAL GROWTH MODELS

As noted earlier, the Armstrong (1981, 1991) steady state hypothesis for crustal growth predicts that Earth's early mantle had an average Nb/U value similar to that of the modern mantle and that this value changed little with time. In contrast the continuous growth models predict a near chondritic value for the early mantle that increases gradually through time. The average Nb/U for the Barberton samples, and for all Archaean basalt-komatiites suites, are 43 and 42 respectively, well above the chondritic value of 34 but below the modern mantle value of 47. It could be argued that the difference between 42 or 43 and 47 is due to depression of Nb/U in Archaean basalts and komatiites by contamination with continental crust. However, the maximum Nb/U in Archaean basalts is 69, which compares with 106 in modern OIBs, suggesting that crustal contamination is not a major factor. The Nb/U data are therefore consistent with a growth model for the continental crust that lies between the extremes of the steady state and continuous growth hypothesis but is closer to the steady state model.

The Nb/U data discussed in this paper allow three constraints to be placed on the rate of growth of the continental crust. Firstly, at least 70 $\pm$ 10 percent of the continental crust was extracted from the mantle by ~3.1 Ga. Secondly, the observation of Hofmann and others (1986) that the average Nb/U of the modern OIB and MORB sources are the same suggests that there was little change in the net mass of the continental crust after 1.5 $\pm$ 0.5 Ga. Thirdly, the absence of a systematic variation the Nb/U of Archaean basalts with time shows that the late Archaean was not a period of rapid continental growth as required by the McLennan and Taylor (1982) hypothesis. These constraints are compared with the various models for growth of the continental crust in figure 12. The Nb/U constraints appear to be most compatible with the model of Reymer and Schubert (1984). However this model requires very rapid continental growth to have occurred between 4.5 and 4.0 Ga. The occurrence of detrital zircons in Archaean sediments, with ages of up to 4.4 Ga, shows that continental crust had indeed begun to form by 4.4 Ga (Wilde and others, 2001). However, zircons older than 4.0 Ga are rare, even in the oldest sediments, suggesting that the amount of crust to have formed between 4.0 and 4.5 Ga was small (Nutman, 2001). Rapid growth of the continental crust prior to 4.0 Ga is also inconsistent with Nd and Hf model ages for Earth's oldest sediments that appear to preclude extensive growth of the continental crust before 4.0 Ga (Jacobsen and Dymek, 1987; Stevenson and Patchett, 1990). The preferred model for growth of the continental crust is shown in figure 12 (curve 8). Note that the form of the curve is not critically dependent on the time allocated to 70 percent extraction of the continental crust (point C in fig. 12), provided it lies between ~2.8 and 3.5 Ga. It is similar to the McLennan and Taylor (1982) model but the onset of rapid growth of the continental crust is pushed back from 3.0 to 4.0 Ga to meet the constraints imposed by the Nb/U data at 3.1 Ga (C in fig. 12) and the lack of evidence of a systematic variation in Nb/U with time in the late Archaean. This conclusion is strengthened if the role of continental crust contamination in Archaean basalts and komatiites has been underestimated, which would result in the percentage of continental crust extracted by ~3.1 Ga being greater than 70 percent. Growth prior to 4.0 Ga is assumed to be low to be consistent with the Nd and Hf model ages of old sediments and with the ages of the zircons extracted from them. The preferred growth curve passes well below the 75 percent continental crust extraction estimated for the Barberton mantle at ~3.8 Ga (B in fig. 12) and it implicitly assumes that the average Nb/U of 43

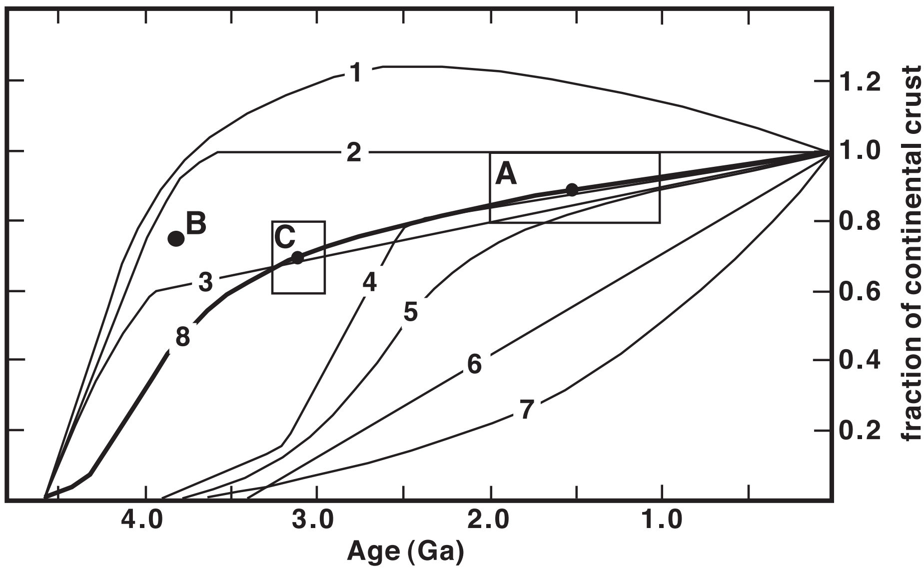

Fig. 12. A selection of growth models for the continental crust. 1 = Fyfe (1978), 2 = Armstrong (1981), 3 = Reymer and Schubert (1984), 4 = McLennan and Taylor (1982), 5 = Veizer and Jansen (1979), 6 = Hurley (1968), 7 = Hurley and Rand (1969) and 8 = this study. A, B, and C are the constraints on growth of the continental crust obtained from the Nb/U data. A is from the observation that Nb/U in modern OIBs and MORBs are the same, which requires little crustal growth after 1.5 Ga; B is the constraint provided by the Barberton data; and C is the constraint provided by the average Nb/U for all late Archaean basalt-komatiite suites. Modified after Taylor and McLennan (1985).

for the Barberton basalts and komatiites is above the average for the mantle at that time. Otherwise it is difficult to rationalize 75 percent continental crust extraction for the Barberton mantle at 3.8 Ga with the constraints from isotopic studies of old sediments. If the Barberton Nb/U value is representative of the mantle at 3.8 Ga, either the Nb/U data, or the data from old sediments have been seriously misinterpreted.

Further Implications of Preferred Continental Growth Model

If the preferred continental growth curve presented in figure 12 is valid it has two further implications for Earth evolution. The first is that it is inconsistent with the hypotheses of continuous, largely irreversible growth of the continental crust. If estimates of the average age of the preserved continental crust of 1.4 to 1.8 Ga, based on Nd and Hf model ages of sediments are correct (Goldstein and Jacobsen, 1988; Stevenson and Patchett, 1990), recycling through the mantle has destroyed much of the 70 percent of the continental crust that had formed by 3.1 Ga. The data are therefore consistent with the early continental crust formation and recycling hypothesis of Armstrong (1968, 1991). However the amount of continental crust required to have formed early in Earth's history, and therefore the amount of crustal recycling required, is less than in the Armstrong hypothesis, especially between 4.0 and 4.5 Ga.

The conclusion that there has been significant recycling of continental crust appears to be inconsistent with the rarity of MORBs and OIBs with Nb/U less that the primitive mantle value of 34, which has been interpreted to indicate that recycled sediments are not an important process in the deep mantle (Hofmann and others, 1986). However, it is consistent with a continental crust-recycling model in which the recycled process is largely confined to subduction zones. That is, if the sediments, which are carried into the mantle at subduction zones, melt or are leached by hydrothermal fluids of elements with continental affinities such as U, Sm, Nd, Lu, Hf, Si et cetera, and if these components are returned to the continental crust via the mantle wedge. Under these circumstances, the OIB and MORB sources will be largely quarantined from the recycling process.

The second implication of the preferred crustal growth model is that the positive ε_{Nd} and ε_{Hf} values seen in Earth's oldest rocks, which are interpreted to indicate that Earth's early mantle was depleted in incompatible elements, cannot be due solely to extraction of continental crust. The formation of a depleted mantle reservoir, with ε_{Nd} of +2 and ε_{Hf} of +4 by 3.9 Ga, requires the reservoir to have had an Sm/Nd and Lu/Hf equal to or greater than that of the modern mantle by 4.5 Ga. If the depleted mantle reservoir is due solely to extraction of continental crust and if it had a mass similar to the mass of the modern depleted reservoir, these increases in Sm/Nd and Lu/Hf require the mass of the continental crust at 4.5 Ga to have been similar to or greater than the mass of the modern continental crust. This, of course, is incompatible with the isotopic and zircon evidence from old sediments. The alternative is that incompatible element depletion in Earth's early mantle is due to extraction of basaltic crust, as first suggested by Chase and Patchet (1988) and Galer and Goldstein (1991). Campbell (2002) has used the relationship between Sm/Nd and Nb/U in the residual mantle, produced by extraction of continental crust, to argue that the elevation seen in Sm/Nd in the depleted mantle is due largely to extraction of basaltic crust in both the Archaean and modern mantles. After all, the lunar mantle reached higher ε_{Nd} and ε_{Hf} early in its history than Earth without requiring extraction of continental crust.

CONCLUSIONS

The following conclusions can be drawn from this work:

1. The average value of 47 for modern OIBs and MORBs is consistent with whole mantle convection and inconsistent with a hypothesis in which the upper and lower mantles convect as separate layers.
2. There is no evidence of a secular variation in the Th/U of the mantle.
3. The average Nb/U ratio of the Barberton basalts and komatiites is 43 which is well above the value of 34 for the primitive mantle and only slightly below the average value of 47 for the modern MORB and OIB sources.
4. The percentage of continental crust that must be extracted from the mantle source region of the Barberton basalts, in order to raise their average Nb/U ratio to 43, is 75 percent of the amount that has been removed from the modern OIB and MORB sources.
5. Other late Archaean komatiite-basalt suites have an average Nb/U ratio of 42, requiring extraction of 70 ± 10 percent of the continental crust during the Archaean. This estimate, and the estimate for the Barberton, could be conservative in that they ignore the possibility that the average Nb/U ratios may have been lowered by contamination by continental crust.
6. The increase in Nb/U must occur within the upper mantle. Because it takes about 300 million years for the material with elevated Nb/U to be cycled through the Archaean mantle and into mantle plumes, the increase in Nb/U recorded in late Archaean basalts and komatiites must have occurred ~300 million years earlier in the mantle.
7. The absence of a systematic variation in Nb/U with time in Archaean basalt-komatiite suites precludes the possibility that the late Archaean was a period of rapid crust growth.
8. The similarity in the Nb/U ratio of modern MORBs and OIBs suggests that the net rate of formation of continental crust over the last 1.5 ± 0.5 Ga is negligible.

9. The constraints from Nb/U in basalts and komatiites suggest that most of the growth of the continental crust occurred between 4.0 and 3.0 Ga.
10. Recycling of the continental crust has been an important process in Earth evolution but less so than envisaged by Armstrong (1968, 1991). Earth's continental crust did not reach a steady state until at least the end of the Archaean.

ACKNOWLEDGMENTS

I wish to thank Grant Cawthorn, Thinus Cloete and Carl Anhaeusser for helping with sample collection, Charlotte Allen for preparing the figures, Barbara Fairchild for carrying out the analyses and Geoff Davies, Nick Arndt and Candace Martin for their critical comments.

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