Niobium/Uranium Evidence for Early Formation of the Continental Crust

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Niobium/uranium ratios in greenstone-belt basalts and gabbros indicate that parts of the Late Archean mantle beneath Western Australia underwent a level of melt extraction, resulting in formation of the continental crust, comparable to that seen in the present mantle. The implication is either that (i) the amount of continental crust that formed before 2.7×10^9 years ago was much greater than generally thought or (ii) crustal growth occurred by severe depletion of small volumes of the mantle rather than by moderate depletion of a large volume of mantle.

Hofmann *et al.* (*1*) showed that the Nb/U ratios of ancient basalts can be used to constrain one of the most fundamental problems in geochemistry—the timing and rate of growth of the continental crust. During the melting processes in the mantle that led to continental crust formation, Nb and U behaved as incompatible elements (*2*) and hence became concentrated in the crust at the expense of the mantle. Niobium, however, was less strongly incompatible than U so the Nb/U ratio of ~10 (*3*) for the continental crust is well below the value of ~30 (*4*) for the primitive mantle. In contrast, during the formation of modern basalts at mid-ocean ridges (MORBs) and ocean island hotspots (OIBs), Nb and U both behave as strongly incompatible elements with nearly identical bulk partition coefficients. As a consequence, Nb/U ratios in the basalts are, for practical purposes, the same as those in the mantle source regions that melted to produce them. Modern MORBs and OIBs have mean Nb/U ratios of 47 (*1*), well above the primitive mantle ratio, which is attributed to removal of the continental crust from their mantle sources. Ancient basalts can be expected to have Nb/U ratios between 47 and 30, depending on the timing of continental crust extraction.

There is uncertainty as to when the bulk of the continental crust separated from the mantle. A range of models varying between the extremes of early (*5*) and late (*6*) crustal growth have been proposed. Arguments based on radiogenic isotopes have been unable to resolve this problem. For instance, the mean age of the continental crust, as inferred from Nd isotopic data for sediments, is ~2.0×10^9 years ago (Ga) (*7*), but it is unclear from isotopic data for Nd, Sr, and Pb in mantle-derived rocks whether this age is the result of successive crustal additions through time, as proposed by Moorbath (*8*), or continental crust formation in the Early Archean and its continuous recycling through the mantle since then, as argued by Armstrong (*5*).

Jochum *et al.* (*9*) used Nb/U ratios to estimate the rate of growth of the continental crust by measuring the trace element abundances of 31 Precambrian basalts and komatiites from a variety of locations. They found Nb/U ratios ranging from ~10 to 50 and attributed the scatter to U mobility during secondary alteration. Nb/Th ratios were used in place of Nb/U, but interpretation of the significance of Nb/Th ratios in ancient basalts is not straightforward (*10*, *11*).

We have reinvestigated the question of obtaining reliable data for Nb/U ratios in Precambrian basalts by measuring the trace element abundances of 43 Late Archean (2.7 Ga) basalts from the Lunnon Formation of the Kambalda-Norseman region of the Yilgarn Craton, Western Australia (Table 1). This formation was chosen because there is no evidence of crustal contamination in the chemistry of the basalts (*12*). Furthermore, its age of 2.7 Ga is ideal to test the hypothesis of early crustal growth. If the bulk of the continental crust formed before 2.7 Ga, the Lunnon basalts should have Nb/U ratios similar to those of modern basalts, whereas if most of the crust grew between 2.7 and 1.7 Ga, as is generally thought (*13*), the ratio should be below 47.

The Lunnon Formation is the basal unit in a 2.7-Ga basalt-komatiite sequence. It is overlain first by komatiites of the Kambalda Komatiite Formation and then by basalts of the Devon Consuls and Paringa Formations. The Devon Consuls and Paringa basalts are rich in silica, magnesia, and incompatible trace elements (*14*), have nonradiogenic Nd isotopic ratios (*15*), and contain zircon xenocrysts (*16*), all of which suggests that they are mixtures of komatiite magma and continental crust (*12*). All the samples used in this study are from diamond drill core and are free from oxidation and shearing. They have undergone typical greenschist facies metamorphism that has destroyed the primary minerals but are free of the late hydrothermal alteration that accompanies gold mineralization in the region. We analyzed the rocks by solution nebulization–inductively coupled plasma mass spectrometry (ICPMS) using the enriched isotope internal standardization method described by Eggins *et al.* (*17*). Concentrations of U vary systematically with Nb and Th, indicating that postmagmatic mobility of U was negligible in these samples. We confirmed this result by carrying out multiple analyses on three gabbro sills that are interlayered with the basalts. In each case, the range of measured Nb/U and Nb/Th ratios lies within 4% of the means (Table 1).

Comparison of Nb/U with Nb/Th, La/Sm, and Th/La (Fig. 1) shows that, for each pair of ratios, the samples define a two–end-member mixing array with Nb/U varying between 32 and 47. It is apparent, from the range of measured Nb/U ratios, that many analyses are needed to characterize

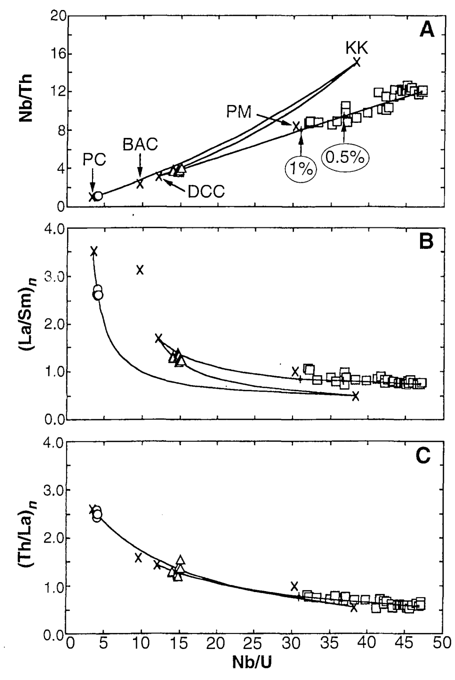

Fig. 1. Nb/U versus (**A**) Nb/Th, (**B**) chondrite-normalized La/Sm, and (**C**) chondrite-normalized Th/La for the Late Archean greenstone basalts [(□) Lunnon basalts, (△) Devon Consuls basalts, (○) Paringa basalts], a Kambalda komatiite (KK) (*9*), the primitive mantle (PM) (chondrites) (*4*), and the bulk Archean continental crust (BAC) (*3*). Also plotted are calculated compositions of hypothetical crustal contaminants of the Devon Consuls (DCC) and Paringa (PC) basalts and mixing curves between components. Tick marks along the mixing curve between the high-Nb/U Lunnon end-member and DCC are shown for 0.5 and 1% crustal contamination. KK, PM, BAC, DCC, and PC are plotted as X's.

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the Nb/U of a suite of basalts. Indeed, much of the scatter in the Nb/U ratios of Jochum *et al.* (*9*) may reflect mixing of the type seen in Fig. 1.

The high Nb/U end-member in the mixing array is basalt derived from mantle that has been depleted in U relative to Nb as a result of continental crust formation. It has a Nb/U ratio of 47, similar to the mean value for modern MORBs and OIBs, implying that the fraction of the continental crust removed from the mantle source region of these 2.7-Ga basalts was similar to the amount removed from modern MORB and OIB source regions. The nature of the other end-member is problematic. It could represent basalt derived from mantle from which no continental crust had been removed, or it could be due to crustal contamination of the high Nb/U end-member.

The compositions of the two most likely crustal contaminants can be calculated from compositions of the Devon Consuls and Paringa basalts which, based on Nd isotope data (*12*), are thought to have formed by 5 and 25% crustal contamination, respectively, of a magma having a composition of the Kambalda komatiite (*18*). Assuming these levels of crustal contamination and using the measured concentrations of Nb, U, Th, La, and Sm for 15 samples of Devon Consuls and Paringa basalts (Table 1), we calculate that the Nb/U ratio of the Devon Consuls contaminant is 12.1 and that of the Paringa contaminant is 3.4. For comparison, the Archean continental crust has an estimated bulk Nb/U ratio of 9.6 (*3*). Mixing curves between either the Devon Consuls or Paringa contaminant and a Lunnon basalt with a Nb/U ratio of 47 pass through the data arrays of Fig. 1. For the mixing curve to the Devon Consuls contaminant (Fig. 1), only ~1% crustal contamination is required to explain the entire spread of the Nb/U measured in the Lunnon basalts. Such a small amount of contamination would not be detectable on the basis of Nd isotope data, because initial ε_{Nd} values (*19*) of the Lunnon basalts would decrease by only ~0.3 units (*20*), which is well within analytical uncertainty on the measurements (*21*).

If the crustal contamination model is correct, the 2.7-Ga mantle source of the Lunnon basalts had the same Nb/U ratio as modern MORBs and OIBs and, hence, had undergone a level of melt extraction, resulting in continental crust formation, comparable to that seen in the present mantle. The Lunnon Formation is 5 km thick and can be traced for 250 km, so the high Nb/U end-member must have been derived from a substantial mantle reservoir. This interpretation suggests that a large amount of the continental crust had already formed by 2.7 Ga. It remains to be seen, however, whether the modern-like Late Archean mantle beneath Western Australia was typical of the sources of most Late Archean basalts; if so, this would be compelling evidence in favor of the Armstrong (*5*) model of early crust formation. Alternatively, the depleted Late Archean mantle we have recognized may have been generated by severe depletion of small domains of the mantle rather than by a more moderate, progressive depletion of a large portion of the mantle.

It is possible, of course, that the range of Nb/U ratios (Fig. 1) is not the result of crustal contamination but instead indicates that the source region of the Lunnon basalts

Table 1. Trace element data for Western Australian basalts and gabbros. Trace element concentrations (reported as parts per million) were measured by ICPMS with external calibration to U.S. Geological Survey standard basalt BHVO-1 (Nb, 19.5; La, 15.5; Sm, 6.17; Th, 1.26; U, 0.42). Precision is ±2% for Th, U, Nb, and the rare earth elements, and ±4% for Nb/U and Nb/Th ratios. KD, Kambalda drill cores; ND, Norseman drill cores; LB, Lunnon basalt; LG, Lunnon gabbro (multiple samples analyzed in sills A, B, and C); PB, Paringa basalt; DCB, Devon Consuls basalt.

Depth (m)	Rock	Nb	La	Sm	Th	U	Depth (m)	Rock	Nb	La	Sm	Th	U
			KD8698A							*KD1029*			
52.4	LB	2.39	3.13	2.34	0.203	0.058	524.6	LGC	2.04	2.56	1.85	0.240	0.060
61.3	LB	2.22	2.65	2.11	0.183	0.051	525.5	LGC	1.99	2.46	1.80	0.226	0.056
80.4	LB	1.95	2.23	1.81	0.171	0.045	543.5	LGC	1.83	2.48	1.74	0.217	0.051
100.4	LB	2.03	2.32	1.92	0.178	0.048	611.4	LGC	1.82	2.39	1.69	0.218	0.053
122.4	LB	1.94	2.27	1.87	0.168	0.044	655.0	LGC	1.94	2.48	1.76	0.230	0.057
131.4	LB	2.12	2.24	1.92	0.169	0.047	659.0	LGC	1.90	2.53	1.74	0.220	0.052
157.3	LB	2.13	2.59	1.99	0.175	0.047	660.5	LGC	1.97	2.46	1.82	0.233	0.056
180.4	LB	2.23	2.73	2.05	0.180	0.049	1281.1	LB	1.77	2.05	1.56	0.177	0.042
201.5	LB	2.39	2.64	2.15	0.199	0.052	1300.3	LB	1.79	2.09	1.64	0.184	0.045
215.4	LB	2.12	2.33	1.90	0.175	0.045	1322.2	LB	1.76	2.17	1.67	0.192	0.046
242.6	LGA	2.22	2.48	1.98	0.181	0.048				*KD1236*			
245.5	LGA	1.96	2.16	1.79	0.169	0.044	49.0	PB	3.21	9.10	2.19	2.84	0.780
253.9	LGA	2.20	2.56	2.03	0.181	0.050	68.0	PB	3.38	9.58	2.19	3.10	0.827
285.4	LB	2.28	2.53	2.07	0.188	0.051	83.0	PB	3.09	8.85	2.12	2.77	0.755
300.4	LB	2.27	2.53	2.08	0.188	0.050	109.2	PB	2.83	8.18	1.94	2.62	0.717
324.2	LB	2.13	2.30	1.89	0.175	0.048	122.5	PB	3.17	9.38	2.16	2.85	0.782
340.2	LB	2.22	2.51	2.00	0.184	0.049	139.9	PB	2.91	8.29	2.01	2.61	0.724
364.6	LGB	2.35	2.56	2.09	0.187	0.051	221.1	DCB	2.95	5.14	2.42	0.764	0.199
366.3	LGB	2.34	2.66	2.15	0.199	0.053	229.9	DCB	2.91	3.75	1.91	0.724	0.192
397.4	LGB	2.06	2.32	1.90	0.174	0.046	246.1	DCB	2.94	4.70	2.23	0.753	0.210
417.2	LGB	2.24	2.50	2.04	0.189	0.052	262.1	DCB	2.73	4.56	2.05	0.704	0.186
467.5	LG	1.96	2.21	1.74	0.221	0.055	278.4	DCB	3.02	4.39	2.20	0.754	0.198
524.1	LB	2.12	2.48	1.78	0.241	0.057	293.8	DCB	2.65	4.43	2.17	0.720	0.188
			ND				309.0	DCB	2.72	4.49	2.36	0.750	0.184
1358*	LG	2.97	2.98	2.40	0.249	0.063	316.4	DCB	2.97	4.46	2.24	0.785	0.200
115†	LB	1.92	2.04	1.78	0.185	0.052	327.7	DCB	2.93	5.13	2.46	0.816	0.199
67.1‡	LB	2.06	2.38	2.04	0.173	0.044				*ND*			
236.1‡	LG	2.98	3.51	2.69	0.291	0.070	140.3§	LB	4.83	5.69	3.64	0.494	0.131
699.95‡	LB	8.83	9.57	6.74	0.873	0.212	217.5§	LG	2.10	2.54	1.93	0.240	0.063
837.8‡	LB	2.23	2.42	2.07	0.190	0.048	322§	LG	9.19	10.50	6.15	1.057	0.287
							401.8§	LB	7.56	8.94	5.37	0.857	0.234

Hole number *5593, †LK7, ‡5577, §5177.

was a heterogeneous mixture of modern-like depleted mantle with a Nb/U ratio of 47 and primitive mantle with a Nb/U ratio of 30. The absence of samples with Nb/U ratios less than the chondritic value supports this interpretation. The source heterogeneity could have formed by incomplete mixing between depleted upper mantle and primitive lower mantle, as predicted by the mantle plume model of (*22*) for greenstones, or simply by variable amounts of continental crust extraction from the primordial upper mantle. In either case, because all initial ε_{Nd} values determined for Lunnon basalts are positive (+2.1 to +3.7) (*12*), including those with Nb/U ratios of ~30 (*23*), this interpretation requires that the subchondritic Nd/Sm ratio of the depleted upper mantle is not related to the formation of the continental crust, as is widely assumed (*5*, *24*). Similarly, continental crust formation could not have been responsible for depleting Th relative to La in the depleted upper mantle because Lunnon basalts, with near-chondritic Nb/U ratios, have subchondritic Th/La ratios (Fig. 1C). The positive initial ε_{Nd} values and subchondritic Th/La ratios of the low Nb/U end-member are consistent with extraction of a now destroyed basalt proto-crust (*25*) from the mantle before formation of the continental crust, assuming, of course, that the basalt proto-crust had a chondritic Nb/U ratio.

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18. A single crustal contaminant cannot produce the two types of enriched basalts. Although Paringa and Devon Consuls basalts have different Nb/U, Nb/Th, La/Sm, and Th/La ratios, consistent with different amounts of crustal contamination by a single contaminant, concentrations of Nb and Sm in the two basalt types are about the same, inconsistent with this interpretation.
19. Initial ε_{Nd} is the deviation of the $^{143}Nd/^{144}Nd$ ratio of a magmatic rock from the chondritic value at the time the rock crystallized.
20. This calculation assumes a hypothetical crustal contaminant with an ε_{Nd} of −5 at 2.7 Ga and a parent magma for the Lunnon basalts with an ε_{Nd} of +3.
21. Lead isotopes are a more sensitive gauge of crustal contamination than Nd and hence, in principle, could be used to distinguish between a primitive mantle and contamination origin for the low Nb/U end-member. Unfortunately, primitive mantle–normalized trace element diagrams for Lunnon basalts are characterized by large positive Pb anomalies, suggesting enrichment in Pb during secondary alteration. Concentrations of Rb, Ba, and Sr, which could provide information about the low Nb/U end-member as well, also have been affected by secondary processes.
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Regulation of NF-κB by Cyclin-Dependent Kinases Associated with the p300 Coactivator

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The nuclear factor κB (NF-κB) transcription factor is responsive to specific cytokines and stress and is often activated in association with cell damage and growth arrest in eukaryotes. NF-κB is a heterodimeric protein, typically composed of 50- and 65-kilodalton subunits of the Rel family, of which RelA(p65) stimulates transcription of diverse genes. Specific cyclin-dependent kinases (CDKs) were found to regulate transcriptional activation by NF-κB through interactions with the coactivator p300. The transcriptional activation domain of RelA(p65) interacted with an amino-terminal region of p300 distinct from a carboxyl-terminal region of p300 required for binding to the cyclin E–Cdk2 complex. The CDK inhibitor p21 or a dominant negative Cdk2, which inhibited p300-associated cyclin E–Cdk2 activity, stimulated κB-dependent gene expression, which was also enhanced by expression of p300 in the presence of p21. The interaction of NF-κB and CDKs through the p300 and CBP coactivators provides a mechanism for the coordination of transcriptional activation with cell cycle progression.

Progression through the eukaryotic cell cycle is controlled by the assembly and activation of specific cyclin-CDK complexes, which provide checkpoints that control entry into each phase of the cell cycle (*1*). Regulation of cyclin-CDK activity is achieved, in part, through the interaction of CDK inhibitory proteins (CKIs) (*2*). Among the CKIs, p21 (also known as WAF1, CIP1, CAP20, or SDI1) is an inhibitor of all CDKs (*2–4*). The amount of p21 mRNA and protein is increased upon DNA damage through a mechanism dependent on the tumor suppressor gene p53 (*5*), and p21 is thought to mediate G_1 checkpoint cell cycle arrest (*6*). Synthesis of p21 is also enhanced in cells that are treated with serum factors, phorbol esters, or okadaic acid and undergo growth arrest in a p53-independent manner (*7*, *8*). These latter agents also activate NF-κB (*9*), which regulates genes involved in the response to stress and infection (*10*). Moreover, the induction of either NF-κB or p21 is associated with growth arrest and cellular differ-

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