STORING EARTH'S MISSING NIOBIUM IN THE TERRESTRIAL COUNTERPART OF EVOLVED LUNAR MAGMA OCEAN MELTS.

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Introduction: The origin of the observed niobium deficit in the bulk silicate Earth (BSE) compared to chondritic meteorites constitutes a long-standing problem in geochemistry. High-precision analyses of terrestrial crust, depleted mantle, and ocean island basalts all show subchondritic Nb/Ta ratios of 8-17 [1-3] compared to the chondritic values of 18.4 for enstatite chondrites and 19.9 for carbonaceous chondrites [4] (Fig. 1). In the absence of significant Nb/Ta fractionation during volatile loss during planetary accretion, a large-scale process fractionating niobium from tantalum needs to be identified, and a superchondritic Nb/Ta reservoir must be 'hidden' in the deep silicate Earth and/or the core.

The only voluminous superchondritic Nb/Ta silicate reservoir analysed to date is found in highly evolved KREEP rocks on the Moon, thought to represent the last fractions of melt remaining at the end of magma ocean crystallization. Their Nb/Ta ratios range up to 22 at Nb concentrations up to 30 ppm [4] (Fig. 1). Here we present high-precision Nb-Ta data for highly evolved, iron-rich rocks associated with a terrestrial anorthositic intrusion with geochemical affinities to lunar KREEP. These rocks exhibit extreme superchondritic Nb/Ta ratios and highly elevated Nb concentrations. We argue that formation of an early enriched crustal reservoir with these characteristics (high Fe, high Nb, superchondritic Nb/Ta) is likely during late-stage terrestrial magma ocean solidification, regardless of whether this is accompanied by anorthositic crust formation). Subsequent deep mantle storage of a minor amount (0.5-1.5 % of the BSE mass) of such a reservoir can readily explain the terrestrial Nb deficit.

Samples and methods: The sample suite is from the Bolangir complex, part of a Proterozoic massif-type anorthosite body that constitutes the largest Indian anorthosite, with a surface exposure of ~500 km² [5]. The anorthosite shows a typical association of anorthosite–leuconorite–norite–jotunite, with a zoning of predominantly anorthosite in the centre towards jotunites that occur as marginal, melanocratic, crosscutting dikes and sheets. The latter rock series comprises ferromonzodiorites and ferrodiorites characterised by extremely high iron contents (10-37 wt% FeO) and enrichment of incompatible elements [6]. Previous studies have interpreted jotunite suites as late stage, differentiated liquids from anorthositic intrusions [7]. For the Bolangir complex, this genetic relationship between anorthosite and jotunite is strongly supported by complementary REE patterns [5].

Isotope dilution analyses for Ta, Lu, Sm, Nd, Hf, Zr, and W, as well as Nb/Ta were carried out on the ThermoFinnigan Neptune multicollector-ICPMS at VU University Amsterdam. Precisions are 0.2% on Lu, Sm, Nd, Hf, and Zr concentrations, and 1% on Ta. Zr/Hf, Lu/Hf and Sm/Nd ratios are precise to ≤ 0.2%, Nb/Ta to 5% [8,9].

Results: The jotunites are extremely enriched in incompatible elements, with Hf concentrations varying from 4 to 82 ppm. Sm-Nd concentrations in the jotunites are extremely high compared to mantle or crustal abundances, ranging from 31 to 83 ppm Sm and 155 to 454 ppm Nd. Nb and Ta concentrations are also extremely high with 83-338 ppm Nb and 3.1-12.8 ppm Ta (Fig. 1). All samples exhibit extreme Nb/Ta ratios (25-31) that exceed values for all terrestrial rocks analysed to date. Lu-Hf and Sm-Nd isotope systematics of the ferrodioritic rocks and associated anorthosites demonstrate isotope equilibrium showing that crustal assimilation of Hf and Nd (and thus Nb and Ta) was minor. Accordingly, the initial Hf and Nd isotope compositions of the anorthosites and the jotunites are almost identical, further corroborating the coupled genesis of both suites.

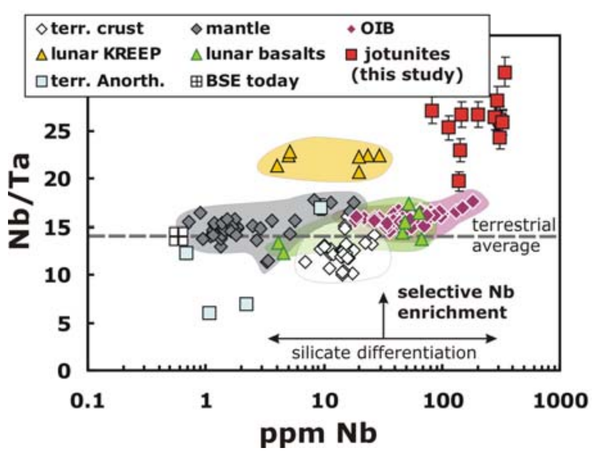

Fig. 1. Literature compilation of high-precision Nb/Ta ratios and Nb concentration data for terrestrial and lunar rocks (from [1-4]). New data from this study are shown as red squares at top right.

Late-stage magma ocean melts - Earth vs. Moon: On the Moon, formation of late-stage Fe-rich liquids accompanied solidification of a global magma ocean and formation of an anorthositic upper crust. The much larger pressure-temperature range in the Earth limits the possibility of anorthositic crust formation from a global magma ocean, because in a deep rooting terrestrial magma ocean, high pressure Al-phases such as garnet suppress extensive plagioclase formation [10]. Consequently, olivine and pyroxene formation are triggered preferentially, with a resulting crust that is thought to be boninitic or komatiitic [11]. The possibility of significant plagioclase fractionation in shallower, smaller-scale magma oceans cannot be discounted. More importantly, in any of the above scenarios late-stage evolved melts would be highly enriched in Fe and incompatible trace elements. Mineral-melt partitioning experiments show that Nb and Ta are highly incompatible in both pyroxene, plagioclase, and garnet [12-14]. More importantly, D_{Nb}/D_{Ta} for these phases range between 0.2 and 0.7. These low D ratios indicate that upon massive fractional crystallization of these minerals from a terrestrial magma ocean, evolved melts become progressively enriched in Nb and Ta with superchondritic Nb/Ta. The strong similarity between residual melts from anorthosite crystallisation on the Moon and boninite/komatiite crystallisation on Earth with respect to incompatible elements render the true nature of the first terrestrial crust less significant with respect to the Nb-Ta budget. We conclude that the jotunites studied here are a realistic (and tangible!) analogue for an early enriched crustal reservoir forming at the end of the solidification of a terrestrial magma ocean.

Storing Earth's missing niobium: A scenario for early crustal formation is suggested here that is accompanied by Nb decoupling from the silicate portion of the Earth, similar to KREEP formation on the Moon. During final cooling of a terrestrial magma ocean, crystallisation of an early enriched crustal reservoir (EECR) was triggered at shallow levels from highly evolved melts. Permanent isolation of this high Nb/Ta upper crustal component from the Hadean bulk silicate Earth was achieved by early subduction and subsequent permanent deep mantle storage, aided by the high density of this Fe-rich reservoir. Deep storage of such a reservoir can readily account for the observed depletion in BSE Nb/Ta. Assuming simple two-component mixing with a chondritic primitive mantle with no Nb in the core, sequestration of ~0.5 wt% of an average EECR (Nb/Ta=25.4, 152 ppm Nb, weighted average from our measurements) is required to fully compensate the Nb deficit of samples from the present-day BSE. If Nb behaved weakly siderophile during core formation in opposition to a lithophile Ta to the extent found experimentally by [15], the mass of the EECR required to mass balance terrestrial Nb/Ta would be lowered to 0.2 % of the BSE mass. These reservoir size estimates are similar to other independent estimates of the size of a hidden silicate reservoir in the Earth [16]. The high density required for permanent deep mantle storage is consistent with the high Fe contents of the rocks discussed here.

Implications for short-lived isotope systems: Our model is consistent with current short-lived ^{142}Nd. Our Sm-Nd concentration data yields a ^{147}Sm/^{144}Nd=0.11. This value is significantly lower than the chondritic value of 0.1966, in general agreement with deep mantle storage of a low Sm/Nd reservoir [17]. In the case of an EECR formed from late-stage melts after pyroxene and garnet crystallization, the Sm/Nd ratio would be somewhat higher, thus having a smaller effect on Nd isotope systematics. Similar systematics have been observed by Lee and co-workers [18] for late-stage Fe-O-S liquids considered as a possible representative for late stage magma ocean melts. Finally, although not presented in this abstract our data are fully consistent with current long-lived ^{176}Hf-^{143}Nd isotope models for early crustal differentiation as well.

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