Is the bulk Earth Nb/Ta chondritic?

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The accessible silicate Earth is characterized by a Nb deficit of ca. 30% relative to most groups of chondrites [1]. This Nb deficit has been attributed to a slightly siderophile affinity of Nb during high-pressure formation of the Earth's core [1,2]. The finding of low Nb/Ta ratios in CV chondrites (ca. 17 [1]), however has challenged this model, as CV chondrites closely resemble the Earth's composition in their relative abundances of volatile and refractory elements. If the bulk Earth indeed had a CV-chondritic or even lower Nb/Ta ratio, the Nb deficit in the silicate Earth would be much less pronounced, and models using Nb/Ta ratios to assess conditions during core formation [e.g., 3,4] would neeed some revision.

In order to investigate the cause for the low Nb/Ta in CV chondrites, we analyzed small ca. 0.6 g slices taken from a single piece of Allende [5], together with an aliquot of the Smithsonian powder that is representative for bulk Allende. Ratios of HFSE were determined at high precision using isotope dilution and the Neptune MC-ICPMS at Cologne-Bonn [6] and are compared to high precision data for REE previously determined at ETH Zürich and RSES Canberra [5, unpulished]. The Smithsonian Allende powder yielded a Nb/Ta of 19.1±0.8 (2σ), within error of values for other chondrite groups (19.9±0.6, [1]). Conversely, the Nb/Ta measured for the small Allende slices span a wide range from 14.2 to 22.0. Ratios of Zr/Nb are correlated with Nb contents and range towards values as low as 10, much lower than the chondritic value (13.5, [3]).

The Nb/Ta systematics found for Allende indicate that in contrast to Zr-Hf, Nb and Ta are not distributed homogenously in CV chondrites. However, the data for the large Smithsonian powder aliquot suggest that the bulk Allende parent body had a Nb/Ta indistinguishable from other types of chondrites. Notably, the Nb/Ta in the small Allende slices are negatively correlated with Tm/Er ratios (0.16 to 0.26). At near-chondritic Tm/Er (ca. 0.16 [7]), the mesured Nb/Ta in the Allende splits scatter around a value of 20, typical of the chondrite average. It has previously been argued that the elevated Tm/Er in many CV chondrites can be attributed to the presence of type II CAIs [5]. Low Nb/Ta ratios occasionally found in CV chondrites may reflect selective enrichment group II CAI.

The co-variation between Nb/Ta and Tm/Er could imply that the bulk Earth exhibits a superchondritic Tm/Er, if it had a low Nb/Ta. This is clearly not the case, as the silicate Earth displays a Tm/Er that is not resolvable from that of CI-chondrites [7]. The Nb/Ta of the bulk Earth should therefore overlap the chondritic value and the Nb deficit in the Earth's mantle reflects its siderophile behaviour.

[1] Münker *et al.* (2003) *Science* **301**, 84-87. [2] Wade & Wood (2001) *Nature* **409**, 75-78.[3] Palme & O'Neill (2003) *Treatise on Geochemistry* **2**, 1-38, Elsevier, Oxford. [4] Corgne *et al.* (2008) *GCA* **72**, 574-589. [5] Stracke *et al.* (2012) *GCA*, in press.[6] Münker (2010) *GCA* 74, 7340-7361. [7] Pourmand et al. (2012) *Chem Geol* **291**, 38-54.

Microchemistry of amphiboles near the roof of a mafic magma chamber

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The Late Neoproterozoic Greendale Complex is a suite of arc-related appinitic rocks ranging from ultramafic to felsic in composition that crystallized at shallow crustal levels under conditions of high pH_2O. Amphibole is the dominant mafic mineral in ultramafic to mafic rocks and displays the extraordinary variability in texture and modal abundance that is characteristic of appinite suites. These features allow sensitivity of amphibole composition (major, trace and REE) to the evolution of water-rich magma to be investigated.

All amphiboles in mafic and ultramafic rocks are calcic, with $(Ca+Na)_B \geq 1.34$ and $Na_B < 0.67$ apfu, with Si^{IV} between 6.1 and 7.3. They predominantly range in composition from tschermakite, to tschermakitic hornblende, to magnesio-hornblende and display a dominance of edenite ($Na,K_A + Al^{IV} = Si^{IV}$) substitution. Although each sample exhibits remarkably uniform $Mg/(Mg+Fe^{2+})$ over a wide range in Si of up to one formula unit, the mafic rock amphiboles are characterized by lower (0.5 to 0.7) $Mg/(Mg+Fe^{2+})$, compared to the ultramafic rocks (0.7 and 0.9). REE and trace element profiles of amphiboles from mafic rocks are remarkably consistent. REE profiles are bow-shaped, and are characterized by depletion in LREE (La/Sm ≈ 0.61), a slight depletion in HREE (Gd/Yb ≈ 1.55) as well as a negative Eu anomaly, which is attributed to co-precipitation of plagioclase. REE and trace element profiles of ultramafic amphiboles are divided into two groups that correspond to different textural settings: Group A amphiboles occur in all specimens analyzed and are very similar to the profiles of the mafic rocks. In contrast, Group B amphiboles display relative enrichment in light REEs (La/Sm ≈ 2.05), have lower ΣREE, and lack a negative Eu anomaly relative to Sm and Gd. Group B amphiboles are more enriched in Th and U and show a more pronounced depletion in Ta, Nb, Ti and Y. Group B amphiboles grew in a reaction relationship with olivine and pyroxene. Groups A and B are virtually indistinguishable with respect to the major elements used for amphibole classification, suggesting that REE and selected trace element data when combined with textural observations may provide important additional insights into phase equilibria and conditions of crystallization.

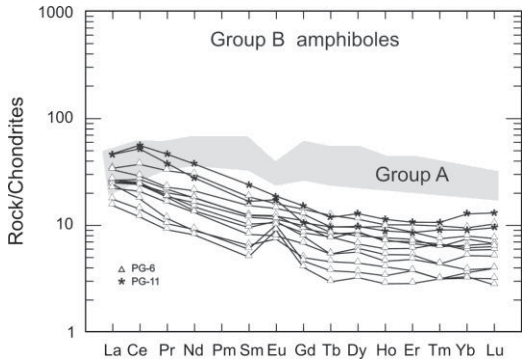

Figure 1. Contrasting REE profiles of amphiboles in ultramafic rocks