

In search of a superchondritic Nb/Ta reservoir: High-precision Nb/Ta and Zr/Hf ratios in ocean island and intraplate basalts

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A compilation of Nb-Ta data for terrestrial samples indicates that all known major reservoirs of the silicate Earth have subchondritic Nb/Ta ratios (<17.5). Superchondritic Nb/Ta ratios have only been reported from a few high-K island arc lavas, some OIBs, eclogite xenoliths and carbonatites. Here we present new high-precision HFSE concentration data (Nb, Ta, Zr, Hf and Lu) for a variety of OIBs from Rurutu, Samoa and the Azores, together with data for continental basalts (Rhön area, Germany). Concentrations were obtained by isotope-dilution (except Nb) using the MC-ICPMS at Münster and a mixed ¹⁸⁰Ta-¹⁸⁰Hf-¹⁷⁶Lu-⁹⁴Zr tracer. The external reproducibility is ±4% for Nb/Ta and ±0.6% for Zr/Hf (2σ), thus improving the analytical resolution nearly by a factor of about 10 compared to previous methods. The new data provide important constraints for a quantification of the HFSE budget of OIB mantle sources. They further provide information about the fate of subducted slabs and on the role of the subcontinental lithosphere in buffering the global Nb-Ta budget.

OIBs from Rurutu island have subchondritic Nb/Ta (14.8-16.7) but superchondritic Zr/Hf ratios (35.5-45.1). Nb/Ta is invariant with Nb concentration, whereas Zr/Hf is highly correlated with Hf concentration. This requires mixing between different reservoirs having the same Nb/Ta ratio. The overall sub-chondritic Nb/Ta ratios in OIBs argue against a super-chondritic Nb/Ta reservoir in the deep mantle as suggested by Rudnick et al. [1]. It is highly unlikely, that such a reservoir can be isolated in the Earth's mantle for a long period of time without being involved into mantle convection, and thus without being sampled by OIB.

Intracontinental primitive alkaline basalts and basanites from the Rhön area (Germany) have Nb/Ta=16.1-18.8. The Nb/Ta ratios are negatively correlated with Zr/Nb ratios, linking Nb/Ta variations with lithosphere - melt interaction. This interpretation is consistent with a previous model that involves HIMU-like mantle melt that assimilated subcontinental lithosphere [2], but requires the subcontinental lithosphere to be superchondritic in Nb/Ta. - *We thank C. Chauvel, S. Jung, M. Regelous and K. Haase who provided samples for this study.*

[1] Rudnick et al. 2000, *Science* 287, 278-281. [2] Jung & Hoernes 2000, *J. Volcanol. Geotherm. Res.* 99, 27-53.

Arsenic in deep groundwater of Switzerland and their environmental impact and health risk

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During the last ten years, enhanced arsenic contents in drinking water have become an important health threat in many countries. In Switzerland about 20'000 people live in areas in which the arsenic concentrations in drinking waters are between 10 µg/l, and 50 µg/l. This paper discusses the geological occurrence, the origin, the environmental impact and the health risks of arsenic in deep groundwaters. i.e. in cold and thermal mineral water, bore holes and tunnels which reach max. values of 3 mg/L.

Three main regions with elevated As-contents in deep waters can be distinguished: 1) Thermal springs occurring in the Molasse zone of Northern Switzerland, which is underlain by Mesozoic and Palaeozoic formations. It also includes thermal waters sampled at various depths of the different bore holes drilled for the radioactive waste repository program 2) The Western Alps zone in the Wallis and adjacent France (Savoy) where a series of thermal springs naturally emerge or occur in tunnels and 3) The Eastern Alps zone of the Rhine Valley and the Engadin, where a series of cold, highly mineralised, CO₂-rich springs occur. In all these areas arsenic originates from veins, containing various arsenate and sulphide minerals rich in As. In most cases they are located in the crystalline basement of Carboniferous or Permian age. In a few places the As-bearing minerals are located in Mesozoic carbonate-mica schists (Bündnerschiefer), which generally contain slightly elevated As-contents (20 ppm). The total arsenic content of all these waters varies between 20 and 2800 µg/l, with a median of about 100 µg/l. Where As(III) is the dominant species, also higher concentrations of dissolved iron(II), i.e. iron reducing conditions, are found. Upon contact with air, these waters locally form ferrihydrite deposits, sorbing effectively arsenic. These deposits contain between 0.5 and 10% As. When As-bearing spring water is percolating through soil horizons rich in organic matter, As is strongly sorbed by Fe-organic matter complexes. These horizons become enriched in As (up to 700 mg/kg). In case no sorption or co-precipitation is possible, As-rich spring waters are quickly diluted by local rivers. Bottled mineral waters are usually filtered and/or de-ironed and do not contain more than 5 µg As/l. Therefore, one can conclude that the environmental and health impact of these waters in Switzerland is almost negligible.