

^{92}Nb - ^{92}Zr in the Early Solar System

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^{92}Nb decays by electron capture to ^{92}Zr with a half life of 36 Ma, thus making this isotope system potentially useful for studies of the early solar system and early terrestrial evolution. Zr and Nb are both lithophile and, thus, were not fractionated from each other during core formation. However, the more incompatible behaviour of Nb relative to Zr during mantle melting makes the Zr-Nb system a particularly useful tracer of early melting processes, such as the formation of early crust and of early magma oceans on planets. High precision Zr isotope data are scarce because TIMS measurements have been hampered by the high first ionisation potential of Zr and the isobaric interference of ^{92}Mo derived from Re filaments on ^{92}Zr .

Using the IsoProbe Multiple Collector-ICPMS (MC-ICPMS) in Münster, we are currently able to obtain a precision of better than $\pm 0.7 \text{ } \epsilon$ ($2 \text{ } \sigma$) for as low as 50 ng of Zr. The ^{92}Zr abundances were analysed as $^{92}\text{Zr}/^{91}\text{Zr}$ and normalised to $^{90}\text{Zr}/^{91}\text{Zr}$ of 4.584, using the exponential law for fractionation correction. $^{92}\text{Zr}/^{91}\text{Zr}$ for samples are given as ϵ -value relative to a "terrestrial" value of 1.53120 ± 15 ($2 \text{ } \sigma$), which was obtained for a solution of AMES pure metal Zr over now 14 months. After quantitative extraction of Zr and Nb from the whole rock matrix by ion-exchange, Zr/Nb was measured with an external precision of better than $\pm 10\%$ at total Zr-yields of generally better than 95% (tested by multiple measurements of rock standards). Except for zircons, chemical separation of Zr from Mo is essential in order to avoid large ^{92}Mo interference corrections on ^{92}Zr . Likewise, efficient chemical separation of Zr from Ti is required to ensure constancy of mass bias and accurate mass bias correction.

In order to evaluate possible variations in the terrestrial Zr isotope composition of different reservoirs, we analysed zircon grains and whole rock samples of different ages and tectonic settings. Compositions of all terrestrial samples overlap with that of the AMES solution within analytical error. Likewise, $^{92}\text{Zr}/^{91}\text{Zr}$ of Archean to Proterozoic rutiles and ilmenites (high Nb/Zr) overlap with that of the AMES solution. Impact spherules from the lower Fig Tree Group of South Africa which, on the basis of Cr isotopes, were suggested to be partially of extraterrestrial origin (Shukolyukov et al. 1998) also agree in their $^{92}\text{Zr}/^{91}\text{Zr}$ with terrestrial rocks.

The presence of ^{92}Nb in the early solar system is indicated by significant ^{92}Zr anomalies in Ca, Al-rich inclusions (CAI) of the Allende meteorite (-2 to -4ϵ) and in a separate of the ordinary chondrite Adrar-003 ($+2.7\epsilon$). ^{92}Zr abundances in bulk chondrites (Allende, Murchison, Orgueil, Sahara 97096) agree with the terrestrial value within analytical uncertainty, thus demonstrating that the silicate Earth has a chondritic $^{92}\text{Zr}/^{91}\text{Zr}$. This observation is supported by "terrestrial" $^{92}\text{Zr}/^{91}\text{Zr}$ in bulk rock samples of the eucrites Juvinas, Millbillillie and Stannern, and the angrite Sahara 99055.

The discovery that the Allende CAI display clearly resolvable ^{92}Zr deficits at Zr/Nb from 50 to 70 provides unambiguous evidence for live Nb⁹² in the solar system, suggesting a minimum value of 0.001 for the initial $^{92}\text{Nb}/^{93}\text{Nb}$. The absence of resolvable ^{92}Zr anomalies in >3.5 Ga old Archean terrestrial rocks and minerals is strong evidence that no remnants of major silicate reservoirs that formed within the first 50 Ma after CAI condensation (magma ocean residue, depleted mantle or crust) are preserved on the Earth. In particular an old magma ocean residue would display clearly resolvable negative ^{92}Zr anomalies because the partitioning of Nb into Mg-perovskite ($K_d = 0.1-1$) is much lower than that of Zr ($K_d = 5-10$; e.g. Kato et al., 1996). A chondritic $^{92}\text{Zr}/^{91}\text{Zr}$ of the silicate Earth furthermore confines the Zr/Nb of the silicate Earth to $\pm 20\%$ of the chondritic Zr/Nb value, since otherwise a resolvable $^{92}\text{Zr}/^{91}\text{Zr}$ would be observed for the silicate Earth. Our ^{92}Nb - ^{92}Zr results are in agreement with Hf-W systematics (Halliday and Lee, 1999) that require formation of the Earth's core and of the major silicate reservoirs to have taken place at least 50 Myr after condensation of the solar system.

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