# Sm-Nd in zircon: An imperfect time capsule

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<sup>147</sup>Sm-<sup>143</sup>Nd and <sup>146</sup>Sm-<sup>142</sup>Nd systems were studied in 3.32-4.02 Ga single zircon grains from Jack Hills metaconglomerate, some of which were previously studied for Lu-Hf. The amount of Nd recovered from zircon grains was between 13-446 pg. The analytical precision of <sup>142</sup>Nd/<sup>144</sup>Nd and  $^{143}\mathrm{Nd}/^{144}\mathrm{Nd}$  ratios varied between 0.004-0.08% depending on the sample size. Nd concentrations in the zircons are 0.9-20 ppm (median 2.7). The <sup>147</sup>Sm/<sup>144</sup>Nd ratios vary from 0.4-1.2 (median 0.87). <sup>143</sup>Nd/<sup>144</sup>Nd ratios are variably radiogenic, from 0.5125 to 0.5346. Combined interpretation of <sup>147</sup>Sm-<sup>143</sup>Nd and U-Pb systems shows that LREE in zircons are a mixture of a primary component with high Sm/Nd (>1.6-2.0), and a secondary, younger component with low Sm/Nd. Determination of initial \_143Nd of ancient zircons with reasonable precision and accuracy is compromised by large errors in <sup>147</sup>Sm/<sup>144</sup>Nd ratios, which propagate to the uncertainty of  $\epsilon^{143}$ Nd, in the best preserved, alteration-free zircons, and by the presence of secondary Nd of unknown age and isotopic composition in more altered zircons.

Sm-Nd isotopic system in zircon is an imperfect time capsule. Initial  $\epsilon^{143}$ Nd of the source rocks of ancient zircons, or the timing of the zircon crystallization may be difficult and in some cases impossible to determine using the <sup>147</sup>Sm-<sup>143</sup>Nd system. Application of the <sup>147</sup>Sm-<sup>143</sup>Nd system to detect the secondary REE component in zircon, and of the <sup>146</sup>Sm-<sup>142</sup>Nd system to study the timing of early planetary differentiation are more promising, but it will require advancement of the analytical procedures to achieve Sm and Nd blanks of 0.2 pg or lower, and ion yields of 20-30% or higher in isotopic analyses. These goals may be within reach of modern isotope geochemistry.

# Geochemical test for branching decay of <sup>176</sup>Lu

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Recent high-precision determinations of the <sup>176</sup>Lu decay constant by decay counting (Nir-El and Lavi 1998) and by geological age comparison (Scherer et al. 2001, 2002, Blichert-Toft et al. 2002, Bizzarro et al. 2003) have produced two incompatible groups of values. The  $\lambda^{176}$ Lu values of 1.86-1.87\*10<sup>-11</sup> y<sup>-1</sup> were determined by decay counting and by age comparisons using terrestrial minerals of Proterozoic age, whereas values of 1.94-1.98\*10<sup>-11</sup> y<sup>-1</sup> were determined in age comparison studies of meteorites.

One possible cause of this discrepancy is branching decay of <sup>176</sup>Lu. The decay of <sup>176</sup>Lu to <sup>176</sup>Yb by electron capture was detected in the early studies of radioactivity of <sup>176</sup>Lu. The reported values of the electron capture fraction  $\lambda_e/(\lambda_e + \lambda_{-})$  in the total <sup>176</sup>Lu decay vary from less than 0.03 (Dixon et al. 1954, Glower and Watt 1957) to 0.67 (Flammersfeld 1947). If the electron capture fraction is close to the upper limit of the reported values, it can explain the 4-6% difference between the  $\lambda^{176}$ Lu values estimated from ca. 4.5 Ga meteorites and younger terrestrial minerals.

In order to get a reliable estimate for the electron capture decay of <sup>176</sup>Lu, we have measured Yb isotopic composition in 2.7 Ga zircons with  $Lu/Yb_N$  (chondrite-normalized) ratios of 1.40 and 1.45, in 1.0 Ga xenotime with Lu/Yb<sub>N</sub>=1.23, using Yb from the 28 Ma Fish Canyon Tuff (FCT) zircon and titanite as the modern reference value. Yb isotopic ratios were measured using a Triton TI mass specrometer at the GSC, corrected for isobaric interference from <sup>176</sup>Lu (negligible in most analyses), and normalized to <sup>172</sup>Yb/<sup>174</sup>Yb=0.68321 using exponential law. Multiple analyses yielded the following average values ( $\pm 2\sigma_m$ ) for the <sup>176</sup>Yb/<sup>174</sup>Yb ratio: 0.4022134  $\pm$ 0.0000017 for the FCT zircon and titanite, 0.4022134  $\pm$ 0.0000019 for the 1.0 Ga  $\,$  xenotime, and 0.4022124  $\pm$ 0.0000033 for the 2.7 Ga zircons. These data yield  $\lambda_{a}/(\lambda_{a}+\lambda) =$ - 0.005±0.015 (2\_) and establish an upper limit of 1% of total decays for the electron capture branch. Branching decay can therefore be eliminated as the cause of the discrepancy in <sup>176</sup>Lu decay constant estimates.

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