

## Unusually depleted Hf isotopic signatures in late Archean carbonatite, Superior Province, Canada: a result of carbonate metasomatism?

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Hf isotope analyses were obtained by laser ablation ICP-MS on single zircons from carbonatite of the 2.68 Ga Beaverhouse Lake alkaline complex, which cuts metasedimentary rocks of the Quetico subprovince in the western Superior Province. The zircons display highly depleted, and variable Hf isotopic signatures with initial <sup>176</sup>Hf/<sup>177</sup>Hf ratios between 0.281360 and 0.281577 corresponding to εHf(t) between +10 and +18. This contrasts with Nd and Hf isotopic ratios from the surrounding silicate phases, which are mildly to moderately depleted. The intrusion is part of a suite of LILE-rich, syn- to post-kinematic complexes, which are interpreted to have formed by partial melting of a metasomatized upper mantle. The Beaverhouse Lake intrusion has high LILE, moderately high LREE, low HREE and variable negative Nb and Ta anomalies in primitive mantle normalized diagrams. The carbonatite is a medium to coarse grained sövite containing minor phlogopite and aegirine-augite and subordinate F-apatite, zircon and monazite. It contains high Ba (<450 ppm) and Sr (<6600 ppm) which is mainly accommodated in calcite (SrO = 1.0-1.2 wt %) and the silicate minerals have high contents of F and very low Cl, confirming an igneous origin. We suggest that the carbonatite formed by small degrees of partial melting of carbonate-bearing upper mantle previously affected by carbonate metasomatism. Carbonate in the mantle is expected to strongly fractionate Lu from Hf leading to elevated Lu/Hf ratios and with time radiogenic Hf isotope ratios (partition coefficients from Hamilton et al., 1989. In: Bell, K. (ed.) Carbonatites: Genesis and Evolution). Rocks originating by partial melting of such a source will inherit highly radiogenic initial Hf isotopic compositions. The mantle is capable of storing large amounts of carbonate at depths beneath 100 km (Wyllie 1987, EPSL 82, 391-397) although carbonate is rarely reported from mantle xenoliths and usually in minor modal amounts. We discuss the implications of the extreme fractionation of Lu/Hf, which is expected from carbonate metasomatism.

## The influence of recycled oceanic crust on the potassium and argon budget of the earth

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The <sup>40</sup>Ar budget of the earth has historically been used as an argument for strong mantle layering. The amount of <sup>40</sup>Ar that has been generated in the earth from the decay of <sup>40</sup>K can be calculated if one can estimate the earth's potassium content. The K content of the silicate earth is commonly estimated at ~250 ppm based on K/U ratios of ~12-13000 in MORB and continental crust, and assuming a chondritic U content for the earth. Given this K content, only ~50% of the <sup>40</sup>Ar generated over earth history currently resides in the atmosphere. Because the upper mantle is thoroughly degassed and contains little <sup>40</sup>Ar, the "missing" Ar has been taken as evidence for a gas-rich (and therefore convectively isolated) lower mantle [1].

An alternative solution of the "missing Ar" problem is that the K content of the silicate earth is substantially lower than 250 ppm. Previous estimates have failed to take into account the composition of recycled oceanic crust, which based on current production rates should comprise some 5-10% of the mantle by mass. Because K is more soluble than U in subduction-generated hydrous fluids, recycled oceanic crust is characterised by extremely low K/U ratios. This is evidenced in the low K/U ratios of eclogites (~1000; [2]) and in HIMU-type basalts (~4000), whose source contains significant quantities of recycled crust. Ocean island basalts span a large range in K/U (~4000-22000). However, the vast majority have K/U values well below the canonical bulk silicate earth value of ~12700. In addition, average K/U ratios from individual island chains are negatively correlated with <sup>206</sup>Pb/<sup>204</sup>Pb, indicating that the low K/U in OIBs is a source feature. The low K/U values in many OIBs is consistent with their derivation from mantle plumes containing variable quantities of subduction-modified oceanic crust, and indicate that OIB reservoirs are generally characterised by low K/U. Inclusion of a recycled crust reservoir in K and U mass balance calculations results in a bulk silicate earth K/U of ~8000, or a K content of ~170 ppm. As a result, much of the "missing" <sup>40</sup>Ar thought to be stored in the deep mantle simply does not exist, with ~75-80% of the earth's <sup>40</sup>Ar residing in the atmosphere or continental crust. The remaining <sup>40</sup>Ar can be accommodated in the convecting mantle without convective isolation of a deep, undegassed reservoir. In short, the <sup>40</sup>Ar budget of the earth is fully consistent with whole mantle convection.

1. Allegre, C.J., Hofmann, A., O'Nions, K., (1996) *Geophys. Res. Lett.* **23**, 3555-3557.
2. Becker, H., Jochum, K.P., Carlson, R.W., (2000), *Chem. Geol.* **163**, 65-99.