Initial ^{176}Hf/^{177}Hf of the Earth and early silicate differentiation

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Investigating silicate differentiation on Earth using the ^{176}Lu-^{176}Hf system requires knowledge of the ^{176}Hf/^{177}Hf evolution of the bulk silicate Earth (BSE). The starting point of this evolution is commonly determined by back-calculating the present-day ^{176}Hf/^{177}Hf of chondrites to the age of the solar system [1]. Relative to this ^{176}Hf/^{177}Hf evolution, most Hadean zircons exhibit less radiogenic ^{176}Hf/^{177}Hf and were interpreted in terms of crust extraction from a primordial mantle at 4.4-4.5 Ga [e.g., 2]. However, Bizzarro et al. [3] argued that the initial ^{176}Hf/^{177}Hf of the angrite Sahara 99555, which is ~4 ε-units below the back-calculated chondrite initial [1], provides a more appropriate initial ^{176}Hf/^{177}Hf of the BSE. Relative to such a revised ^{176}Hf/^{177}Hf evolution of the BSE [3], Hadean zircon populations show both enriched and depleted signatures, which was inferred to imply continuous crustal growth throughout the Hadean [3].

To better constrain the initial ^{176}Hf/^{177}Hf of the BSE we have initiated a Lu-Hf study on primitive meteorites, complemented by investigations of KREEP-rich lunar rocks, which provide the signature of a strongly enriched reservoir that formed at ca. 4.4 Ga [4]. Our data for low-Lu/Hf phases in primitive meteorites, which should directly provide the initial ^{176}Hf/^{177}Hf of the solar system, overlap with the back-calculated chondrite initial [1]. Moreover, we show that the ^{176}Hf/^{177}Hf of KREEP at ~3.9 Ga is ~5.5 ε-units below the contemporaneous ^{176}Hf/^{177}Hf of chondrites, yielding a two-stage model age of ca. 4.4 Ga, assuming a chondritic Lu-Hf isotopic evolution for the bulk Moon. This Lu-Hf model age of KREEP is fully consistent with other, independent estimates for the age of KREEP. In contrast, the two-stage model age of our KREEP-rich lunar rocks relative to the revised BSE evolution of [3] is ca. 4.0 Ga and thus ca. 400 Myr too young. Thus, our new data do not support the revised initial ^{176}Hf/^{177}Hf of the BSE based on Sahara 99555 [3], but rather indicate that the back-calculated chondrite composition [1] is a reliable estimate for the initial ^{176}Hf/^{177}Hf of the BSE.

[1] Bouvier et al. (2008) EPSL 273, 48–57. [2] Kemp et al. (2010) EPSL 296, 45-56. [3] Bizzarro et al. (2012) G3 13, Q03002. [4] Carlson & Lugmair (1979) EPSL 45, 123–132.

The structural role of iron in pantelleritic glasses

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The main objects of this work are to determine the effect of oxygen fugacity and composition on the structural role of Fe in silicate glasses representative of pantelleritic magmas. Since many studies have investigated melts using glasses as a structural analogue [1, 2, 3], we have focused on the structural environments of Fe and S in synthetic glasses to relate their behaviour to natural magma with the same composition.

Several glasses have been synthesized under controlled oxygen fugacity conditions (from air to iron-wustite buffer) and with different (Na+K)/Al ratios. In fact, alkali content is known to affect strongly the Fe oxidation state in silicate glasses [4], but it is still controversial to which extent alkali can modify Fe structural role in glasses/melts. Hydrothermal syntheses have been carried out at 1.5 kbar and temperatures between 800°C and 1000°C. Additionally, glasses were produced by melting in a Ar/H$_2$ gas mixing furnace at ambient pressure and at 1250°C.

Water incorporation in the glasses has been characterized by Karl-Fischer titration (KFT) and IR spectroscopy. Additionally, the redox state of iron in the glasses has been determined by colorimetric wet-chemical analyses. Preliminary Fe K-edge X-ray Absorption Spectroscopy data allowed to study the kinetic of Fe reduction under anhydrous conditions. Here we present preliminary results on Fe oxidation state, coordination number and geometry [5]. The results will be useful for understanding the role of Fe in the polymerization of the silicate melt and the interaction Fe-S.

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