Hf-W constraints on the formation and differentiation of the Moon

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Hf-W chronometry is well suited to investigate the timescales of early lunar differentiation because Hf/W ratios are variable amongst the products of the lunar magma ocean [1,2]. Application of Hf-W chronometry to lunar whole-rock samples however is hampered by the production of ^{182}W via neutron-capture of ^{181}Ta during prolonged cosmic-ray exposure of the lunar surface [3]. Almost all lunar samples contain some metals, which contain virtually no Ta and hence no cosmogenic ^{182}W. The age of magma ocean crystallization that has been derived from the W isotope composition of lunar metals is ~40 Myr after the start of the solar system [4], apparently inconsistent with the ~200 Myr age obtained from ^{146}Sm-^{142}Nd systematics [5,6]. Here we present new W isotope data for metals from a comprehensive set of lunar samples. Our new data are significantly more precise than most of the earlier data, mainly because we processed ~4 times more material than was used in earlier studies [4]. All lunar metals separated from KREEP-rich samples, low- and high-Ti mare basalts have indistinguishable $^{182}W/^{184}W$ ratios, which are identical to those previously reported for KREEP [4]. In contrast to earlier studies [4,7] we do not find systematic variations in the $^{182}W/^{184}W$ ratios of lunar samples, despite the large variations in Hf/W ratios of the source areas. This indicates that solidification of the lunar magma ocean continued until after the effective life-time of ^{182}Hf (i.e., >60 Myr) and might have continued until ~200 Myr, as indicated by ^{146}Sm-^{142}Nd systematics [5,6]. Our new data reveal that the lunar and terrestrial mantles have indistinguishable W isotope compositions, which could indicate that the Moon mainly consists of material derived from the Earth's mantle. This however is inconsistent with constraints from dynamical simulations of the giant impact. Alternatively, W isotopes re-equilibrated during the giant impact, as has been proposed to account for the similarity in O isotope composition of the Earth and Moon [8]. Whether this process can effectively equilibrate W isotopes remains to be investigated.

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Dynamic metal speciation analysis by stripping chronopotentiometry at scanned deposition potential (SSCP)

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In the broad context of stripping voltammetric techniques, the depletive mode of stripping chronopotentiometry, SCP, has fundamental advantages for metal speciation analysis. Complete voltammetric potential-current curves are inherently rich in information content: as measurements are made from the foot of the wave to the limiting deposition current region the relevant part of the stability distribution and corresponding parts of the rate constant distribution are scanned. Conventional DC steady-state voltammetry lacks the necessary sensitivity for measurements at environmentally relevant concentrations, however analogous curves, denoted as SSCP waves, can be constructed by plotting the magnitude of the SCP stripping peak as a function of deposition potential. Analogous to the Deford-Hume expression for voltammetric waves, speciation parameters derive from the change in half-wave deposition potential that occurs on complexation, and the magnitude of the limiting plateau. The distinctive features of SSCP include (i) an effective getting around part of the Nernstian extension of the reoxidation process, leading to (ii) greater resolution than conventional stripping voltammetries, (iii) a certain insensitivity to electrochemical irreversibility, especially at a microelectrode, (iv) practically freedom from induced metal ion adsorption interferences, (v) no requirement for excess ligand during stripping, and (vi) ability to provide a certain unambiguous measure of any chemical heterogeneity in the metal speciation. In case of kinetic currents, i.e. systems with limited association/dissociation rates, invoking the Koutecky-Koryta approximation allows a rigorous expression to be obtained for the full SSCP wave. These features are illustrated by practical examples.

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