

## A HIGH-PRECISION CADMIUM STABLE ISOTOPE STUDY OF APOLLO LUNAR SOILS

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**Introduction:** Pioneering studies of Apollo lunar soils have revealed a geochemical dichotomy in the lunar regolith reflecting the dominance of mare and highland lithologies, with variable admixtures of Procellarum KREEP Terrane, and differences in their exposure to galactic cosmic rays [1]. Cadmium, with a half-mass condensation temperature of 652K [2], exhibits a stronger depletion in the bulk Moon and larger stable isotope fractionation in lunar samples [3,4,5] compared to the Earth. In contrast to other volatile elements (e.g., K, Zn, Ga), cadmium has the unique potential to trace thermal neutron capture (*n.c.*) effects which are reflected by an enrichment in <sup>114</sup>Cd due to neutron absorption by <sup>113</sup>Cd (cross-section: 2.10<sup>4</sup> barns). Thus, a Cd isotope study of lunar soils provides a means to understand the origin of volatile elements depletion and processes of stable isotope fractionation at the lunar surface as well as gather information on the formation, evolution and composition of the Moon.

**Samples and Methods:** Lunar soils from Apollo 12 (n=5) and Apollo 16 (n=7) missions were selected to cover a large range of maturity and include the most immature trench samples 12032 and 12033 which have been reported to contain abundant K- and P-rich glass [6]. The samples were acid-digested at the University of Cologne while chemical separation of Cd and isotope measurements, performed by TIMS (ThermoFisher Triton) using a <sup>106</sup>Cd-<sup>108</sup>Cd double spike for instrumental mass bias correction [7], were done at the Max Planck Institute for Chemistry in Mainz. The isotopic compositions are expressed as  $\epsilon^{112/110}\text{Cd}$  relative to NIST SRM3108 Cd [8]. The amounts of Cd analyzed varied from ~2 to 20 ng (blanks of 8 to 20 pg were negligible) – with an analytical uncertainty on  $\epsilon^{112/110}\text{Cd}$  ranging from  $\pm 1$  to  $\pm 0.2$ , respectively. Since measurement of <sup>113</sup>Cd by TIMS is compromised by odd-even isotope effects [7,9], the *n.c.* effect was derived from the <sup>114</sup>Cd/<sup>112</sup>Cd ratio, normalized to <sup>110</sup>Cd/<sup>112</sup>Cd to remove the natural stable isotope fractionation effects.

**Results and discussion:** The Cd concentrations are on average lower in Apollo 12 than Apollo 16 soils and are associated to large Cd stable isotope variations. The  $\epsilon^{112/110}\text{Cd}$  (~0 to +110) of Apollo 12 soils co-vary with the maturity index, whereas Apollo 16 soils show a more restricted range (+60 to +90) with no clear relationship with soil maturity. Likewise, *n.c.* effects are positively correlated with the maturity index for Apollo 12 soils. In contrast, no clear correlation is observed for Apollo 16 soils which are relatively uniform, except for two soils collected at Stone mountains which exhibit the highest *n.c.* effects. There is a clear Cd isotope dichotomy in  $\epsilon^{112/110}\text{Cd}$ -Cd space where Apollo 12 and Apollo 16 soils define two distinct negative correlations. These can be interpreted in terms of either Rayleigh fractionation due to evaporative Cd loss imparted by micrometeorite impacts, or binary mixing involving distinct components. Given that the isotope fractionation factor inferred from the slopes of the two regressions lines falls below the theoretical kinetic isotope fractionation factor ( $\alpha^{112/110}\text{Cd} = 0.9910$ ), the two correlations are best explained by mixing involving at least three components – mare basalt, highland feldspathic crust and Procellarum KREEP. Importantly, the Apollo 12 correlation intersects the Bulk Silicate Earth value corresponding also to the isotope composition of the most immature and KREEP-rich soil 12033. The remarkable positive correlation between  $\epsilon^{112/110}\text{Cd}$  and the *n.c.* effect in Apollo 12 soils constrains the isotopic compositions of the mare and KREEP components to be, respectively, isotopically heavy and light. A Cd isotopic composition of KREEP comparable to the bulk Earth value may, in turn, suggest that the Moon and Earth share a similar Cd isotope signature which bears important implications on the lunar and terrestrial volatile elements depletion and models of formation of the Moon. In particular, a Cd isotope similarity in the Earth-Moon system would imply Moon formation from a well-mixed vapor disk without significant Cd isotope fractionation imparted by volatile loss during and following the giant impact.

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