The chlorine-isotopic composition of lunar KREEP from magnesian-suite troctolite 76535

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ABSTRACT

We conducted in situ Cl isotopic measurements of apatite within intercumulus regions and within a holocrystalline olivine-hosted melt inclusion in magnesian-suite troctolite 76535 from Apollo 17. These data were collected to place constraints on the Cl-isotopic composition of the last liquid to crystallize from the lunar magma ocean (i.e., urKREEP, named after its enrichments in incompatible lithophile trace elements like potassium, rare earth elements, and phosphorus). The apatite in the olivine-hosted melt inclusion and within the intercumulus regions of the sample yielded Cl-isotopic compositions of 28.3 ± 0.9‰ (2σ) and 30.3 ± 1.1‰ (2σ), respectively. The concordance of these values from both textural regimes we analyzed indicates that the Cl-isotopic composition of apatites in 76535 likely represents the Cl-isotopic composition of the KREEP-rich magnesian-suite magmas. Based on the age of 76535, these results imply that the KREEP reservoir attained a Cl-isotopic composition of 28–30‰ by at least 4.31 Ga, consistent with the onset of Cl-isotopic fractionation at the time of lunar magma ocean crystallization or shortly thereafter. Moreover, lunar samples that yield Cl-isotopic compositions higher than the value for KREEP are likely affected by secondary processes such as impacts and/or magmatic degassing. The presence of KREEP-rich olivine-hosted melt inclusions within one of the most pristine and ancient KREEP-rich rocks from the Moon provides a new opportunity to characterize the geochemistry of KREEP. In particular, a broader analysis of stable isotopic compositions of highly and moderately volatile elements could provide an unprecedented advancement in our characterization of the geochemical composition of the KREEP reservoir and of volatile-depletion processes during magma ocean crystallization, more broadly.

Keywords: Apatite, Mg-suite, Apollo, volatiles, moon, magma ocean, melt inclusion, phosphates

INTRODUCTION

The Moon formed in the aftermath of a giant impact between the proto-Earth and Theia (Canup and Asphaug 2001; Hartmann and Davis 1975; Lock et al. 2018) between 60 and 120 million years after the birth of the solar system at 4.567 Ga (as defined by the ages of calcium-aluminum rich inclusions within CV meteorites; Connelly et al. 2012). After the Moon coalesced into a distinct body, it underwent differentiation to form a small metallic core and molten silicate mantle, the latter of which is referred to as the lunar magma ocean (LMO). As cooling proceeded, the LMO crystallized to form a cumulate mantle comprised of mostly ferromagnesian silicates with progressively higher Mg/Fe ratios with depth (Charlier et al. 2018; Elardo et al. 2011; Elkins-Tanton and Grove 2011; Lin et al. 2017; Rapp and Draper 2018; Snyder et al. 1992). The LMO liquid became progressively enriched in Fe and incompatible trace elements as crystallization continued, and a primary flotation crust of ferroan anorthosite formed after about 70–80% crystallization (Charlier et al. 2018; Elkins-Tanton and Grove 2011; Lin et al. 2017; Rapp and Draper 2018; Snyder et al. 1992). After 88–98% crystallization, the upper part of the cumulate mantle became rich in Fe-Ti oxide cumulates (Charlier et al. 2018; Elkins-Tanton and Grove 2011; Lin et al. 2017; Rapp and Draper 2018; Snyder et al. 1992), and the final residual liquid that remained uncrysallized after about 99% crystallization was enriched in incompatible elements and termed urKREEP (Warren 1988; Warren and Wasson 1979) after the incompatible elements potassium (K), rare earth elements (REE), and phosphorus (P). The abundance of cool, dense, Fe-rich cumulates at the top of the mantle and hot Fe-poor cumulates at the base of the lunar mantle resulted in a density instability that instigated cumulate mantle overturn (Hess and Parmentier 1995; Ringwood and Kesson 1976), resulting in a redistribution of cumulates in the lunar mantle that set the stage for secondary crust production on the Moon (Shearer et al. 2006; Wieczorek et al. 2006).

The fate of urKREEP during cumulate mantle overturn is poorly constrained, but a KREEP-like component in products of secondary volcanism is evident in many lunar sample types, including plutonic rocks from the lunar highlands, some mare basalts, and some impact melt rocks (Shearer et al. 2006). A pure sample of urKREEP is not preserved in any lunar samples, so the composition of urKREEP must be inferred from samples with a KREEP component (Taylor et al. 2006; Warren 1988; Warren and Wasson 1979). Given that urKREEP represents a primordial geochemical reservoir on the Moon, establishing its isotopic and chemical composition is important for constraining geochemical mixing models and for determining the bulk composition of the Moon, particularly for the origin and onset of moderately and highly volatile element depletion in the Moon (Barnes et al. 2016; Boyce et al. 2018; Day and Moynier 2014; Day et al. 2020; Dhalwal et al. 2018; Hauri et al. 2015; Kato et al. 2015; Lock et al. 2018; McCubbin et al. 2015; Wang and Jacobsen 2016). In particular, chlorine is one of the most incompatible moderately volatile elements, so the Cl-isotopic composition of KREEP represents the isotopic composition of the largest Cl reservoir on the Moon at the end of LMO crystallization.