

CONDENSATE ZINC ON THE SURFACE OF THE MOON EVIDENCED FROM THE ‘RUSTY ROCK’, 66095. James M.D. Day^{1,2}, Frédéric Moynier², Charles K. Shearer³ ¹Scripps Institution of Oceanography, University of California San Diego, La Jolla, CA 92093 (jmdday@ucsd.edu); ²Institut de Physique du Globe de Paris, 75238 Paris cedex 05, France; ³Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131.

Introduction: Recent examinations of Apollo samples using Zn isotopes have shown that mare basalts dominantly exhibit enrichments in the heavy isotopes of Zn, translating to $\delta^{66}\text{Zn}$ values ($\delta^{66}\text{Zn} = [({}^{66}\text{Zn}/{}^{64}\text{Zn})_{\text{sample}}/({}^{66}\text{Zn}/{}^{64}\text{Zn})_{\text{Lyon standard}} - 1] \times 1000$) of +1.4 to +1.6‰ [1,2]. These results have been interpreted to reflect kinetic isotopic fractionation of Zn in response to volatile element loss from the Moon, either during the giant impact [1], and/or during a lunar magma ocean phase [3]. However, there are a subset of mare basalts and ferroan anorthosites with low $\delta^{66}\text{Zn}$ (to as low as -11.4‰) and moderately high Zn contents, which do not appear to fit this paradigm. Instead, these samples have been interpreted to reflect the presence of isotopically light condensate Zn on the lunar surface [1-3].

Here, we examine these issues using the ‘Rusty Rock’. The ‘Rusty Rock’, 66095, is a fine-grained, sub-ophitic to ophitic melt-rock that contains a wide variety of basaltic to anorthositic lithic clasts [4,5]. A remarkable aspect of 66095, which has been considered akin to the pyroclastic bead deposits at the Apollo 15 (15426) and 17 (74220) sites, is the unusual enrichments in ²⁰⁴Pb, Cd, Bi, Br, I, Ge, Sb, Tl, Zn and Cl (e.g., [6-11]), which indicate that portions of these samples contain an anomalously high volatile component. This raises the question of how volatile and moderately volatile elements were inherited in these rocks; through endogenous, or exogenous processes.

Methods: Three fragments of 66095 were studied. Two fragments represented breccia material with no large clasts (.421 and .430); fragment .425 was composed of anorthosite-rich material, with black glass. .425 and .430 were broken into sub-fragments and powdered (splits A and B), while .421 was completely powdered. All powders were analyzed for Os isotope and HSE abundance (Os, Ir, Ru, Pt, Pd, Re) systematics and for >40 major-, minor- and trace-element abundances at SIO using methods described previously [12]. Sequential leaching experiments using H₂O, HCl, HNO₃ and HF were performed on portions of powders to examine the location of Zn and other elements. Zinc isotopic analyses were performed at IPG-Paris, using methods outlined previously [2]. Elemental mapping was done using established methods, at UNM [11].

Results: Fragments of 66095 have broadly flat chondrite-normalized HSE patterns, but with notable relative enrichment in Re, with measured ¹⁸⁷Os/¹⁸⁸Os

ranging from 0.122 to 0.137. These compositions are consistent with $\sim 0.6 \pm 0.2\%$ impactor contribution to the fragments that we examined. Bulk-rocks and residues have relatively flat CI-normalized rare earth element (REE) patterns, similar to prior results [13], but leachates are enriched in the light REE, P, Ni and Zn, relative to residues. Leachates, residues and whole-rocks have high Pb (3.5-10.3 $\mu\text{g g}^{-1}$) and Zn (87 to 7099 $\mu\text{g g}^{-1}$) contents. Zinc isotopic compositions for bulk rocks, leachates and residues are the lowest measured to date for any Solar System materials, with $\delta^{66}\text{Zn}$ ranging from -8 to -14‰ (Figure 1). We also examined a fragment of Apollo mare basalt 14053. This sample has previously been shown to have isotopically light Zn [2]. Sequential leaching demonstrated that the silicate portion accessed using HF-HNO₃ acid attack yielded $\delta^{66}\text{Zn}$ (+1.6‰); identical to that of previously studied mare basalts [1,2].

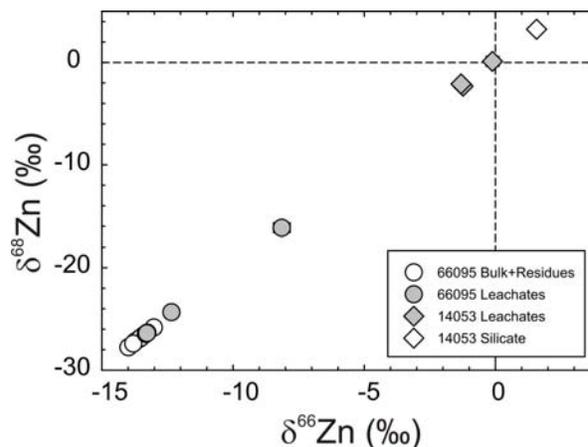


Figure 1: $\delta^{66}\text{Zn}$ versus $\delta^{68}\text{Zn}$ for bulk rocks, residues and leachates of Apollo samples 66095 and 14053. Uncertainties (2σ) are smaller than symbols.

In order to identify the phases responsible for hosting Zn and other moderately volatile elements in 66095, we expanded the investigations of [11] to examine a range of mineral phases (Figure 2). Phases rich in Zn include high Zn-Fe-S phases (sphalerite), as well as troilite. Phases enriched in Cl appear associated with sulfides and metallic iron, but Cl has also been redistributed as low temperature alteration products, including Cl-bearing akaganéite [FeO(OH, Cl)] and lawrencite [FeCl₂] [11], whereas Zn appears to be mostly sited within stoichiometric S-rich phases.

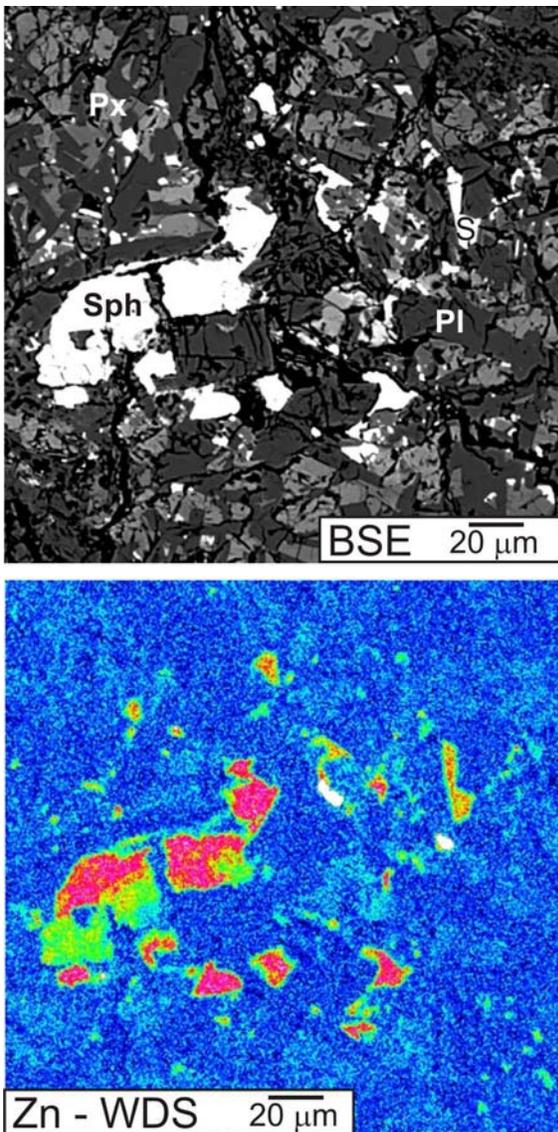


Figure 2: BSE and WDS X-ray maps (Zn) illustrating the location of Zn within sphalerite, troilite, and metallic iron in 66095. Matrix materials are dominantly plagioclase (pl) and pyroxene (px).

Discussion: Fragments of material that we analyzed have a relatively limited estimated impactor contribution (~0.6%), compared with fragments of 66095 measured previously (up to 10% impactor contribution [14]). Thus, despite ubiquitous evidence for volatile element enrichment in fragments of 66095 [6-11], impactor contributions vary significantly, suggesting that additions from impacts may not solely be responsible for volatile enrichments in 66095.

The sub-ophitic to ophitic texture of 66095 is evident in fragments of the samples that we studied (Figure 2), where S-rich phases that dominantly host Zn

appear to have formed interstitially to silicate grains. These observations offer the possibility that the Zn isotopic signature of 66095 was inherited during or prior to impact-driven melting to create the 66095 melt rock. In contrast, it has been shown that Cl was dominantly preserved as lawrencite in 66095, prior to alteration to akaganéite, and that low temperature alteration effects have redistributed Cl within the sample [11]. A secondary, hydrothermal origin for Cl, versus a primary impact melt association for sulfides rich in Zn may account for the extremely light Zn isotopic character that contrasts so strongly with the enrichment in the heavy isotopes of Cl in 66095 ($\delta^{37}\text{Cl} = +14$ to $+15.6\%$ [11]). Alternatively, kinetic isotopic fractionation of Zn and Cl likely occurred as very different speciations (ZnS versus HCl/FeCl₂, for example), leading to differing isotope systematics for the two elements.

Previous studies have shown enrichment in the heavy isotopes of Zn, as well as potentially Cl, K and S, in lunar mare basalts [3]. Our new results for Apollo mare basalt 14053 support the concept that mare basalts with light Zn isotope compositions have been affected by condensate Zn. This Zn was likely added to the exteriors of samples from vapor plumes generated either during exhalative eruptions, or from impact-gardening, at the lunar surface. Results from 66095 indicate that portions of the lunar crust may be enriched in condensates of volatile elements inherited from heat-induced vaporization at or close to the lunar surface. A Pb-Pb age of 3.8 Ga has been reported for 66095 [6], indicating that isotopically light condensate Zn was present on the lunar surface at this time. Thus, the Zn isotopic composition of 66095 supports models that invoke loss of Zn from the lunar interior during magma ocean differentiation, outgassing and impacts, and its partial preservation on cold, crustal rocks at the surface.

References: [1] Paniello et al. (2012) *Nature*, 490, 376-379; [2] Kato et al. (2015) *Nature Comm.* DOI: 10.1038/ncomms8617; [3] Day & Moynier (2014) *Phil. Trans. A Math. Phys. Eng. Sci.* 372, 20130259; [4] Garrison & Taylor (1980) *Proc. Conf. Lunar Highland Crust*, 395-417; [5] Hunter & Taylor (1981) *LPS*, **XII**, 261-280; [6] Nunes & Tatsumoto (1973) *Science*, **182**, 916-920; [7] Hughes et al. (1973) *Lunar Sci.* **IV**, 400-402; [8] Krahenbuhl et al. (1973) *PLSC*, **4**, 1325-1348; [9] Allen et al. (1975) *PLSC*, **6**, 2271-2279; [10] Jovanovic & Reed, 1981) *PLPSC*, **12**, 295-304; [11] Shearer et al. (2014) *GCA*, **139**, 411-433; [12] Day et al. (2015) *M&PS*, **50**, 1750-1766; [13] Wänke et al. (1981) *LPS*, **XII**, 1136-1138; [14] Ebihara et al. (1992) *PLPSC*, **22**, 417-426.