LUNAR APATITE – A RELIABLE SHOCK-RESISTANT HYGROMETER AND IMPACT-SENSITIVE Pb-Pb CHRONOMETER?

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Introduction: Apatite ($Ca_5[PO_4]_3[F,Cl,OH]$) is one of the most versatile minerals among terrestrial and planetary samples [1]. It is receiving rapidly increasing attention as a key tracer of the volatile budget [e.g. 2] and absolute age [e.g. 3] of planetary materials. However, little attention has been given to understand how impact processes affect the structure of apatite and the associated consequences on element and isotopic mineral chemistry. Here we focus on variably shocked lunar Mg-suite apatite, in order to investigate if the level of shock-deformation reflected in microtexture of apatite correlates with the H content (reported from hereon in terms of equivalent H_2O) and its δD isotopic composition. Moreover, we determined the Pb-Pb age of the exact same apatite (and associated merrillite) grains in order to discriminate whether the particular H_2O-δD signature is correlated with the Pb-Pb isotopic disturbance caused by the samples' impact history.

Samples: When it comes to studies of water in lunar apatite, most lunar lithologies ranging from basaltic [e.g. 4] to more evolved lithologies [5] have been thoroughly investigated. However, correspondingly little work has been done [6] on apatite in samples from lunar highlands. In this study, six different samples of Mg-suite norite, troctolite and gabbro were selected from the Apollo 17 collection, based on increasing levels of shock deformation [7]: unshocked S1 troctolite 76535, brecciated S2 anorthositic troctolite 76335, breccia 76255 with troctolite, norite and gabbro clasts (S2, S3 and recrystallized) within impact melt, 73235 S3 shocked troctolite, 72255 (Civet Cat fragment, S3-4), and 78236 & 78236 S5-S6 shocked norites. Albeit numerous geochronological investigations of most of these Mg-suite samples exist [summerized in 8], there has been only one *in situ* phosphate age determination in Mg-suite apatite and merrillite [3].

Methods: H_2O content and δD were obtained by Cameca NanoSIMS 50L located at The Open University, using a previously established protocol [4,6]. Pb-Pb isotopic measurements were performed using CAMECA 1280 ion microprobe at the NordSIMS facility, located at the Swedish Museum of Natural History (Stockholm), following previously reported protocols for Ca-phosphate analyses [3]. In nine different polished thin sections, we located 36 grains of apatite suitable for H_2O, δD and Pb-Pb analyses. Additional Pb-Pb measurements were performed on 15 merrillite grains. EPMA analyses of apatite were performed at the OU, using Cameca 50X instrument.

Results: Two distinct types of apatite were observed. The ***primary apatites*** are those preserved in the primary, albeit shock-metamorphosed, mineral association. The ***secondary apatites*** are found associated with impact melt, only in sample 76255. These are either heavily annealed and most likely recrystallized in contact with impact melt, or freshly crystallized from the melt in the case of euhedral apatite. There is no compositional difference observed between these two textural types. Merrillite is only found in primary form.

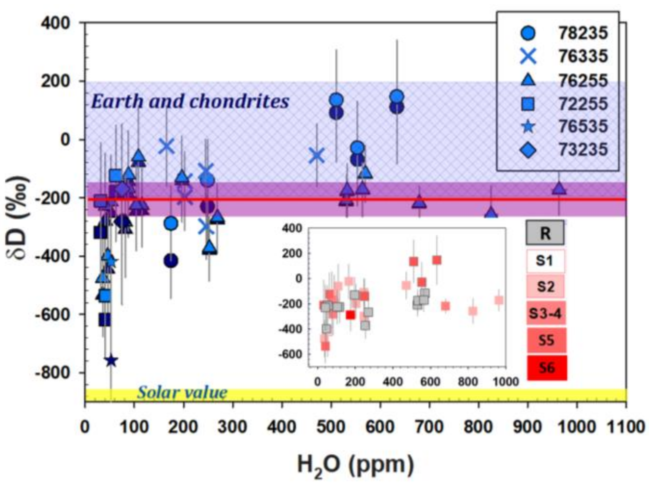

Figure 1. *H_2O-δD diagram of shocked apatite from a range of Mg-suite rocks. δD is corrected for cosmic ray D production after [9] (light blue) and after [13] (dark blue). The inset shows different shock stages of primary (S1-S4).*

H_2O-δD content. Apatite in shocked Apollo 17 rocks shows a wide range in water concentrations, as well as in δD values, albeit the variations within a single sample are relatively limited (Fig. 1). Total range of water content measured in Mg-suite apatites is 31 to

964 ppm, with δD values ranging from +147 ± 224 to -535 ± 56 ‰ (2σ) (CRE correction for D after [9]). A weighted average over 36 analysed spots is -199 ± 48 ‰ (2σ). No difference in H_2O-δD systematics is seen between primary and secondary apatite.

Pb-Pb ages of phosphates. All analysed samples are presented in Fig. 2, except for 78235 and 78236 in which individual $^{207}Pb/^{206}Pb$ ages span from 4236 ± 29 (2σ) Ma to much younger ages, implying substantial Pb loss in phosphates in both samples (see ref. 10).

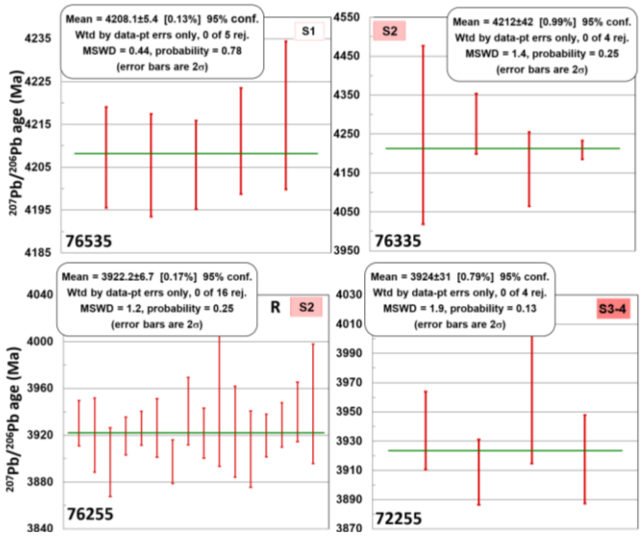

Figure 2. *$^{207}Pb/^{206}Pb$ ages (Ma) of apatite and merrillite in different Mg-suite samples. Different shock stages of primary grains (S1-S4) and recrystallized (R), secondary apatite are annotated.*

Discussion: Our study reveals that shocked Mg-suite apatite record variable H_2O and δD, which does not correlate with the level of shock deformation they experienced (Fig. 1). The extent to which H_2O-δD were affected during an impact largely depends on initial water abundance. Regardless of the level of shock, water-poor primary apatite exposed to shock deformation appear to show very low δD, most likely as a result of incorporating D-poor hydrogen. Potential source of D-poor hydrogen is regolith, that can get incorporated inside impact melt during an impact [11]. On Moon that has regolith as a significant source of D-poor water, shock-induced microtexture of apatite can be promoting mixing and hence reduction of the δD value. On the other hand, apatite that contains more than ~100 ppm H_2O is unlikely to disturb its isotopic systematics significantly. Pb-Pb systematics of the unshocked apatite (S1, 76535) is undisturbed, implying cooling of the rock below Pb-Pb closure temperature (~450 ºC) at ~4.2 Ga. This is ~100 Ma younger than what is interpreted as the rock's crystallization age [12]. Similar is the case for the petrogenetically related S2 troctolite 76335. The brecciation caused by an impact gives rise to a greater spread in Pb-Pb ages, however, the age of ~4.2 Ga is close to its crystallization age [8 and refs. therein]. Although primary apatite in the sample 76255 experienced similar level of deformation (S2, one grain S3), the heat from the impact melt that surrounds the clasts in which phosphates are found is sufficient to accommodate almost complete age resetting (~3.92 Ga) of all grains. The secondary apatite that is recrystallized in the melt of this sample is ~3.92 Ga old, too. This is in agreement with the Pb-Pb phosphate ages of impact melt breccias found within the same boulder [3]. At higher stages of shock (S3-4 in 72255), where apatite and merrillite show high crystal-plastic deformation [7], Pb-Pb resetting to ~3.92 Ga is complete in all but one grain. The resetting is concordant to Pb-Pb phosphate ages found in different clasts of the 72255 breccia [3]. At the highest stage of shock deformation (S5 and S6, 78235&78236), highly deformed and recrystallized apatite and merrillite show great spread in Pb-Pb ages and substantial Pb loss [10].

Conclusions: We determine the mean value of the primordial water reservoir that sourced Mg-suite rocks to be of -199 ± 48 ‰, confining with the lower end of the range for terrestrial and chondritic samples. Apatite can be considered a reliable hygrometer if it contains ~100 ppm H_2O or more, despite undergoing severe microtextural disorder and complete or partial resetting of Pb-Pb systematics in course of an impact. Based on the correlative microtexture and *in situ* Pb-Pb systematics, we find that apatite shows a great potentials to be utilized as a thermochronometer of impact events.

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