NOBLE GAS ELEMENTAL RATIOS REVEALED BY STEPWISE COMBUSTION AND CRUSHING METHODS IN THE LUNAR DHOFAR 1436 METEORITE.

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Introduction: Dhofar 1436 is a gas-rich lunar feldspathic impact melt breccia [1,2]. A combination of noble gas, nitrogen, carbon stepwise crushing and heating methods was performed for this meteorite and the preliminary results were published in [3]. In particular this study revealed that Dhofar 1436 contains large amounts of trapped noble gases in voids and/or defects accessible by crushing. The origin of this component is related to an impact event which caused a reset of the K-Ar system 4.1 ± 0.1 Ga ago (updated value) and induced release, mobilization, fractionation and redistribution of gases (radiogenic, re-implanted ^{40}Ar [e.g., 4], solar, cosmogenic) that accumulated before the impact event in regolith material of the Moon. Here we discuss in detail noble gas elemental abundances identified by stepwise combustion and crushing methods in Dhofar 1436.

Experimental techniques: Noble gases (He, Ne and Ar) from a whole rock (WR) sample of 117.5 mg and 19.78 mg were studied by stepwise crushing with cumulative number of strokes of 5000 and 12100 in Heidelberg University (HD) and at the Open University (OU), respectively. WR sample of 3.12 mg and powder samples retained after crushing analyses were stepwise heated at the OU.

Results and discussion: It should be noted that only totals and stepwise crushing data reflect truly *in situ* elemental ratios, e.g., ^{4}He/^{20}Ne and ^{20}Ne/^{36}Ar. Stepwise heating data do not, as these can be principally affected by diffusional fractionation upon stepwise heating extraction. As light noble gases can be more easily extracted by thermally driven diffusion, this effect would be recognizable by too high ^{4}He/^{20}Ne and ^{20}Ne/^{36}Ar ratios in low temperature extractions which then gradually turn to anomalously low ^{4}He/^{20}Ne and ^{20}Ne/^{36}Ar ratios in high temperature extractions. Hence, we will focus our considerations on totals and stepwise crushing data.

In all analyses the ^{4}He/^{20}Ne, ^{4}He/^{36}Ar and ^{20}Ne/^{36}Ar ratios are strongly fractionated, i.e., the light noble gases are depleted, relative to the heavy ones compared to the solar wind (SW) composition. Similar fractionation is observed for subsolar noble gases in enstatite chondrites [5 and reference therein]. The elemental abundances are also similar to other lunar samples [e.g., 6, 7]. The mechanism of fractionation is considered to be diffusive loss of the light noble gases [8]. The detection of fractionated noble gases released by crushing indicates that additional mechanisms like solubility controlled degassing fractionation may play a role [9]. It is likely that in Dhofar 1436 the 4.1 ± 0.1 Ga ago event having mobilized preexisting noble gas components (SW, radiogenic, cosmogenic, re-implanted ^{40}Ar) caused the fractionation, resulting in significant loss of SW He and Ne.

Fig. 1 shows that the ^{4}He/^{20}Ne and ^{4}He/^{36}Ar ratios observed during stepwise crushing extractions are clearly lower than in unfractionated solar wind and in the cosmogenic component produced by galactic cosmic rays. Only upon prolonged crushing after >2000 strokes, the ratios show a trend towards the cosmogenic component (Fig. 1). This is consistent with the more cosmogenic character of the isotopic ratios (^{4}He/^{3}He, ^{21}Ne/^{22}Ne) in advanced crushing steps [3].
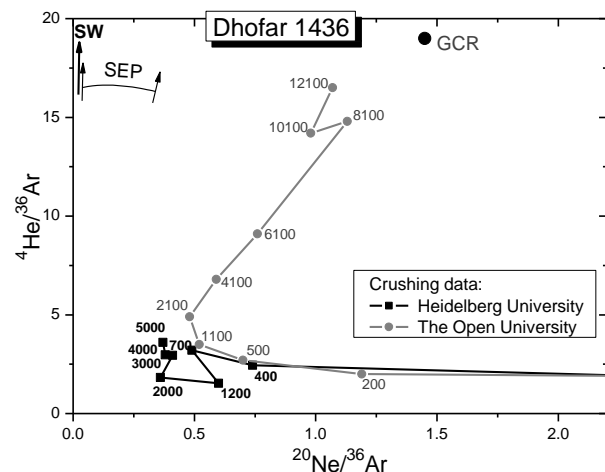

Fig. 1. Elemental abundance plot of ^{20}Ne/^{36}Ar vs. ^{4}He/^{36}Ar ratios for Dhofar 1436 crushing data. Other components plotted include solar wind (SW; [10]), fractionated solar wind (SEP; [11]: range based on step 16 of ilmenite 79035/3 and step 13 of pyroxene 71501/1) and cosmogenic component produced by galactic cosmic rays (GCR; [12]: average value for 0-150 cm radius using chemical composition of Dhofar 1436). Labels near data points indicate cumulative number of strokes.

Basically the elemental ratio variations in crushing steps can be explained by successive opening of

voids\inclusions of different sizes. It should be noted that a significant increase of the ^{4}He/^{20}Ne and ^{4}He/^{36}Ar ratios cannot be explained solely by admixing of nucleogenic or cosmogenic ^{4}He. Another source of ^{4}He could be mechanical breakdown of the crystal structure releasing radiogenic ^{4}He, causing significant effects on the measured ^{3}He/^{4}He ratios during crushing experiments [13-15]. However, in Dhofar 1436 the ^{3}He/^{4}He ratio systematically increases with crushing steps and there is no indication of the *in situ* radiogenic ^{4}He contribution in the advanced crushing steps. A higher production rate of cosmogenic He compared to cosmogenic Ne and Ar [12] also cannot explain a factor of 10 increase of the ^{4}He/^{20}Ne and ^{4}He/^{36}Ar ratios during progressive crushing, since the contribution of cosmogenic ^{4}He to the ^{4}He budget is very low (<0.1% in the Dhofar 1436 sample crushed at HD). The increase of these ratios obviously reflects a truly different elemental ratio of the fractionated SW component between crush-accessible sites varying in size, e.g., between larger and smaller voids. The increase of ^{20}Ne/^{36}Ar during progressive crushing is also observed but less pronounced compared to the He/Ne and He/Ar ratios and is demonstrated by more intensive crushing performed at the OU (Fig. 1). The analogous increase of ^{4}He/^{20}Ne and ^{4}He/^{36}Ar ratios with progressive crushing is also reported for the L-chondrite Ghubara [16] and seems to be controlled by very similar processes.

The elemental ratios of cosmogenic ^{3}He, ^{21}Ne and ^{38}Ar released by crushing are strongly fractionated compared to the production rate ratios of these isotopes calculated according to [12,17,18] for the Dhofar 1436 chemical composition. For example, (^{3}He/^{38}Ar)$_{cos}$ is mostly ≤0.1 in individual crushing steps when compared to literature or model values of >1.9. We can't completely exclude the influence of diffusional fractionation upon stepwise heating at low-medium extractions in the WR sample, but notably the analysis of (^{21}Ne/^{38}Ar)$_{cos}$ in the steps 700-1300 °C of the Dhofar 1436 WR combustion experiment shows that this ratio is unfractionated at 700-1100 °C ranging between 1 and 3 and becomes strongly fractionated (≤0.1) at 1200-1300 °C, that is also the main degassing peak of the elementally fractionated solar-like Ne, orphan Ar and nitrogen with the lightest isotopic composition [3]. This strengthens the association of vesicles and the high temperature components [3], but further adds the conclusion that they also contain fractionated cosmogenic gases. Nevertheless, it should be noted, that the fractionation of the solar wind component is stronger (a factor of c. 80 for ^{20}Ne/^{36}Ar and at least 2000 for ^{4}He/^{36}Ar) than for the cosmogenic noble gases (up to a factor of c. 20 for ^{21}Ne/^{38}Ar and c. 100 for ^{3}He/^{38}Ar).

Summary: Noble gas elemental ratios released during crushing can be interpreted by mixing of variably fractionated solar and cosmogenic components. The significant fractionation of the cosmogenic gases suggests that the main part of cosmogenic nuclides in Dhofar 1436 was accumulated early over a long time period (hundreds of Ma according to cosmic ray exposure age spectrum from Ar-Ar dating; our unpublished data), redistributed and fractionated during the main impact event 4.1±0.1 Ga ago and trapped into voids. The fractionation of accumulated solar and cosmogenic noble gases could have happened before formation of Dhofar 1436 caused by solar heating of regolith. The amount of cosmogenic gases with unfractionated composition in tracks of late accumulation is obviously low. Later "solar heating" or late mild-impacts were likely not responsible for the main component of high temperature fractionated cosmogenic gases as temperature extractions ≤1100 °C do not show fractionation of cosmogenic gases. The solar and cosmogenic components were strongly fractionated, however, fractionation of the solar wind component is stronger than for cosmogenic noble gases. The increase of the ^{4}He/^{20}Ne, ^{4}He/^{36}Ar and ^{20}Ne/^{36}Ar elemental ratios upon progressive crushing likely point out disequilibrium distribution of the gases between the voids of different sizes that can be caused by the dynamics of the shock metamorphism process.

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