HIGH ^{40}AR/^{36}AR RATIOS OF TRAPPED ARGON FROM MARTIAN INTERIOR AND ATMOSPHERE IN SHERGOTTITES

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Introduction. A ^{40}Ar/^{36}Ar ratio of 3000±500 was determined by Viking for Martian atmospheric argon [1] and hence the high ^{40}Ar/^{36}Ar ratios found in shergottites [2] are usually interpreted as atmospheric argon trapped from the recent Martian atmosphere. With time, isotopic data on shergottites were gradually changing the scientific view about Martian atmospheric argon. For instance, Bogard and Garrison [3] suggested that atmospheric argon has ^{40}Ar/^{36}Ar no greater than ~1900, substantially different from the Viking measurements. But there is no generally accepted certain value of the ^{40}Ar/^{36}Ar ratio for the Martian atmosphere so far.

We performed comprehensive high-resolution ^{40}Ar-^{39}Ar stepwise heating analyses on whole rock and handpicked mineral separates of several Martian shergottites (Shergotty, Zagami, SaU005, Dhofar019). Additionally some non-irradiated samples were measured to check the contribution of interfering Cl-derived ^{38}Ar in neutron-irradiated samples. Here we discuss the results concerning the presence of trapped argon with high ^{40}Ar/^{36}Ar ratios.

Methodological aspects. High ^{40}Ar/^{36}Ar ratios of 1000-3000 were found for argon in EETA 79001 [2, 4], Zagami [5, 6], Shergotty [3, 6] and SaU005 [7]. Many studies inferred the presence of atmospheric components from high $^{40}Ar_{total}/^{36}Ar_{trapped}$ ratios only, i.e. not corrected for *in situ* radiogenic ^{40}Ar or inherited ^{40}Ar, or only with a rough correction for radiogenic argon based on K concentrations – which are variable. On the other hand, Ar-Ar isochron analysis appropriately corrected for cosmogenic and Cl-derived argon is a powerful tool to unequivocally identify a trapped high ^{40}Ar/^{36}Ar component [3, this work]. However, this correction is also not without drawbacks: For example, Bogard and Garrison [3] used a method to resolve cosmogenic ^{36}Ar suggesting the application of the lowest ^{36}Ar/^{37}Ar ratio of the sample. This approach is restricted in a sense, that it can be used mainly for mineral separates from which cosmogenic isotopes - produced from different target elements (Ca, Fe, K) - are released congruently, thereby neglecting incongruently degassing impurities or inclusions. Moreover, the fraction with the minimum ^{36}Ar/^{37}Ar ratio may still contain trapped Ar. Resolving cosmogenic argon and trapped argon by using endmember compositions based on ^{36}Ar/^{38}Ar ratios (as mainly done in this study) is also not unproblematic due to the presence of Cl-derived argon in Ar-Ar dating. Principally, this could be quantified by simultaneous measurements of unirradiated samples. For example, in this study the ^{36}Ar/^{38}Ar ratios of non-irradiated Shergotty pyroxene are significantly higher than those of the irradiated sample.

Results and discussion. High $(^{40}Ar/^{36}Ar)_{trapped}$ ratios in our study were found for Shergotty pyroxene melt inclusions (~1500), however, these are likely overestimated due to Cl-induced ^{38}Ar. Similarly, $(^{40}Ar/^{36}Ar)_{trapped}$ ratios of ~2000 for Shergotty pyroxene reported by [6] may be overestimated, as only the K content of pyroxene crystals was used to calculate *in situ* radiogenic argon, instead of the bulk K content of the separate, which is – as in our case – very likely dominated by K-rich melt inclusions in pyroxene and hence, may be significantly variable from sample to sample. While these considerations just advise to caution about uncertainties of $(^{40}Ar/^{36}Ar)_{trapped}$ values, it is ascertained that high $(^{40}Ar/^{36}Ar)_{trapped}$ ratios are reality. In this study, highest $(^{40}Ar/^{36}Ar)_{trapped}$ ratios were also found for Shergotty glass (~1800), maskelynite (~1200), and SaU005 glass (~1200). Taken at face, these results are compatible with above mentioned studies.

Another important point is related to the identification of the high $(^{40}Ar/^{36}Ar)_{trapped}$ component as Martian atmospheric argon, which has become ambiguous: Schwenzer et al. [6] found that only a very small proportion of the high $(^{40}Ar/^{36}Ar)_{trapped}$ argon is accompanied by Martian atmospheric xenon with high ^{129}Xe/^{132}Xe ratios. Indeed, most of the high $(^{40}Ar/^{36}Ar)_{trapped}$ argon component must be ascribed to the Martian interior. Similarly, Bogard and Park [8] assigned the high ^{40}Ar/^{36}Ar excess argon found in Zagami maskelynite to a magmatic component inherited from the Martian interior, and our results are as well consistent with these conclusions. Until recently, Martian mantle argon was considered to have low ^{40}Ar/^{36}Ar ratios: For instance, Wiens [9] estimated the ^{40}Ar/^{36}Ar ratio of the mantle component present in EETA 79001 to be between 430 and 680, Swindle et al. [10] suggested a component in the same meteorite with ^{40}Ar/^{36}Ar <300, Bogard and Garrison [3] concluded a ^{40}Ar/^{36}Ar ratio of <500 for the Martian mantle. Taking all results into account, Martian interior (or mantle) argon may be characterised by very distinct heterogeneous compositions. Incidentally, this was also recently inferred for the terrestrial lithospheric mantle, where mantle argon (evaluated by correlations with solar type neon) in diferent lithospheric samples was found to have highly variable $^{40}Ar/^{36}Ar$ ratios [11].

Incorporation of trapped argon. Atmospheric noble gases are ubiquitous on Earth and noble gas geochemists perform huge efforts to search rocks not contaminated by atmospheric gases with pristine mantle noble gases. For Martian rocks, the presence of Martian atmospheric gases is rarely found and - in shergottites - generally attributed to shocked phases, incorporated somehow by the shock process [2, 12]. It was suggested that the scatter in "Martian atmospheric" $^{40}Ar/^{36}Ar$ ratios determined in different shergottites is related to the shock pressure of shergottites and could be due to the mixture of different components (e.g., Martian atmosphere and mantle) and their inhomogeneous distribution [12, 13]. However, there is no definite correlation between shock pressures and the $^{40}Ar/^{36}Ar$ ratios of trapped argon: For example, the glass sample from SaU005, a heavily shocked shergottite (40-45 GPa [14]), contains a trapped component with $^{40}Ar/^{36}Ar$ of ~1200, while Shergotty experienced a lower shock pressure (30.5±2.5 GPa [14]) and shows $(^{40}Ar/^{36}Ar)_{trapped}$ ratios up to 1800. Moreover, analyses of the same EET79001,27 inclusion conducted by different laboratories demonstrate a wide range of $(^{40}Ar/^{36}Ar)_{trapped}$ ratios [13]. Particular for Shergotty, our own data and those by [3] display data almost linearily aligned in a three isotope plot. If the trapped component with $^{40}Ar/^{36}Ar$ of ~1800 is a mixture of Martian atmosphere and mantle, and the result of shock implantation, this would require equilibration of atmospheric and mantle argon mobilised during the impact. If mantle argon was not mobilised during the impact and equilibrated with Martian atmospheric argon, we would expect different phases hosting the two trapped components with likely different degassing behaviour. This would result in a scatter of data plotting in a triangle between one radiogenic and two trapped compositions in a plot of $^{36}Ar_{trapped}/^{40}Ar_{total}$ versus $^{39}Ar/^{40}Ar_{total}$, as is indeed observed for many shergottite samples [3; this study]. To explain the linear Shergotty data, we suggest considering a different possibility, that the high $^{40}Ar/^{36}Ar_{trapped}$ ratios found are not from "true" Martian atmosphere but could be implanted from an "impact" generated transient atmosphere. A recent study on L chondrites [15] demonstrated that capture of gases from a temporal atmosphere is possible. Any addition of mobilized gases from crustal or mantle rocks during impact could significantly increase the $^{40}Ar/^{36}Ar$ ratio of trapped argon.

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