

COLD DESERT ALTERATION OF MARTIAN METEORITES: MIXED NEWS FROM NOBLE GASES, TRACE ELEMENTS AND OXYGEN ISOTOPES. S. P. Schwenzer¹, M. Anand¹, I. A. Franchi¹, J. M. Gibson¹, R. C. Greenwood¹, S. Hammond¹, R. Haubold², S. Herrmann², S. P. Kelley¹, U. Ott², and A. G. Tindle¹, ¹The Open University, CEPSAR, Walton Hall, Milton Keynes MK7 6AA, UK; s.p.schwenzer@open.ac.uk; ²Max-Planck-Institut für Chemie, J.-J.-Becher-Weg 28, 55128 Mainz, Germany.

Introduction: Currently, about 30% of the known Martian meteorites have been found in Antarctica, with some rare samples such as the orthopyroxenite AHL84001 amongst them [1]. We have previously shown [2, 3] that terrestrial weathering in hot and cold deserts can cause elemental fractionation of air incorporated into those meteorites, which complicates the quantification of the noble gas components. This can cause serious contamination, partially obscuring the extraterrestrial heavy noble gas signatures [e.g., 2] by, for example, mimicking the Martian interior component [4]. This is a critical problem because key inferences have been made on the basis of these noble gas signals (e.g. Martian atmosphere in EETA79001, fractionated or ancient Martian atmosphere in ALH84001 (see [5]), and they are the finds that have a well documented history). In this study we investigate the rim and interior of ALHA77005 and RBT 04261 Martian meteorites to characterise terrestrial air contamination, and derive potential correction procedures.

Samples and methods: We obtained rim and interior samples of ALHA77005 (splits 225 (rim), 226 (close to rim), and 227 (interior), thin section 54, thick section 230); and of RBT 04261 (splits 34 (rim), 35 (close to rim) and 36 (interior), thin section 43, thick section 42). Note, that the terrestrial residence ages for the meteorites are different: 190 ± 70 kyr for ALHA77005 [6], and less than 60 kyr for RBT 04261 [7]. Microscopy, virtual microscope documentation, and electron microprobe analyses (Cameca SX 100) were done at the OU. Each split was gently crushed. For Ar-Ar analyses ~40 bulk rock grains were handpicked, irradiated at McMaster reactor (Canada), and measured by melting grains individually by laser heating for Ar isotope analysis (MAP215-50). In addition stepwise heating was performed on a larger grain of each sample. For the five-noble gas measurements ~50 mg were heated in five steps and measured using the standard protocol [2]. Mineral trace-element measurements were made using an Agilent 7500s ICP-MS coupled with a UV (213 nm) laser system. Synthetic doped glass NIST 612 was used for external calibration. Oxygen isotope analyses were undertaken at the OU using an infrared laser-assisted fluorination system [8]. $\Delta^{17}\text{O}$ values have been calculated using a linearized format [9]. Samples were analyzed both untreated and after leaching in a solution of ethanolamine thioglycollate (EATG), which

has proved to be efficient at removing terrestrial weathering products, without significantly disturbing the primary oxygen isotope composition of the sample [10].

Mineralogy: Microscopic and microprobe investigation confirmed that weathering effects in these meteorites from Antarctica are minimal. Along cracks Ca, Si and S enrichment, and Fe and Mg depletion occur in ALHA77005. RBT 04261 has some fusion crust, which is intact and visible alteration is minimal, which is in line with its shorter terrestrial residence time.

Trace elements: A number of silicates (olivine, pyroxene, feldspar) were analyzed from both meteorites for their trace element contents. We specifically analyzed cores, rims and other areas of mineral grains located near large cracks to cover the possible spectrum of trace element variations. Our preliminary analyses of the data suggest limited variations in trace element concentrations from different areas of mineral grains from both meteorites although there are subtle compositional differences which could be ascribed to the effects of terrestrial weathering.

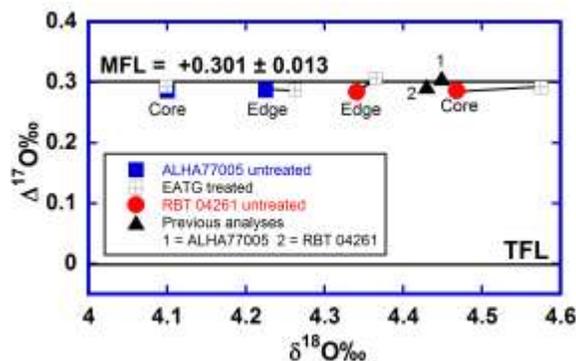


Fig. 1 Oxygen isotope composition of core and edge samples from ALHA77005 and RBT 04261. TFL = terrestrial fractionation line. MFL = Martian Fractionation Line [12, linearized].

Oxygen isotopes: ALHA77005 and RBT 04261 show contrasting behaviour (Fig. 1). In the case of RBT 04261 the core of the sample is slightly heavier with respect to $\delta^{18}\text{O}$ than the edge. This is in keeping with previous studies which indicate that oxygen isotope compositions are shifted to lighter values by Antarctic weathering processes [11]. However, this shift is small, being about 0.2‰ for the EATG-washed samples and therefore just above the level of precision of the measure-

ments, which for $\delta^{18}\text{O}$ are $\pm 0.16\text{‰}$ (2σ) [8]. This suggests that the level of terrestrial alteration experienced by RBT 04261 is very small. ALHA77005 shows the opposite trend with the core region being isotopically lighter than the exterior. Again these differences are subtle. One possible explanation of this behaviour is that the outer portion of the sample has experienced mild non-Antarctic weathering or exchange post recovery, possibly as a result of interaction with the terrestrial atmosphere; ALHA77005 was collected 27 years prior to RBT 04261. Previous analyses of both samples obtained at the OU are also shown in Fig. 1.

Noble gases: *Ar-Ar.* Ar-isotopes give information about the composition of the sample: ^{37}Ar is derived from Ca and ^{38}Ar is derived from Cl upon irradiation. A plot of $^{37}\text{Ar}/^{39}\text{Ar}$ vs $^{38}\text{Ar}/^{39}\text{Ar}$ for ALHA77005 shows a clear difference between interior and exterior with the exterior sample exhibiting higher ^{37}Ar and ^{38}Ar values than the interior sample. Average $^{37}\text{Ar}/^{39}\text{Ar}$ is 235 ± 302 and 120 ± 250 , $^{38}\text{Ar}/^{39}\text{Ar}$ 0.73 ± 0.86 and 0.30 ± 0.42 , for exterior and interior samples, respectively. Note that the error on the individual measurement is small ($<10\%$) and the above variation reflects mineralogical differences between individual grains, i.e., the exterior sample has more Ca and Cl, and a larger inter-grain-variation in the concentration of these elements. In RBT 04261 average $^{37}\text{Ar}/^{39}\text{Ar}$ is 35 ± 78 and 95 ± 194 , $^{38}\text{Ar}/^{39}\text{Ar}$ 0.13 ± 0.15 and 0.26 ± 0.37 , for exterior and interior samples, respectively. However, the variation is caused by one single outlier in each sample, without which $^{37}\text{Ar}/^{39}\text{Ar}$ is 17 ± 12 and 65 ± 79 , $^{38}\text{Ar}/^{39}\text{Ar}$ 0.11 ± 0.11 and 0.21 ± 0.30 , for exterior and interior, respectively. We take the higher values (and larger variation) as indicator for terrestrial weathering.

Helium was measured in three samples of each meteorite: exterior, close to surface and interior. In both meteorites the close-to-surface sample has the highest $^4\text{He}/^3\text{He}$ ratio. ALHA77005 has lost almost all its radiogenic ^4He through impact metamorphism [13]. RBT 04261 shows much higher $^4\text{He}/^3\text{He}$ ratios indicating a significant amount of radiogenic ^4He to be preserved. This observation is likely related to the higher shock metamorphic overprint in ALHA77005 compared to RBT 04261 rather than weathering.

Table 1. Cosmic ray exposure ages.

RBT04261	T ₃	T ₂₁	T ₃₈
34	1.79	2.81	2.85
35	2.16	3.07	3.81
36	2.74	2.91	4.29
ALHA77005	T ₃	T ₂₁	T ₃₈
225	4.47	5.41	3.34
226	4.60	4.39	2.43
227	4.50	5.71	3.43

Exposure ages: Cosmic ray exposure ages averaged over all three splits and isotopes are 4.25 Ma and 2.94 Ma for ALHA77005 and RBT 04261, respectively. Our value for ALHA77005 is higher than literature values (2.5 to 3.4 Ma [1]). For RBT 04261 our average value agrees within error with the age of 3.0 ± 0.6 measured by [7].

Neon. On a $^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ plot spallation, solar cosmic irradiation and atmospheric contribution (Mars and Earth) can be distinguished. All samples from this study plot within or close to the spallation field. ALHA77005 shows somewhat lower than regular GCR spallation $^{21}\text{Ne}/^{22}\text{Ne}$ in the exterior and interior, but not in the close to the surface sample. All samples have a small atmospheric contribution, which could be either Martian or terrestrial. In contrast, all RBT 04261 samples fall into the regular GCR spallation range in cosmogenic $^{21}\text{Ne}/^{22}\text{Ne}$, and only the exterior sample has a very small atmospheric contribution which we assume is terrestrial.

Kr/Xe. Heavy noble gases are severely influenced by terrestrial air. In ALHA77005 the exterior sample has a pure air signature in all temperature steps, while the interior exhibits a mixture of air and Martian atmosphere. Moreover, the exterior sample has a 17 times higher ^{132}Xe (air) concentration than the two other samples. In RBT 04261 all three samples fall onto the Martian interior [4] point in the $^{84}\text{Kr}/^{132}\text{Xe}$ space, however, they show air ratios (or higher) in their $^{136}\text{Xe}/^{132}\text{Xe}$. Concentrations of ^{132}Xe match the exterior sample of ALHA77005. We conclude that the Kr/Xe signature is dominated by fractionated air.

Conclusions: The heavy noble gas evidence clearly demonstrates significant terrestrial contamination of the exterior of ALHA77005, and some contamination of its interior. However RBT 04261 exhibits much less terrestrial noble gas contamination and may be free of contamination in its interior. The difference between the two samples probably reflects their different terrestrial exposure histories. In contrast, the oxygen isotope and mineral trace-element data for both meteorites suggest minimal terrestrial alteration.

References: [1] Mars Meteorite compendium: <http://curator.jsc.nasa.gov/antmet/mmc/>. [2] Mohapatra, R. K. et al. (2009) *GCA* 73, 1505–1522. [3] Schwenger, S. P., et al. (2009) *Polar Science*, doi:10.1016/j.polar.2009.06.00. [4] Ott, U. (1988) *Geochim. Cosmochim. Acta*, 52: 1937–1948. [5] Swindle T.D. (2002) Martian Noble Gases. *Reviews Min.*, 47: 171–190. [6] Schultz, L. & Freundel, M. (1984) *Meteoritics*, 19, 310. [7] Nishiizumi, K., and Caffee, M. W. (2010) LPSC XLI, abstract #2276. [8] Miller M. F. et al. (1999) *Rapid Commun. Mass Spectrom.* 13, 1211–1217. [9] Miller M. F. (2002) *GCA* 66, 1881–1889. [10] Martins Z. (2007) *MAPS* 42, 1581–1595. [11] Greenwood R.C. and Franchi I. A. (2004) *MAPS* 39, 1823–1838. [12] Franchi I. A. et al. (1999) *MAPS* 34, 657–661. [13] Schwenger, S. P. et al. (2008) *MAPS*, 43, 1841–1859.

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