

**AN ALMOST INFINITE SINK FOR TIGHTLY BOUND XENON: ETCHED SHERGOTTY AND (LESS SO) ETCHED NAKHLA.** U. Ott, Max-Planck-Institut für Chemie, Joh.-J.-Becherweg 27, D-55128 Mainz, Germany (ott@mpch-mainz.mpg.de).

**Introduction:** Among the (stable) noble gases xenon is the least noble, a fact that is evident in a number of physical-chemical processes that can be a first step in its eventual introduction into solids. Ionization and adsorption, e.g., favor Xe over the lighter noble gases and lead to elemental fractionation [1]. Also solution in liquids generally favors Xe, and often has been discussed as a key process for achieving the fractionated noble gas elemental patterns often associated with alteration products. A case in point are the nakhlite meteorites, which contain – relative to Martian atmosphere – fractionated gases [2], and where iddingsite has been considered a possible host phase [3].

Here I report results of etching experiments on Martian meteorites. These were performed some time ago, with the aim of shedding light on the carrier phases of the Martian atmospheric and interior gas components. The interest at the time was in the fate of the indigenous components, and we reported only relevant observations obtained on Nakhla [4]. Additional results for Nakhla are reported in [5].

**Experimental:** Samples of Shergotty, Nakhla and Chassigny were treated with 6N HCl and, in order to limit re-precipitation of dissolved phases, weak HF.  $\text{AlCl}_3$  was added to avoid formation of insoluble fluorides. In spite of this, the initial residue from mostly olivine Chassigny of ~32 % by weight was found to consist almost totally of precipitated silica gel. This was dissolved by additional HF treatment which left a tiny residue of ~0.5 weight % containing only little gas (<1% of the initial inventory for all noble gases). Residues from Shergotty and Nakhla amounted to ~32 and ~87 wt. %, respectively.

**Residue compositions:** Small amounts were investigated by SEM/EDX.

*Nakhla.* We found essentially pyroxene only. As expected, the chemical treatment appeared to have dissolved olivine and the less abundant labile alteration phases. Nakhla contains ~15 % olivine [6], which is consistent with the observed weight loss.

*Shergotty.* SEM/EDX observations also showed mostly pyroxenes. While augite and pigeonite in Shergotty are about equally abundant [6], we observed mostly augite grains in our SEM inspection of the residue. The SEM observations need to be taken with a grain of salt, however, as the noble gas data on much larger samples show that it was rather difficult to obtain by random sampling a representative sample.

**He, Ne, Ar mass balance:** Results are summarized in Table 1. Two splits were analyzed both from the

Nakhla residue and the Shergotty residue: N-R11 (~17% of total residue) and N-R12 (~24 %) from Nakhla, Sh-R11 (~19%) and Sh-R12 (~21%) from Shergotty. Mass balance is calculated by comparing the abundances measured in the residue splits to abundances in the bulk nakhlite (average of abundances given in [2]) and taking into account the weight yields.

Table 1. Mass balance (%) for He, Ne, Ar.

nuclide	N-R11	N-R12	Sh-R11	Sh-R12
$^3\text{He}$	61	95	21	5
$^4\text{He}_{\text{rad}}$	36	98	6	3
$^{21}\text{Ne}$	106	91	31	22
$^{36}\text{Ar}_{\text{trap}}$	--		18	29
$^{38}\text{Ar}_{\text{cos}}$	126	113	27	24
$^{40}\text{Ar}$	77	84	13	68

*Nakhla:* In spite of the large difference in He, averaged data show retention consistent with the observed weight loss. Only cosmogenic Ar is somewhat high, in line with the low concentration of the major target element Ca in the dissolved olivine (<0.4 wt. %; [7]).

*Shergotty:* There are major losses of noble gases. The low recovery of  $^3\text{He}$ , which is a cosmogenic product produced in roughly equal abundance on all target elements cannot be due to an overestimate of the weight yield, since a) we did not observe major precipitates in our SEM examinations and b) this would have diluted Ne and Ar to the same extent, whereas yields of cosmogenic Ne and Ar are not very different from the weight yield. The ~70% recovery of  $^{40}\text{Ar}$  (radiogenic and/or Martian atmosphere) suggests that – although not observed in the SEM – a significant amount of feldspar survived. In fact, if feldspar were the major constituent of the residue, this could explain the low He contents, since feldspar suffered significant losses of cosmogenic  $^3\text{He}$  [8].

**Kr, Xe mass balance:** A summary is given in Table 2. Three points are remarkable: 1) the high abundances of  $^{84}\text{Kr}$  and  $^{132}\text{Xe}$  in the Shergotty etched samples and in Nakhla R12 (not in Nakhla R11, however) of obviously terrestrial origin; these also prevent us from doing mass balance calculations for  $^{129}\text{Xe}$  as a marker of Martian atmospheric contributions; 2) the low Kr/Xe ratios; and 3) the retentive siting of Xe in the Shergotty residue.

*High abundances.* Concentrations in units of  $10^{-12} \text{ cm}^3 \text{ STP/g}$  for  $^{84}\text{Kr}$  amount to 303 (N-R12), 324 (Sh-R11) and 56 (Sh-R12), those for  $^{132}\text{Xe}$  amount to 126 for N-R12; for the Shergotty samples they are as high

as 1104 (Sh-R11) and 686 (Sh-R12). If taken up from Xe in solution in the acid, the trapping efficiency must have been on the order of a percent.

Table 2. Mass balance (%) for Kr and Xe.

nuclide	N-R11	N-R12	Sh-R11	Sh-R12
$^{84}\text{Kr}$	24	685	167	29
$^{132}\text{Xe}$	80	998	3178	1975
$^{129}\text{Xe}^*$	~7	--	--	--

$^{129}\text{Xe}^*$  is the excess  $^{129}\text{Xe}$  over  $^{129}\text{Xe}/^{132}\text{Xe} = 1.03$  (the Martian interior Xe found in Chassigny [2]).

**Krypton to Xenon ratio.** For Nakhla R12  $^{84}\text{Kr}/^{132}\text{Xe}$  is as low as 2.4, for the Shergotty residues it is even lower: 0.29 (Sh-R11) and 0.08 (Sh-R12). Low Kr/Xe ratios have been observed in Martian meteorites found in hot deserts, in particular, and the name *EFA* has been coined to describe a low  $^{84}\text{Kr}/^{132}\text{Xe}$  (~2) component [9]. Even lower values have been found in terrestrial samples that have been studied in a search for effects on noble gas budgets associated with weathering in terrestrial environments (e.g., [10]). Often the action of water has been invoked, however fractionation of Kr/Xe by solution in water is only about a factor of 2 [1], which has led to the suggestion of more complicated scenarios involving multiple episodes of adsorption/desorption [10]. The data obtained here show existence of a process that can lead to even more severe fractionation than observed in these studies.

**Xenon retentivity.** It has been suggested that the *EFA* component can be removed by stepwise heating [e.g., 9, 10]. The results of our etching experiments show that this cannot be taken for granted. Krypton acquired in the etching is quantitatively released in a 800 °C step preceding total gas extraction both in the case of the Nakhla and the Shergotty residues. This is also true for Xe in the Nakhla residue, but the situation for Xe in Shergotty is completely different, and Kr/Xe is even more fractionated in the gas left after heating to 800 °C:  $^{84}\text{Kr}/^{132}\text{Xe} = 0.026$  (Sh-R11) and 0.038 (Sh-R12). Figure 1 shows the release pattern from the Sh-R12 sample, where in an effort to remove the air contamination we performed a total of 5 heating steps at 800 °C, with step #4 for 210 minutes rather than our usual heating time of 30 minutes. To allow for the different heating times the gas release per minute is shown. Also shown are the  $^{84}\text{Kr}/^{132}\text{Xe}$  ratios. Air Kr is essentially removed already after the first 800 °C 30-minute heating, and Kr in the 1800 °C step amounts to ~12% of what is left in an untreated sample after 800 °C heating [2]. In contrast, there is further Xe release upon repeated heating at 800 °C. Furthermore, a total extraction at 1800 °C, performed after release at 800 °C seemed to have fallen to an acceptable level in step

5, showed that almost half had still been retained.  $^{84}\text{Kr}/^{132}\text{Xe}$  decreases from 0.18 in the first step to zero in the following steps and with release of indigenous Kr increases again to 0.06 in the final extraction.

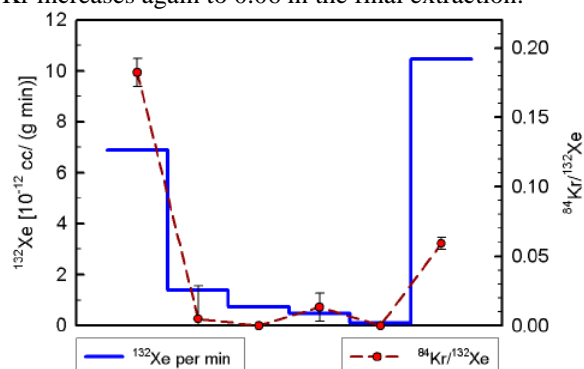


Fig. 1. Release of  $^{132}\text{Xe}$  normalized to heating time and  $^{84}\text{Kr}/^{132}\text{Xe}$  in step-heating of Shergotty R12. The first five steps were at 800 °C, the final step at 1800 °C.

**Summary and implications:** Results of acid etching Nakhla and Shergotty show significant amounts of Kr and Xe from air can be acquired, with Xe extremely tightly bound. Details of the process need to be investigated in more detail, and we plan closer examination of the remaining residue material by SEM/EDX and Raman spectroscopy. Alteration of meteoritic materials by a similar process may introduce air that will be difficult to distinguish from indigenous gases based on release characteristics. While acidic etching may not play an important role on Earth, we note the high Cl and S content of Martian surface materials [11] and the evidence for acidic weathering of Mars [12]. Acidic weathering may have played a role in creating the elementally fractionated Martian component observed in the nakhlites and in ALH 84001.

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