TRAPPING OF ANCIENT MARTIAN ATMOSPHERE IN METEORITE ALH84001. J. A. Whitby¹, J. D. Gilmour and G. Turner ¹Earth Sciences Department, University of Manchester, Manchester M13 9PL, United Kingdom. email: James.Whitby@man.ac.uk

Introduction: The fourteen known martian meteorites have been used to place many constraints on the nature and evolution of martian volatiles, particularly by means of study of the noble gases. Trapped gases within shock-glasses from the Shergottite EET79001 are widely interpreted as providing a more precise analysis of the modern martian atmosphere than that provided by robotic probes or remote observation, particularly for isotopic measurements [1]. The Chassigny meteorite contains gases of a distinct composition, believed to sample a reservoir other than the martian atmosphere, perhaps from the mantle [2].

Noble gas contents of martian meteorites have generally been interpreted as mixtures of terrestrial air, modern martian atmosphere and the martian mantle, with contributions from spallation and *in situ* radioactive decay [1, 2]. Simple mixing between these reservoirs coupled with elemental fractionation cannot however explain all observations, particularly for ALH84001 [3, 4, 5], which is distinguished from the other martian meteorites by its composition [6] and much older crystallization age [7,8].

ALH84001 has relatively high concentrations of trapped noble gases, despite a lower abundance of shock glasses than the shergottites. Moreover, these are elementally fractionated in favour of the heavy noble gases when compared with the martian atmosphere. It has been suggested on the basis of nitrogen and xenon isotopic ratios that some of the trapped gases in ALH84001 reflect the composition of the martian atmosphere at an earlier epoch [3, 4]. Modeling of the evolution of the martian atmosphere [9], coupled with the proposal that the trapped gases were incorporated in one of the shocks experienced by ALH84001 suggest that an event at 3.9Ga may have been responsible [3,4,10,11].

Various suggestions have been made for the location and trapping mechanism of the various gas components within ALH84001. Mathew et al. [5] suggested by analogy with Zagami and EET79001 that the atmospheric component resides in shock-produced glass. Gilmour et al. [3] demonstrated that the minor phases of shock-produced feldspathic glass, carbonate and apatite could not account for the observed abundance of excess ¹²⁹Xe, and that orthopyroxene was the host for the majority of the trapped atmospheric component. They suggested that it was incorporated by a shock event at 3.9Ga after adsorption of noble gases onto grain surfaces. Rao et al. [12] prefer a model in which noble gases from aqueous solution are trapped on fine grained material in the granular bands and then redistributed by a later shock.

To further investigate the location of martian atmospheric xenon in ALH84001, and in particular to test the hypothesis of shock implantation into orthopyroxene after adsorption (which is expected to result in an inhomogenous spatial distribution of xenon within grains) we prepared a mineral separate for acidetching. Initial results are presented here.

Experimental: Interior chips of ALH84001 (allocation ,287) were crushed in a stainless-steel mortar and the 250-500µm fraction was rinsed with acetone in an ultrasonic bath to remove adhering fines. An orthopyroxene enriched separate was produced by manually discarding grains that clearly contained carbonate, maskelynite or chromite. This mineral separate was divided into three aliquots which were either untreated, treated with 2% nitric acid for 48 hours, or treated with 20% nitric acid for 48 hours. Etch solutions were retained for chemical analysis. The isotopic composition of xenon trapped within the pyroxene was then determined using the RELAX mass spectrometer in conjunction with laser stepped heating [15].

Results: Figure 1 shows ¹²⁹Xe versus ¹³²Xe for gas released in all temperature steps for both etched and untreated samples (hollow and solid symbols respectively). After rejecting 4 points potentially affected by terrestrial atmosphere a ¹²⁹Xe/¹³²Xe ratio of 2.03 ± 0.07 is obtained which is in good agreement with previous observations of ALH84001 whole rock [3, 4, 5, 13, 14], density separates [4], and laser-probe on pyroxene [3].

Abundances for trapped xenon are at the low end of the range of reported values for ALH84001 bulk rock $(4.7-39\times10^{-12}\text{cm}^3\text{STP}^{132}\text{Xe})$ [3] or pyroxene enriched density separates $(28.9\times10^{-12}\text{cm}^3\text{STP}^{132}\text{Xe})$ [4], which do however show considerable variation from aliquot to aliquot. Analysis of the etch solutions indicates that the 20% acid dissolved about 1% of the sample mass, and the 2% acid about 0.5%. The composition of the solution is consistent with most of the mass loss being due to dissolution of orthopyroxene. Despite the small mass loss in etching there is a measurable difference in the concentrations of trapped xenon between the acid etched samples and the untreated samples, the latter having a slightly higher concentration, but similar total ¹²⁹Xe/¹³²Xe ratios, see Table 1.

Discussion: These preliminary data indicate that a disproportionate amount of the martian atmospheric component in ALH84001 orthopyroxene grains is removed upon etching after crushing, suggesting that this component may be concentrated near the surface of grains. ¹²⁹Xe/¹³²Xe ratios for the etched and unetched pyroxene do not show the difference expected if the interior of the grains contained a greater fraction of Chassigny like gas.

The concentrations and elevated 129 Xe/ 132 Xe ratios observed support the previous conclusion that orthopyroxene is indeed the host phase for most of the martian atmospheric xenon in ALH84001[3]. The narrow range of values observed for the 129 Xe/ 132 Xe ratio, its consistency in etched and unetched samples, and the value of 2.03 ± 0.07 as distinct from the modern atmospheric ratio of 2.6 ± 0.05 [1] are consistent with previous suggestions that there is a single trapped atmospheric component in ALH84001 which is more primitive than the modern martian atmosphere.

Consideration of the primitive nature of the trapped xenon and the timing of shock events that may have implanted gases into the orthopyroxene [10, 11] (and other phases) imply that the trapped xenon in ALH84001 may be representative of the martian atmosphere 3.9 billion years ago. The value for 129 Xe/ 132 Xe of 2.03 ± 0.07 at 3.9Ga is consistent with modelling of the evolution of the martian atmosphere [9], and implies that the outgassing rate since then has been relatively low in agreement with the low 40 Ar content of the modern atmosphere. Estimates of the actual rate of xenon outgassing between 3.9Ga and the present day depend on assumptions made regarding the relative proportions of radiogenic 129 Xe and a (Chassigny type?) mantle component.

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Fig. 1: Step-heating data from four aliquots of orthopyroxene separate. Solid data points are from untreated orthopyroxene, open data points from acid etched orthopyroxene. Error bars are smaller than data-symbols.

Etch	ID	Mass/mg	¹³² Xe	¹²⁹ Xe _{XS}	¹²⁹ Xe/
					Ae
none	2	1.980	7.9	7.2	1.93
none	3	1.719	5.3	5.3	2.04
2%	4	2.342	4.4	5.0	2.16
20%	7	1.675	4.2	3.9	1.94

Table 1: Concentrations (10⁻¹²cm³STP/g) for trapped ¹³²Xe, excess ¹²⁹Xe (over Chassigny ¹²⁹Xe/¹³²Xe value of 1.03) and total ¹²⁹Xe/¹³²Xe ratio summed over all temperature steps for crushed orthopyroxene from ALH84001 either untreated, etched in 2% nitric acid, or 20% nitric acid.