

OXYGEN AND NOBLE GAS ISOTOPE CONSTRAINTS ON THE ORIGIN OF ALH84001 CARBONATE.

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Ar-Ar laser probe studies, Xe isotope analyses of individual minerals, and ion microprobe analyses of oxygen isotopes in ALH84001 carbonate have been made in order to constrain the conditions and timing of its formation.

The widely quoted preliminary Ar-Ar age for carbonate of 3.6 Ga measured by Knott et al. [1] has been reassessed on the basis of an improved treatment of blank and background corrections [2]. Our preferred age, based on Ar released by lasering the particular sub-microgram carbonate grain referred to by Knott et al., is $3,750 \pm 150$ Ma [2]. This age is not significantly different from our best estimate of the whole rock stepped heating age of $3,920 \pm 80$ Ma or the weighted mean laser probe age of the meteorite as a whole $3,900 \pm 100$ Ma [2]. It is important to realize that the potassium and argon bearing phase dated is not the carbonate itself, but rather the maskelynite intimately associated with it. Whether the age indicates the time of carbonate formation is therefore dependent entirely on whether the carbonate was deposited hot or cold. If, as first suggested by Mittleheldt [3] the carbonate was deposited at high temperatures ($600 - 700^\circ\text{C}$) then it is likely that the argon in the associated maskelynite (or feldspar as it probably then was) would have been degassed. In this case the Ar-Ar age would indicate the time of carbonate formation. Alternatively, if, as suggested by Romanek et al. [4], the carbonate was deposited cold, it is unlikely that the maskelynite/feldspar would be outgassed, and the apparent age of 3.8 Ga would be only an upper limit to the formation age of the carbonate.

Xenon isotopes have been measured in individual mineral grains of ALH84001 in a series of experiments involving; (a) combined Xe and CO_2 filament stepped heating analyses, (b) laser probe analyses of individual mineral grains in polished sections, and (c) laser stepped heating analyses. This has allowed us to determine the gas contents of some of the mineral phases present in the meteorite (orthopyroxene, maskelynite, apatite and carbonate) [5]. In some cases neutron irradiated samples have been analysed to allow determination of iodine contents. The maximum $^{129}\text{Xe}/^{132}\text{Xe}$ ratio observed in our experiments is 2.4 and is indistinguishable from estimates of the present day martian atmospheric value (in EET79001 glass) and from the components released in similar analyses of Nakhla (Fig.1)

In addition, there is no correlation of ^{129}Xe with excess ^{128}Xe (from neutron irradiation of ^{127}I), such as might arise if live ^{129}I were present when the iodine-bearing phase in ALH84001 formed. This indicates an I-Xe age ≥ 40 Ma (later than the Bjurböle chondrite), corresponding to a ^{129}Xe retention age $\leq 4,520$ Ma. Within error this is consistent with the Sm-Nd age of 4,560 Ma [6,7].

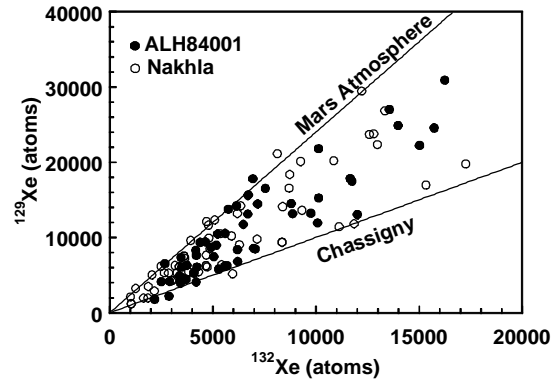


Figure 1

As previously reported [5], the atmospheric ^{129}Xe is located mainly in orthopyroxene. Comparison with our Ar-Ar data and published noble gas analyses of bulk samples indicate that the Xe/Ar ratios in the pyroxene are much higher than those in the (present day) martian atmosphere, i.e. xenon is trapped preferentially to argon. We think it likely that this trapping occurred by shock implantation of xenon which was preferentially adsorbed on mineral surfaces at the low temperatures in the martian crust.

The concentration of martian atmospheric ^{132}Xe in the carbonate is estimated in filament stepped heating analyses by measuring the partial pressure of the associated CO_2 release - a molecular mass of 100 g mole^{-1} is assumed. In measurements on irradiated samples this CO_2 release correlates well with a low temperature release of ^{131}Xe produced by the action of neutrons on Ba. Both sets of experiments indicate ^{132}Xe concentrations up to $3 \times 10^{-11} \text{ ccSTP/g}$ (derived indirectly from the small ^{129}Xe excess). This is similar to the values observed for the orthopyroxene but, because of the low abundance of carbonate in the meteorite, the contribution to the total atmospheric xenon budget of ALH84001 is very small. This observation indicates that trapping of martian atmosphere in ALH84001 by hydrothermal processes is relatively unimportant and, in particular, cannot account for the Xe/Ar fractionation.

In principle the concentration of martian atmospheric xenon in the carbonate is affected by its deposition temperature, the partial pressure of xenon in the atmosphere at the time of trapping, possibly the nature of the fluid (i.e. the $\text{CO}_2\text{-H}_2\text{O}$ ratio), and whether shock implantation is involved. In practice there are too many unknowns to make anything but semi-quantitative comparisons with terrestrial carbonates, other authigenic minerals, and with surface

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waters. Allowing for the (present day) difference in partial pressure between Mars and Earth, the concentration of ^{132}Xe in martian air saturated water (MASW) would be 2.9×10^{-11} ccSTP/g at 0°C and 1.2×10^{-11} ccSTP/g. at 25°C . These values are comparable to the concentrations measured in ALH84001 carbonate and indicate that trapping of surface water alone cannot account for the observed ^{132}Xe content. Concentrations of xenon in sedimentary authigenic minerals on Earth (speleothem and chert), vary over four orders of magnitude, from 10^{-12} to 10^{-8} ccSTP/g [8,9] indicating that trapping mechanisms in low temperature aqueous environments can produce large enrichments of the noble gases relative to ASW. Whether high concentrations can be produced in high temperature environments is not known, but intuitively seems less likely.

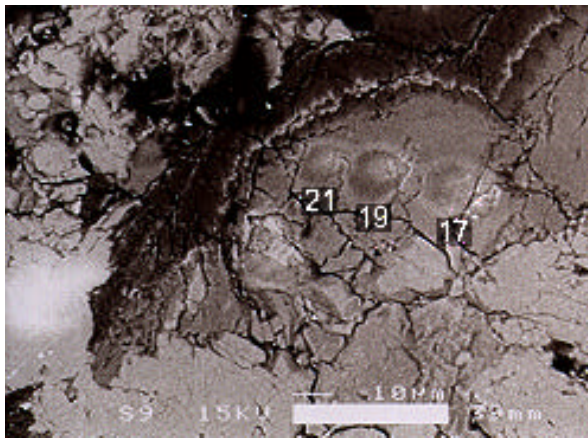


Figure 2.

Isotopic analyses of oxygen isotopes in the carbonate have been made using the Isolab 54 ion microprobe. The objective of this work, which is ongoing, is to see whether any evidence exists for isotopic exchange between the carbonate and surrounding pyroxene. Preliminary analyses (spot size $15\ \mu\text{m}$) are illustrated in figure 2 for the Ca-Fe rich cores. The analyses were calibrated with reference to four standards of calcite, magnesite, siderite and a carbonatite. A relatively large matrix effect ($\sim 18\%$ favouring ^{18}O) was observed in calcite and carbonatite relative to magnesite and siderite. Because of the low Ca content (~ 14 mole%) the magnesite and siderite standards were used for calibration and, for the time being, a uniform 2.5% correction has been applied for the matrix effect from Ca. Matrix effects are being investigated more fully and currently limit the accuracy of the ratios indicated in figure 2 to $\pm 2\%$. At this stage the three analyses are indistinguishable within error.

The mean $\delta^{18}\text{O}$ value of 19% lies in the middle of the range measured by Romanek et al.[4], 16.4% to 22.6% , using stepped dissolution. Modelling the dissolution kinetics, they inferred end member values of 13.3% and 22.3% , for the inner (Ca-Fe rich) zones and rims (Mg-rich), respec-

tively. Our spatially resolved data do not conflict with their analyses. Romanek et al. chose to interpret the carbonate as a low temperature ($<100^\circ\text{C}$) product, in contrast to Mittlefehldt and Harvey and McSween [10], who used cation distributions to infer a formation temperature of $>650^\circ\text{C}$, followed by rapid cooling. Based on the arguments below the oxygen data are consistent with either interpretation.

Whatever formation model for the ALH84001 carbonate is correct, the generation of heavy oxygen in martian carbonate, starting with a primary silicate mantle reservoir of oxygen with $\delta^{18}\text{O} \sim 4\%$, appears to require *at some stage* a low temperature isotopic exchange between water and CO_2 [11]. According to the Romanek et al. view, this exchange occurred as an integral part of the low temperature hydrothermal processes which deposited the carbonate. It seems equally plausible that the carbonate was generated by interactions involving CO_2 which was already enriched in ^{18}O . This could either be CO_2 generated by impact or volcanic volatilization of a pre-existing crustal carbonate reservoir or a reservoir of atmospheric CO_2 frozen within the crust. The additional requirements for the high $\delta^{18}\text{O}$ to survive and be incorporated in ALH84001 carbonate are that high temperature interactions with the silicate, during which cations are acquired, are dominated by CO_2 , and furthermore H_2O must be essentially absent. As has already been stressed [10], this latter condition appears to be required by the absence in ALH84001 of hydrated minerals.

A final piece of evidence supporting a water free environment, and by implication the Harvey and McSween view, may be provided by the $\text{Cl}/^{36}\text{Ar}$ ratio. Because of the difficulty of distinguishing terrestrial and martian ^{36}Ar in ALH84001, this ratio is not well established but is at least $\sim 10^6$ [12]. For comparison with the terrestrial environment, the ratio in sea water (salinity 3%) is $\sim 10^7$ and in the most saline groundwaters may reach 10^8 . Allowing for the difference in partial pressure of atmospheric ^{36}Ar between Mars and Earth, the ALH84001 ratio would translate to a terrestrial $\text{Cl}/^{36}\text{Ar}$ ratio of $\sim 2 \times 10^3$, an unrealistically low value if generated by hydrothermal fluids. In conclusion we believe that the isotopic and noble gas data does not conflict with a high temperature origin for ALH84001 carbonate. It is not obvious, however, that an initial high temperature deposition of the carbonate necessarily precludes the subsequent evolution of living organisms.

References: [1] Knott et al. (1995) *L.P.S.C. XXVI*, 765-766. [2] Turner et al. (1997) *GCA* (in press). [3] Mittlefehldt (1994) *Meteoritics* **29** 214-221. [4] Romanek et al. (1994) *Nature* **372** 655-657. [5] Gilmour et al. (1996) *Meteoritics* **31** A51. [6] Jagoutz et al. (1994) *Meteoritics* **29** 478-479. [7] Nyquist et al. (1995) *L.P.S.C. XXVI* 1065-1066. [8] Ozima and Podosek (1983) *Noble Gas Geochemistry* [9] L. K. Ayliffe (pers. comm.) [10] Harvey and McSween (1996) *Nature* **382** 49-51. [11] Clayton and Mayeda (1988) *GCA* **52** 925-927. [12] Ash et al. (1995) *Meteoritics* **30** 483.