IRON ISOTOPE FRACTIONATION IN ZONED CARBONATES FROM ALH84001. K. J. Theis[1]*, I. Lyon[1], R. Burgess[1] and G. Turner[1], [1]School of Earth, Atmospheric and Environmental Sciences, The University of Manchester, Manchester, M13 9PL, UK. (karen.j.theis@student.manchester.ac.uk). *Author previously known as KJ Gildea.

Introduction: The chemically and mineralogically zoned carbonates within the oldest martian meteorite, ALH84001 (a coarse grained orthopyroxenite) have been the subject of intense study [1-9] since McKay et al [3] suggested that they may contain evidence for life. Whilst these studies have revealed a convoluted history, there remains no consensus on the mechanism and temperature of carbonate formation. If we are to determine whether conditions on Mars were once favourable to life or that life may even have existed on the surface then the formation temperature of these secondary minerals must be constrained. Previous studies have focused on oxygen and carbon isotope analysis [6,9-12] which appear to confirm a low temperature origin whilst others [2,13,14] have cited evidence for rapid crystallization, lack of co-existing hydrous minerals and carbonate geo-thermometry to indicate a high temperature origin. The question remains: were the carbonates formed by low temperature evaporation/precipitation and therefore able to support life or was high temperature rapid crystallisation/alteration responsible and therefore less favourable to life existing? The aim of this study is to constrain the carbonate formation temperature from the iron isotope composition of the zoned carbonates relative to martian bulk silicate isotopes. ALH84001 bulk silicate δFe^{57} isotope value have been reported as -0.027±0.051 by Poitrasson et al [15].

Samples and preparation: The zoned carbonates were removed from a pristine fragment of ALH84001. The fragment is approximately 6.0 x 5.5mm in size and, as shown in figure 1, there are numerous areas of orange-stained zoned carbonates on the surface of the fragment.

Figure 1. Photograph of the fragment of ALH84001 used in this study prior to the removal of the surface carbonates.

The carbonates were removed from the meteorite using a carbide tipped micro-drill bit and were soft enough that they could be gently scraped away from the surface using very little force. This also helped to ensure that no silicates would be removed during this process. A preliminary experiment with terrestrial carbonates revealed that 10mls of 2% HNO_3 solution is sufficient to fully digest a carbonate sample of up to 20mg without any additional iron being leached from silicates that may have been intergrown with the microcrystalline carbonates.

Once the powdered carbonates had been dissolved in a 2% HNO_3 solution for 1 hour, the solution was filtered to remove any remaining silicate residue before being introduced to the ICP-MS for analysis.

Mass Spectrometry: Analyses were carried out on a Nu Plasma double focusing multiple-collector ICP-MS using pseudo high resolution mode. The sample and standard solutions were introduced by a Nu Instruments DSN-100 desolvating nebuliser to remove the majority of the carrier solvent and thus minimise the effects of ArN, ArO and ArOH which interfere with ^{54}Fe, ^{56}Fe and ^{57}Fe respectively. The pseudo high resolution mode enables mass resolution of any remaining isobaric interferences and iron isotopes to obtain a flat-topped iron 'shoulder' for high precision isotopic measurements [16].

The reproducibility and accuracy of the Nu Plasma ICP-MS has been determined by continuous measurements of an in-house Johnson-Matthey (JM) iron standard bracketed by the IRMM014 iron isotope standard (JRC Reference Laboratory for Isotopic Measurements) over a period of three years. Results were calculated using the standard delta notation: $\delta^{56,57}Fe = [\{(^{56,57}Fe/^{54}Fe)_{sample}/(^{56,57}Fe/^{54}Fe)_{IRMM014}\}-1 *1000]$. We found that $\delta^{56}Fe=0.35\pm0.03‰$ and $\delta^{57}Fe=0.53\pm0.04‰$ for the JM standard which is in good agreement with accepted values. Each measurement cycle consisted of a single block of 30 readings repeated 3-6 times (bracketed each time with IRMM014 Fe solution). The ALH84001 carbonate sample analysis was repeated 6 times and bracketed with a Mg:Ca matrix matched IRMM014 Fe solution. Quoted uncertainties are ±1σ.

Matrix effects: Mixtures of standard solutions of Mg:Ca:Fe in known concentrations have revealed that the presence of Fe suppresses the Mg signal but has no effect on Ca. Thus, to accurately determine the correct Mg:Ca:Fe composition of the ALH84001 carbonate

solutions of Fe and Mg mixtures were analysed to fully determine the effect of the suppression. Results showed that this effect can be easily corrected. For the carbonate composition the correction was a 28% increase of the Mg concentration giving the Mg:Ca:Fe composition of the ALH84001 carbonate sample shown on the ternary diagram in figure 2.

The presence of Mg and Ca in Fe solutions is also known to affect the ionisation of the Fe causing a matrix effect. The resulting fractionation is biased towards the lighter isotope and thereby requires a correction. Fe isotope standards JM and IRMM014 were mixed with known concentrations of Ca and Mg solutions to assess the isotopic effects. These experiments revealed that there was no significant fractionation effect on the resultant iron isotope variations between the JM Fe solution and the IRMM014 Fe solution if the composition of the standard (IRMM) and sample (JM) matrix solutions were matched.

Results: The composition of the ALH84001 carbonate analysed for this study is Mg:34%, Ca:30% and Fe:36%. When plotted on the ternary diagram (fig. 2) taken from Holland et al, [9], it can be seen that the sample matches the compositions of carbonates from other studies quite well thus confirming that the iron analysed in this study is from the carbonates and not from silicates.
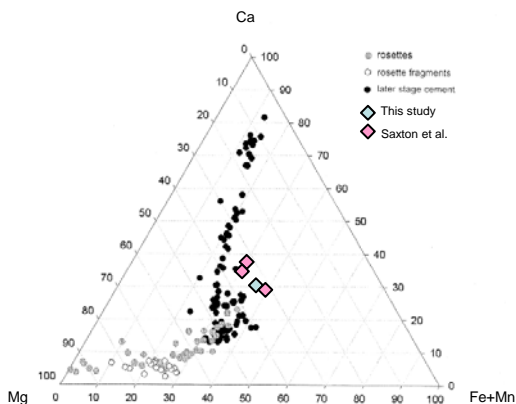

Figure 2. Modified from Holland et al, [9] showing the compositions of different carbonate phases in ALH84001, the composition of the carbonate sample from this study (green) and also 3 data points from Saxton et al, [6] showing zoned carbonates of a similar composition (red) .

The iron isotope fractionation relative to IRMM014 is $\delta^{56}Fe=-0.62\pm0.11‰$ and $\delta^{57}Fe=-0.83\pm0.15‰$ for the zoned carbonates.

Discussion: Assuming that the carbonate was derived from an iron reservoir having an Fe isotope composition as determined in martian silicates then it is possible to obtain a temperature range for carbonate precipitation. If the fluids were in equilibrium with the surrounding silicate rock then the temperature can be estimated using the Mossbaüer spectrum data of Polyakov and Mineev [17] shown in figure 3. By using 1 and 2σ to provide a minima and maxima for this data the overall temperature range would be $83 \pm 67^{o}C$ (2σ).
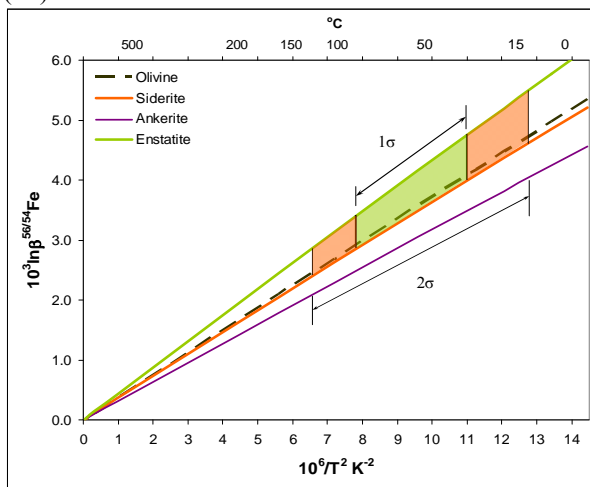

Figure 3. Diagram showing the temperature required for δFe^{56} of -0.6‰ fractionation between orthopyroxenite and ALH84001 carbonate based on the data for enstatite and siderite taken from Polyakov and Mineev [17].

The results of this study confirm a low temperature origin for these secondary minerals.

References: [1] Mittlefehldt D. W. (1994) *MAPS, 29,* 214–221. [2] Harvey R. P. & McSween H.Y. (1996) *Nature, 382,* 49-51 [3] McKay D. S. et al. (1996) *Science, 273,* 924-930. [4] Scott E. R. D. (1998) *MAPS, 33,* 709-719. [5] Treiman A. H. (1998) *MAPS, 33,* 753-764. [6] Saxton J. M. et al. (1998) *EPSL, 160,* 811-822. [7] Eiler J. M. et al. (2002) *GCA, 66,* 1285-1303. [8] Corrigan C. M. & Harvey R. P. (2004) *MAPS, 39,* 17-30. [9] Holland G. et al. (2005) *GCA, 69,* 1359-1369. [10] Romanek C. S. et al. (1994) *Nature, 372,* 655-657. [11] Jull A. J. T. et al. (1995) *MAPS, 30,* 311-318. [12] Valley J. W. et al. (1997) *Science, 275,* 1633-1638. [13] Scott E. R. D. et al. (1997) *Nature, 387,* 377-379. [14] Scott E. R. D. et al. (1998) *Meteorit. Planet. Sci. 33,* 709-719. [15] Poitrasson F. et al. (2004) *EPSL, 223,* 253-266. [16] Weyer S. & Schwieters J. B. (2003) *Int. J Mass Spectrom. 226,* 355-368. [17] Polyakov V. B. & Mineev S. D. (2000) *GCA, 64,* 849-865.