

**DETERMINING THE CARBON ISOTOPIC COMPOSITION OF ALH84001 ROSETTES WITH NANOSIMS** T. Tomkinson<sup>1</sup>, A.W. Needham<sup>1,2</sup>, D. Johnson<sup>1</sup>, C. Guillermier<sup>1</sup>, I.A. Franchi<sup>1</sup>, A. Hagermann<sup>1</sup>, I.P. Wright<sup>1</sup> and M.M. Grady<sup>1,2</sup>. <sup>1</sup>PSSRI, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK (t.o.r.tomkinson@open.ac.uk), <sup>2</sup>Dept. of Mineralogy, The Natural History Museum, London, SW7 5BD, UK.

**Introduction:** Martian meteorite samples provide an insight into the lithosphere, atmosphere and hydrosphere of Mars and thus can help us to determine the environments in which they formed. Formation of secondary alteration products are particularly intriguing since such components can help cast light on their likely fluvial origins. The motivation to search for carbonates on Mars is that these minerals are associated with water, carbon dioxide and an alkaline pH; all conditions hospitable for most terrestrial life. The classification of geological eras and identification of phyllosilicates by the OMEGA team [1] suggest that primordial Mars was a ‘warm and wet’ environment (Phyllosian era). In addition to detecting phyllosilicates [2] CRISM also detected carbonates in the form of magnesite [3]. The Phoenix lander also detected surface deposits of carbonates in the form of calcite [4].

**ALH84001:** The oldest known martian meteorite we have on Earth; the carbonates within ALH84001 precipitated ~3.9 Gy ago [5]. Of all the current martian meteorites ALH84001 has the most abundant carbonate morphology (1 % vol) and varied in mineralogy, especially the carbonate “rosettes”, with an ankerite core commonly surrounded by an alternating layer of siderite-magnesite-siderite. The ancient age (perhaps similar to that of CRISM’s magnesite discoveries), abundance, isotope and mineralogy variations make ALH84001 an ideal candidate to provide insights into the primordial martian conditions.

**Isotope compositions:** The ion microprobe  $\delta^{13}\text{C}$  measurements of carbonates in ALH84001 varies from +27 to +64‰ [6, 7] additional studies by acid dissolution and stepped combustion of bulk material fall within this range [8, 9, 10]. The variation in  $\delta^{13}\text{C}$  requires a significant change in fluid composition and/or temperature during formation. Because of the small size of these rosettes (50-250  $\mu\text{m}$ ), few studies have related the 10’s of micron mineralogical variations with  $\delta^{13}\text{C}$ . To rectify this issue we are using The Open University’s (OU) Cameca NanoSIMS 50L (Secondary Ion Mass Spectrometer), an instrument that combines sub-micron ion beam spot sizes with high sensitivity, making it an ideal analytical tool for studying microscale isotope variations with alternating mineralogy.

**The sample:** Split 246 from ALH84001 was broken into three pieces with a carbonate rich chip set in K rapox resin (but not covered thereby reducing con-

tamination sources). Where topography appeared to be an issue (>10  $\mu\text{m}$  [11]) a focused ion beam (FIB) was used to obtain a submicron smooth surface. The sample was coated with a 30 nm thick gold layer to avoid charging; however, this material, along with any contamination, is sputtered away during the first phase of NanoSIMS isotope analysis. Initial characterization of the sample was conducted using a scanning Dual beam FEI Quanta 3D electron microscope (SEM) at 15 kV. Qualitative element maps and point analysis were produced for the sample with emphasis on the carbonate rich-region (Figure 1). Within the orthopyroxene (Figure 1 – green) only two phases of carbonate were observed (ankerite and magnesite) but surrounding these carbonates are fine grain 10-50  $\mu\text{m}$  spots of Fe-sulphides commonly associated with observations of siderite and magnetite [12]. A 3D image was taken of the top rosette from Figure 1 before using the FIB to gain an idea of its initial topography (Figure 2). The image shows a rosette sitting roughly ~5  $\mu\text{m}$  proud of the orthopyroxene, this in contrast to the samples studied by Thomas-Kerpta et al [12] where carbonates are observed flush to the surrounding material.

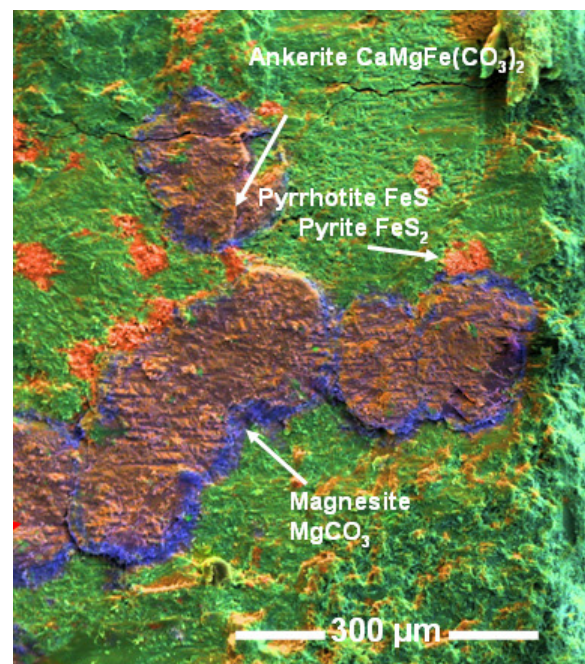


Figure 1 – False coloured secondary electron image. Green - Si, Red – Fe, Blue – Mg.



Figure 2 - 3D image of rosette created with MeX software.

**Standards:** The carbonates that we are using for instrumental mass fractionation (IMF) and matrix corrections are dolomite, calcite, magnesite, ankerite and siderite. All the carbonate standards have been mapped with EDX, XRD analysed and calibrated to a NIST 19 reference on a Thermo-Finnigan DELTA Advantage mass spectrometer for VPDB and VSMOW values.

**Analytical:** Carbon isotopic analysis of the carbonates has been undertaken by isotopic imaging (10-15  $\mu\text{m}$ ) and point analysis (5  $\mu\text{m}$ ) with the  $\text{Cs}^+$  ion beam. Monitoring of  $^{28}\text{Si}$ ,  $\text{MgO}$ ,  $\text{CaO}$  and  $\text{FeO}$  provided an indication of contamination and mineralogy. Analysis were conducted with a primary beam of 15pA and a mass resolving power  $>6000$  ( $M/\Delta M$ ). Extensive pre-sputtering was required to remove surface contamination, residual areas excluded with L'image software. The analytical precision achieved was  $\pm 2.5\%$  ( $2\sigma$ ) with an integration time of 40 minutes per point on spot sizes  $5 \times 5 \mu\text{m}$  for ankerite, calcite, siderite, magnesite and dolomite with good reproducibility of IMF and matrix effects. Two 15  $\mu\text{m}$  lines of analysis will run parallel across the rosettes covering all the isotopes mentioned above. A cameca SX100 electron microprobe (OU) will then be used to quantitatively characterize the mineralogy at each analysis site.

**Implications:** Current models include enrichment of isotopes through Raleigh distillation [13], rapid temperature variations [14] or evaporation models [15]. Two hypotheses have also been suggested to account for the isotope enrichment: in which either mixing has occurred between fluids of different isotopic reservoirs or an interaction of atmospheric  $\text{CO}_2$  with high pH surface fluids has occurred [6]. We anticipate that once we have acquired profiles across several rosettes, we

should be able to distinguish between different formation models.

**References:** [1] Bibring, J.-P. et al. (2006) *Science*, 312, 400-404. [2] Mustard, J. F. et al. (2008) *Nature*, 454, 305-309. [3] Ehlmann, B.L. et al. (2009) *Science*, 322, 1828-1832. [4] Boynton, W. V. et al. (2009) *Science*, 325, 61-64. [5] Borg, L.E. et al. (1999) *Science*, 286, 90-94. [6] Niles, P.B. et al. (2005) *GCA*, 69, 2931. [7] Valley, J.W et al. (1997) *Science* 275, 1633-1637. [8] Jull, A.J.T. et al. (1997) *JGR* 102, pp. 1663-1669. [9] Grady, M.M. *Meteoritics* 29, 469. [10] Jull, A.J.T., et al. (1998) *Science*, 279, 366-369. [11] Kita, N. T. et al. (2009) *Chemical Geology*, 264, 43-57. [12] Thomas-Keprta K.L. et al. (2009) *GCA* 73, 6631-6677. [13] Leshin, L.A. et al. (1998) *GCA*, 62, 3. [14] Eiler, J.M. et al. (2002) *GCA*, 66, 1285. [15] Warren, P.H. (1998) *JGR*, 103, 16759.