Reduced Martian Carbon: Evidence from Martian Meteorites. Everett K. Gibson, Jr.¹, David S. McKay¹, Kathie L. Thomas-Keprta², Simon J. Clemett², Colin T. Pillinger³, Ian P. Wright³ and A.P.Verchovsky³. ¹KR Astromaterials Research Office, NASA Johnson Space Center, Houston, TX 77058, ²ESCG, NASA Johnson Space Center, Houston, TX 77058, ³Planetary Sciences and Space Research Institute, The Open University, Milton Keynes, U.K. (everett.k.gibson@nasa.gov)

Identification of indigenous reduced carbon species on Mars has been a challenge since the first hypotheses about life on Mars were proposed. Ranging from the early astronomical measurements to analyses of samples from the Martian surface in the form of Martian meteorites. The first direct attempt to analyze the carbon species on the surface was in 1976 with the Viking GC-MS in-situ experiment which gave inconclusive results at two sites on Mars [1]. With the recognition in 1983 that samples of the Martian surface were already present on Earth in the form of Martian meteorites by Bogard and Johnson [2] new opportunities became available for direct study of Mars's samples in terrestrial laboratories. Carbon isotopic compositional information suggested a reduced carbon component was present in the Martian meteorites [3-5]. Polycyclic aromatic hydrocarbons associated with carbonate globules in ALH84001 were later identified [6,7]. Jull et al [8] noted that an insoluble component was present within Nakhla and more than 75% of its C lacked any ¹⁴C, which is modern-day carbon contaminant. This carbon fraction was believed to be either indigenous (i.e. Martian) or ancient meteoritic carbon phase. Within the fractures of Nakhla and ALH84001, Fisk et al [9,10] identified reduced carbon-enriched areas. Gibson et al. [11] using a combination of NanoSIMS, Focused Electron microscopy, Laser Raman Spectorscopy and Stepped-Combustion Static Mass Spectrometry analyses the presence of possible indigenous reduced carbon components within the 1.3 Ga old Nakhla.

NanoSIMS analysis of Nakhla's interior samples [11] showed the presence of an optically dark dendritic material fracture-filling reduce carbon phase which showed a direct correlation between C- and CN- abundances. In addition, Laser Raman Spectrometry identified an apparent complex mixture of carbonaceous compounds associated with the Nakhla dendritic material and the iddingsite produced by the alteration of primary silicates within the meteorite.

Stepped combustion static mass spectrometry analysis of the iddingsite-rich phases containing the dark dendritic materials was able to distinguish different C- and N-bearing components present within Nakhla. Three distinct carbon components were identified in Nakhla. Α low-temperature C component released below 300°C was predominantly terrestrial contamination with a carbon isotopic composition of -22 to -24‰. A reduced C-bearing component with isotopic composition of ~-16 to -20‰ was measured in the 400 to 550°C intervals. Possible presence of a pre-terrestrial secondary carbonate with a carbon isotopic composition of >+5‰ was released at $T > 550^{\circ}$ C. The isotopic composition of the reduced C-component was identical to values of -18 to -20% reported earlier by Jull et al. [8] and Stepton [12]. Gibson et al. [11]'s analyses were the first isotopic measurements of directly imaged high molecular weight carbonaceous components in Nakhla. Previous measurements were from bulk Nahkla samples with no direct observation of the C-bearing phases. The nitrogen isotopic composition of the reduced Ccomponent was ~+5‰. It is clear that the organic phases are associated with the iddingsiterich alteration regions of Nakhla. The fluids associated with the iddingsite production seen within Nakhla and other SNC samples along with the carbonate globules within ALH84001 were carriers of the reduced carbon hydrocarbon components. The recent study by Thomas-Keprta et al. [13] clearly showed that a unique population of magnetites, with a possible biogenic signatures, were formed from aqueous fluids in which possible reduced carbon-bearing components were present.

From the evidence contained within ALH84001's carbonate globules formed at 3.9 Ga (in the first 600,000 million years of Martian history) it is suggestive that abundant water reservoirs and movement of aqueous fluids within the planet's crust was occurring. These aqueous fluids were also the carriers of the unique magnetites trapped within the carbonates observed n

ALH84001 [13]. In addition, the association of the PAH's enrichment in the magnetite-bearing carbonate globules of ALH84001, strongly suggests reduced carbon being present in the martian aqueous reservoirs at 3.9 Ga. The estimated ages of the alteration produces (i.e. iddingsite) within the 1.3 Ga Nakhla are around 600,000 million years ago [14]. The presence of the reduced dark dendritic materials in the iddingsite-rich fractures of Nakhla are suggestive of introduction of carbon components in the "recent past" on Mars. With the evidence of reduced-carbon phases present in the fluid reservoirs on Mars 3.9 Ga years ago and at 600,000 million years ago as observed in Nakhla, the possibility of reduced carbon components present within the current near-surface fluid reservoirs on Mars must not be ruled out. It may be possible that the recent fluid discharges observed within the solar heated walls of craters and within channel walls may be carrying reduced organic components. However, with the UV irradiation experienced by the surface of Mars, the resident time for these reduced carbon phases may be limited. Should the deposits bearing the carbon-rich fluids become buried, the probability of survival for the organic components greatly increase.

Suitable sites for reduced-carbon rich components are present on Mars. The recently identified "mud volcanoes" and "springs" locations on Mars as identified by Oehler and Allen [15] are candidate sites. We must use the right tools to positively identify the signatures of life. Until the proper suite of analytical instruments are on the Martian surface or a well-characterized sample is returned from Mars, the Martian meteorites are our only hope for unraveling the nature of the reduced carbon components present on Mars and the signatures of life on Mars.

References:

[1] Biemann K. et al., (1977) J.G.R. 82, 4641-4658. [2] Bogard D.D. and P. Johnson (1983) Science 221, 651-654. [3] Carr R.H. et al. (1985) Nature 314, 248-250. [4] Wright I.P. et al. (1989) Nature 340, 220-222. [5] Grady M.M. et al. (1994) MAPS 24, 469. [6] McKay D.S. et al., (1996) Science 273, 924-930. [7] Clemett S.J. et al., (1998) Faraday Discuss. 109, 417-436. [8] Jull A.T.J. et al. (2000) GCA 64, 3763-3772 [9] Fisk M.R. et al., (2005) LPSC XXXVI, Abst. 2275. [10] Fisk M.R., et al. (2006) Astrobiology 6(1), 48-68. [11] Gibson E.K. et al. (2006) LPSC XXXVII, Abst. 2039. [12] Sephton M.A. (2002) Planet. Space Sci. 50, 711-716. [13] Thomas-Keprta K.L. et al. (2009) GCA 73, 6631-6677 [14] Swindle T.D. and Olson E.K. (2004) MAPS 39, 755-766. [15] Oehler D.Z. and Allen C. (2010) Astrobiology (in press) and this meeting.