

**Mars Sample Return: Stable isotope targets with return samples.** J Farquhar, Department of Geology and ESSIC, University of Maryland, College Park, 20742.

**Introduction:** The return of samples from Mars will provide a unique opportunity to study the present and past environments and surface of Mars. It is inevitable that this effort will be driven by what we already have learned about the atmosphere, surface, and deep planet from studies that use remote sensing techniques, robotic and in-situ techniques, and that derive from the suite of meteorites (SNC) that have been attributed a Martian origin. It is also anticipated that the types of studies that will be undertaken with earth-based techniques on the first return samples will reshape our understanding of the environments and their evolution on Mars and will likely inform further exploration, science, and return sample missions.

Past experience with the Apollo missions has demonstrated that the full importance of these samples and the studies that characterize them will be difficult to gauge, but that the impact on our understanding of Mars, its surface environments, and its evolution are likely to be profound. A number of tests will inevitably be devised as the community gears up for the arrival of such samples and more tests will be developed once they arrive in terrestrial laboratories.

The purpose of this abstract is not to cover all, or even most, of the potential targets for terrestrial-based geochemical investigations of samples from a first (or first few) sample return(s), but to highlight a few questions that could be addressed with return samples using mass spectrometric techniques that focus on light-stable isotopes (H, C, N, O, and S). An undercurrent here will be on approaches used to study samples on Earth, techniques that allow for determination of microscopic variations in isotopic composition, at high precision with rare species, or with minute amounts of sample.

**Ground Truth for SNC Meteorites:** A sample return will provide ground truth for assertions about the SNC meteorites, which while extremely important in shaping our understanding of Mars comprise a sample set is limited. *The diversity of samples that inform us about the surface environments of Mars will be significantly expanded with return samples.*

The SNC meteorites have been important in shaping our understanding of Mars. These meteorites have been attributed a Martian origin and appear to preserve important information about the chemistry and isotopic variations using a number of compelling lines of evidence that include dynamical considerations associated with delivery from their parent, trapped gases, their young geologic ages, as well as other mineralogical characteristics [1-3]. These meteorites also possess

silicate minerals that have a diagnostic oxygen isotope composition [4, 5]. Silicate minerals from the SNC meteorites are documented to lie on a characteristic mass-fractionation line and the return of samples will provide an important direct measure for the triple oxygen isotope composition of silicate minerals at Mars's surface. Such an exercise will be relevant for evaluating the veracity of hypotheses made about Mars on the basis of data obtained from this suite of samples, and potentially for constraining assimilation or exchange with other Martian surface pools of oxygen.

**Other targets for return samples:** Among the big questions about Mars are the conditions that prevailed in earlier times in Mars' history. This includes a number of questions and a handful of these might focus on understanding past temperatures and climate, the availability of water in the regolith, an understanding of the nature and variability of atmospheric composition, the transfer of atmospheric signals to the surface and the oxidation of the surface by interactions with atmospheric species.

A number of studies of SNC meteorites have brought Secondary Ion Mass Spectrometry to bear on interpreting the variability of the isotopic composition of phases such as carbonates in the SNC meteorites. These studies have documented variability in stable isotope compositions at small scales and provided important constraints on temperature and fluids that existed in near surface environments.

*Determining the hydrogen isotope variations of return samples.* Likewise, the hydrogen isotopic composition of SNC meteorites has been demonstrated to be highly evolved as a result of escape processes [6,7]. Investigations using a number of microanalytical and macroanalytical techniques are likely therefore to be a prime target for further investigation of interactions between hydrogen-containing surface pools and deeper planetary reservoirs.

*Determination of the temperatures of surface weathering environments using isotope fractionations and clumped isotopes in phases such as carbonate.* Recent developments in high precision techniques, techniques that rely on the site occupancy of isotopes, and techniques that provide high spatial resolution and high accuracy and precision will continue to evolve [8-10]. These techniques also provide a way of obtaining information about surface conditions that are unique and valuable for shaping our understanding of the surface evolution of Martian environments.

*Determination of the isotopic composition of gases and solid phases in return sample as a measure for*

*atmospheric composition.* The potential exists for preservation of important information about the fractionations between atmospheric species. High-precision measurements of terrestrial atmosphere have proven highly valuable for constraining the types of chemical reactions and chemical pathways that are relevant in the terrestrial element cycles. It is anticipated that similar measurements (such as the carbon isotope fractionation between carbon dioxide and carbon monoxide, or the  $^{16}\text{O}/^{17}\text{O}/^{18}\text{O}$  of atmospheric oxygen-possibly carbon dioxide) provide similarly valuable constraints for understanding Mars atmospheric chemistry [11-14].

*Determination of the extent to which oxidized species with anomalous  $^{17}\text{O}$  have interacted with the silicates during weathering reactions or with water in Martian near surface weathering environments.* The presence of an anomalous  $^{17}\text{O}$  signal in carbonate and hydrous silicates [15-17] from the SNC meteorites indicates the presence of a pathway for transfer of an atmospheric oxygen signal from the atmosphere into the regolith. The amplitude of the signal may depend on parameters that include the amount of available water and the rates of oxidation of the surface by the atmosphere. The amplitude of this signal is uncertain with the present SNC samples.

*Determination of the oxidation pathways that led to the formation of sulfate.* Sulfate appears to be a very important feature of Mars surface environments and the indications from the SNC meteorites point to anomalous oxygen and sulfur. This signal suggests an atmospheric oxidation pathway, but the pathway is uncertain in large part because of the paucity of samples with clear signals [17-19]. Return samples have the potential to provide samples that can be used to characterize this signal and therefore to characterize the oxidation pathways and chemistry of sulfur in the Martian atmospheric environment.

*Integration of reaction textures and the relationship to isotopic variations.* The past decade has seen dramatic improvements in the capabilities of microanalytical techniques, including significant improvements in spatial resolution and precision with SIMS techniques as well as improved capabilities and more widespread use of cutting edge techniques in electron microscopy. The applications and expertise with these techniques will continue to improve and has the potential to provide new types of information and insights into past temperatures, changing conditions, and rates of change.

These examples are but a few of the types of research questions that might be addressed with return samples, or the variety of additional tests that will be devised to understand atmospheric composition, for

textural analysis of samples or even the detection of very rare compounds. Return samples with surface weathering, of soil and sediments, and of atmospheric gases (trapped, adsorbed, or free) have the potential to carry important information about past temperatures of Mars's surface environments, the pathways for oxidation of the Martian regolith, and the presence, composition, and amounts of water in near surface environments.

1. Mcdowell, HY. 1994... Meteoritics 29 (6): 757-779.
2. Mcdowell, Hy. 1985. Rev Geoph 23 (4): 391-416.
3. Bogard, Dd; Nyquist, Le; Johnson, P. 1984. GCA 48 (9): 1723-1739
4. Clayton, RN; Mayeda, TK. 1996. GCA 60 (11): 1999-2017.
5. Franchi, IA; Wright, IP; Sexton, AS; Pillinger, CT. 1999. MAPS 34 (4): 657-661.
6. Leshin, LA; Epstein, S; Stolper, Em. 1996. Geochimica Et Cosmochimica Acta 60 (14): 2635-2650.
7. Watson, LL; Hutcheon, ID; Epstein, S; Stolper, EM. 1994. Science 265 (5168): 86-90.
8. Eiler, JM Earth And Planetary Science Letters, 262 (3-4): 309-327
9. Valley, JW; Eiler, JM; Graham, CM; Gibson, EK; Romanek, CS; Stolper, EM. 1997. Science 275 (5306): 1633-1638.
10. Eiler, JM; Valley, JW; Graham, CM; Fournelle, J. 2002. Geochimica Et Cosmochimica Acta 66 (7): 1285-1303.
11. Bhattacharya, Sk; Savarino, J; Thiemens, Mh. 2000. Geophysical Research Letters 27 (10): 1459-1462.
12. Eiler, JM; Kitchen, N; Rahn, Ta. 2000. Experimental Constraints On Geochimica Et Cosmochimica Acta 64 (4): 733-746.
13. Thiemens, MH History and applications of mass-independent isotope effects Annual Review Of Earth And Planetary Sciences, 34: 217-262 2006
14. Thiemens, MH Science, 283 (5400): 341-345 JAN 15 1999
15. Romanek, et al. 1994. Nature 372 (6507): 655-657.
16. Farquhar, J; Thiemens, MH; Jackson, T. 1998. Science 280 (5369): 1580-1582.
17. Farquhar, J; Thiemens, MH. 2000. Journal Of Geophysical Research-Planets 105 (E5): 11991-11997.
18. Farquhar, J; Savarino, J; Jackson, TL; Thiemens, MH. 2000. NATURE 404 (6773): 50-52.
19. Farquhar, J; Kim, ST; Masterson, A. 2007. Earth And Planetary Science Letters 264 (1-2): 1-8.