

**MARS SAMPLE RETURN: WHICH SAMPLES AND WHY.** C. R. Neal<sup>1</sup>, <sup>1</sup>Dept. of Civil Eng. & Geological Sciences, University of Notre Dame, Notre Dame, IN 46556, USA, neal.1@nd.edu.

**Introduction:** With NASA making a decision to launch a sample return mission to Mars by 2020, there is much development that needs to be done so we are ready to meet this deadline. The Curation and Analysis Planning Team for Extraterrestrial Materials (CAPTEM) produced papers 1998 and 2000 [1,2] that documented the challenges involved in returning samples from Mars to Earth and keeping them in their pristine condition. There is a tendency to consider that this sample return opportunity will be the only one so we should return the best samples to determine if life ever evolved on the red planet and whether the climate was ever much thicker, warmer, and wetter than at present. In order to achieve this, the sample return mission should be “Christmas-treed” with instruments to identify each sample through extensive analyses on the surface. Then, once these samples are collected they have to be maintained in their pristine state during the long return journey to Earth. However, in this time of modest budgets, such a sample return mission will probably be cost-prohibitive, especially if the samples are collected over an extended period by a rover. Therefore, it is time to re-examine this scenario and to see if sample return will yield significant scientific return for a mission that is less than “perfect”.

From orbital and surface observations, it is apparent that igneous, volcanoclastic, and sedimentary materials are present on the Martian surface. All tell a part of the story regarding the evolution of Mars and this story will be unraveled best through study in Earth-based laboratories. However, the samples that are studied here on Earth must remain unchanged since collection on Mars. So how tolerant are the different types of samples to different environmental conditions that will be encountered during sampling, storage, take off from Mars, return to Earth, re-entry and landing, and finally curation?

**Materials.** The previous work published in 2000 [2] gave recommendations on the type of materials that would be acceptable from a sample containment standpoint, noting that (as far as possible within mission constraints) only pure, homogeneous materials should be used for components that come into contact with the samples.

- ◆ Low-Zn aluminum (i.e., not the 7000 series alloys) - the 6061 alloys (i.e., alloyed with Mg and Si) are acceptable;
- ◆ Low sulfur stainless steel that contains no molybdenum and is compatible with electropolishing and passivating in nitric acid;
- ◆ Titanium alloys should be as pure as feasible given

the required physical and metallurgical properties;

- ◆ Unplasticized Teflon that would impart organic contamination recognizable as non-biogenic;
- ◆ Tungsten carbide used for the drill bits should be pure WC and sample contamination documented through drilling experiments on Earth.

It is important that flight spares be created of all components that contact the samples and that these spares be stored for subsequent analysis to document homogeneity and purity.

**Mineral Stability.** The compositions of the various minerals now known to be present at the Martian surface will, in some cases, pose challenges in returning them to Earth and keeping them in their pristine state. For example, clay minerals and hydrated sulfates contain loosely bound water (+/- hydroxyl) molecules that could be dislodged due to temperature and pressure fluctuations. For example, clay minerals can dehydrate between 300-500 K. While this may not seem to be as great loss, being able to measure the pristine  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  of these waters could shed light on the Martian hydrologic cycle. Differential dehydration during collection, storage and transport of samples containing clay minerals will fractionate the isotopic signatures. For Jarosite, dehydration from the hydronium site occurs at 260°C and dehydroxylation occurs between 450-480°C [3]. For other hydrated sulfates, temperature and relative humidity determined the stability of a given phase. Hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ) forms from Epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) at 16-20°C at relative humidities <60%. Kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) forms from Hexahydrate as relative humidity drops below 20-45% [4,5]. Hexahydrate dehydrates rapidly ( $\leq 24$  hours) to a variety of secondary products (Starkeyite: 4  $\text{H}_2\text{O}$ ; Sanderite: 2  $\text{H}_2\text{O}$ ; Kieserite: 1  $\text{H}_2\text{O}$ ) at 75°C [6]. Such changes would radically affect H and O isotope compositions especially if the sample cache was not sealed. However, igneous rocks and minerals would certainly be tolerant of moderate fluctuations in temperature without much change in their pristine state.

**Sample Containment:** As the samples will be contained for a relatively long period, the container should not compromise sample integrity. In addition, temperature control could be important for preserving sensitive biologic/sedimentary chemical signatures. If Teflon is to be used, it should be PFA or FEP and applied as a baked-on coat to the metal of the sample container, rather than a separate insert. This protocol reduces the number of parts to be manipulated, and the possibility that the sleeve could come loose, preventing sample insertion, is avoided. Mixing of samples is considered

undesirable if a petrologically diverse suite of samples is returned from different areas around the landing site(s).

**Sterilization:** While the probability of the returned samples containing viable organisms cannot be demonstrated to be zero, it is considered to be extremely low [7-9]. It has been suggested that if a sample contains no organically bound carbon or demonstrably viable organisms, it be released for scientific study [2]. If sterilization is required, we recommend that heat and chemicals NOT be used as these methods severely compromise sample integrity; at present, the preferred sterilization method is high-dose gamma radiation [10] and it is recommended that this method be further explored.

**Curation:** Long-term curation of Martian samples on Earth will utilize procedures and protocols developed for lunar samples, cosmic dust, and meteorites that will preserve the integrity and pristinity of returned samples. However, protocols need to be reviewed and modified to meet the challenges of curating samples in the long term. For example, storage of the samples should be  $\leq 240$  K and under an inert atmosphere (e.g., nitrogen) for long-term preservation of low-temperature chemical signatures and prevention of isotopic exchange. The need to keep bio-organic contamination out of the sample containers and the curation facility will require an examination of air filtration requirements and protocols.

**Sample Return Strategy.** If the cost of undertaking the monitoring during return and curation of the samples once here swallows up the entire budget of the Mars program, the knee-jerk reaction is to continue pushing sample return off into the dim and distant future. Orbital and surface rovers will continue to be the way Mars is explored, although I would say this would be with diminishing returns. This is because the level of sophistication needed for in situ analytical equipment to give us accurate age dates and geochemical data would again drive the budget for such mission into the realm of unsustainability. Sample return is essential for giving points of ground truth for orbital remote sensing data. It is required so that absolute ages can be determined to give at least one fixed point to the cratering history of Mars, as well as for understanding the sequence of processes that have affected the Martian surface and interior. While impact melts and igneous materials are ideal for this, several papers written since the discovery of Jarosite (and potentially other hydrated sulfates) on Mars have noted that this mineral can be used to obtain age data using argon methods (e.g., [11]). Data indicate little to no Ar loss at 90°C for 12-14 hours [12].

The strategy proposed here is to return samples from Mars that will be the most stable in the varying conditions that they will experience not only during return to Earth, but also during their curation. Such materials would be volcanic in nature, although sedimentary samples containing jarosite could also be included. The samples would need to be well documented on the surface but this does not mean that every piece of analytical equipment be taken to Mars in order to do this. Pictorial documentation, a Raman spectrometer, and an APXS should be sufficient. While this initial sample return would probably not address MEPAG Goals 1 and 2 (Is there life and Mars? and Past climate history, respectively), it will address Goal 3 – Determine the evolution of the surface and interior of Mars. It will do this without breaking the budget and will dramatically advance our understanding of Mars far beyond that of another orbiter or rover mission. If samples are returned to address MEPAG goals 1 and 2, but we do not have good environmental control on them, answers will not be definitive because of the changes that could have occurred to samples during the return to Earth.

**References.** [1] Jones J.H. & Treiman A.H., (1998), *Lunar & Planetary Info. Bull.* **85**. [2] Neal (2000) *JGR Planets* **105**, 22,487-22,506. [3] Alpers C.N. et al. (1992) *Chem. Geol.* **96**, 203-226. [4] Vaniman D.T. et al. (2004) *Nature* **431**, 663-665. [5] Chipera S.J. et al. (2005) *LPSC XXXVI*, #1497. [6] Chipera S.J. et al. (2005) *LPSC XXXVII*, #1457. [7] NRC (1997) *Mars Sample Return: Issues and Recommendations*, 47 p. National Academy Press; [8] Mars Expeditions Strategy planning Group (1996) *The Search for Evidence of Life on Mars*. <http://www.hq.nasa.gov/office/oss/mccleese.htm>, 8 p.; [9] Space Studies Board (1998) National Research Council, 100 p.; [10] Allen C. C. (1999) *JGR* **104**, 27,043-27,066. [11] Papike J.J. et al. (2006) *GCA* **70**, 1309-1321. [12] Vasconcelos P.M. et al. (1994) *GCA* **58**, 401-420.