CONSTRAINING OUR UNDERSTANDING OF THE ACTIONS AND EFFECTS OF MARTIAN VOLATILES THROUGH THE STUDY OF RETURNED SAMPLES. iMOST Team (T. D. Swindle¹, F. Altieri, H. Busemann, P. B. Niles, R. Shaheen, M. P. Zorzano, Y. Amelin, E. Ammannito, M. Anand, D. W. Beaty, L. G. Benning, J. L. Bishop, L. E. Borg, D. Boucher, J. R. Brucato, K. A. Campbell, B. L. Carrier, A. D. Czaja, V. Debaille, D. J. Des Marais, M. Dixon, B. L. Ehlmann, J. D. Farmer, D. C. Fernandez-Remolar, J. Fogarty, D. P. Glavin, Y. S. Goreva, M. M. Grady, L. J. Hallis, A. D. Harrington, E. M. Hausrath, C. D. K. Herd, B. Horgan, M. Humayun, T. Kleine, J. Kleinhenz, N. Mangold, R. Mackelprang, L. E. Mayhew, F. M. McCubbin, J. T. McCoy, S. M. McLennan, H. Y. McSween, D. E. Moser, F. Moynier, J. F. Mustard, G. G. Ori, F. Raulin, P. Rettberg, M. A. Rucker, N. Schmitz, E. Sefton-Nash, M. A. Sephton, D. L. Shuster, S. S. Siljestrom, C. L. Smith, J. A. Spry, A. Steele, I. L. ten Kate, N. J. Tosca, T. Usui, M. J. Van Kranendonk, M. Wadhwa, B. P. Weiss, S. C. Werner, F. Westall, R. M. Wheeler, J. Zipfel.) ¹Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721-0092 USA; tswindle@lpl.arizona.edu.

Introduction: Volatiles have clearly played a key role in the evolution of Mars' atmosphere, hydrosphere and geosphere, with effects ranging from the geomorphological evidence for outflow channels and valley networks early in Mars' history to formation of alteration products in rocks to the current seasonal changes in the polar caps. It is clear that the absolute and relative abundances of various volatiles have changed through time via volcanic degassing, atmospheric loss, and interactions with the crust.

In addition to studying the current Martian atmosphere and ancient trapped gasses in Martian sedimentary, igneous and impact samples, there is considerable knowledge to be gained by examining the compositions of sedimentary rocks, regolith and secondary minerals that are especially sensitive to climatic influences such as obliquity-driven changes. For example, results from the Curiosity rover indicate that it is possible to obtain high resolution chemostratigraphic climate records from rhythmically bedded sedimentary rocks using in situ measurements [1]. Analysis of selected returned samples from such in situ records would be extremely important in confirming and fully understanding such records. In addition, there is growing capability of applying a variety of radiometric techniques to dating of the time of sedimentation and obtaining such dates from climate-sensitive sedimentary sequences would greatly help to tie down the timescales of past climate changes.

This is a provisional report from the iMOST subteam on key samples needed to understand volatiles.

Volatiles subobjectives:

1) Determine the original source(s) of the planet's volatiles, and the initial isotopic compositions of the constituent gases in the atmosphere. Determining the original composition is complicated by the processes that occurred on the planet during its history, but there are some isotopes (such as the triple-isotope system of O in rocks and the lightest isotopes of Xe [2,3]) that are expected to change little, and be highly diagnostic of their origin.

2) Understand crustal-atmospheric interactions and feedbacks, especially for C, O, S, N, Cl, and H, in order to interpret present and past geochemical cycling on Mars. Although present conditions are much different than those earlier in Mars' history, many of the crustalatmospheric interactions are expected to be similar, so quantifying the current interactions will provide constraints on the past history of volatiles.

3) Quantify the history of the composition of the atmosphere, and the history of contributions from the interior (e.g. H, C, N, O, noble gases and radiogenic products). Changes in the Martian atmosphere with time are clearly coupled to changes in the Martian environment. Outgassing (most likely volcanic, but perhaps related to impact) is the primary source of volatiles for contributions to the atmosphere, and it should be possible to put constraints on the amount of outgassing by determining the history of the composition, elemental, molecular, and isotopic, of the Martian atmosphere trapped in rocks and secondary minerals.

4) Assess temporal variations in the composition of the present-day atmosphere. CO_2 , Ar, N_2 , O_2 , H_2O , CO, and other compounds have been measured in-situ to vary during the year [4,5,6]. It is unknown the amount, variability and role on heterogeneous catalytic reactions with the regolith of oxidizing volatiles such as H_2O_2 . Measure the oxidation capacity of the atmosphere by constraining the odd oxygen cycle (O_3 -O) using oxygen triple isotopes and determine the role of peroxy radicals in the removal of organic matter in the soil and regolith [7,8].

References: [1] Milliken R. E. et al. (2015) *LPS XLVI*, Abstract #2339. [2] Clayton R. N. (1993) *Annu. Rev. EPS*, 21, 115-149. [3] Pepin R. O. (2000) Space *Sci. Rev.*, 92, 371-395. [4] Trainer et al. (2016) *LPS XLVII*, Abstract #1739. [5] Encrenaz T. (2015) *A&A*, 578, A127. [6] Franz H. B. et al. (2015) *PSS*, 109-110, 154-158. [7] Shaheen et al., 2010, PNAS, 107(47), 20213-18, [8] Thiemens and Heidenreich III (1983) Science, 219:1073-1075.