**RB-SR GEOCHRONOLOGY BY LASER ABLATION OF NEUTRAL ATOMS BY MINIATURE MASS SPECTROMETRY ON SULFATE MINERALS: POSSIBLE APPLICATIONS FOR IN-SITU ANALYSIS ON MARS.**

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**Introduction**: The recent discovery of jarosite at the Meridiani Planum region of Mars suggests that aqueous solutions were once present on Mars. Absolute age dating of Martian jarosite would give further insight into Martian fluvial processes as well as aid in establishing future Martian landing sites for possible sample return missions. Absolute age dating of Martian surface processes will enhance our understanding of Martian geologic time scales as well as allow the calibration of relative dating techniques such as crater dating. Because sample return missions are unlikely in the near future, we propose an in-situ dating technique of jarosite using the JPL developed laser ablation electron impact ionization miniature-mass spectrometer (LA-EI-MMS). We suggest that the Rb-Sr isotope system may be the most amenable geochronometer that can be used for Martian rocks because other widely used systems such as Sm-Nd, Lu-Hf, U-Pb, or K-Ar systems will be exceedingly low in concentrations, require very high precision isotope ratio analysis, or significant sample manipulation to perform the analysis. In contrast, Sr concentrations in many rock forming minerals are high (>100ppm) and because of the wide range in Rb/Sr ratios and the relatively short decay of $^{87}$Rb (e.g., compared to $^{147}$Sm) there are wide ranges in $^{87}$Sr/$^{86}$Sr ratios which can produce meaningful isochrons or model ages if an $^{87}$Sr/$^{86}$Sr isotope ratio precision greater than ~0.02% can be produced [1].

**MMS Capabilities:** The miniature mass spectrometer (Figure 1) developed at the Jet Propulsion Laboratories is designed to be deployed on a lander style space craft and measure chemical as well as isotopic compositions of Martian samples. The MMS uses 3 to 5 W of power in operation and is ~1.5Kg including the housing, power supply, and pump. The mass spectral analysis is performed by the introduction of laser ablated neutral atoms into the electron impact ionization source of the MMS. The MMS with modified CCD detector array has a dynamic mass range of $10^5$, can simultaneously analyze a mass range of 2 to 250 and has a mass resolving power of 315. To evaluate the potential of the MMS to measure isotopic composition over the Sr mass range (84-88) independent of laser ablation processes, krypton was inlet into the MMS and analyzed. The $^{82}$Kr/$^{84}$Kr, $^{83}$Kr/$^{84}$Kr, and $^{86}$Kr/$^{84}$Kr ratios can be analyzed to a precision of 0.02% and the mass spectrum is shown in figure 2. The resolution of the MMS with modified CCD detector array is suitable for Rb-Sr mass analysis.

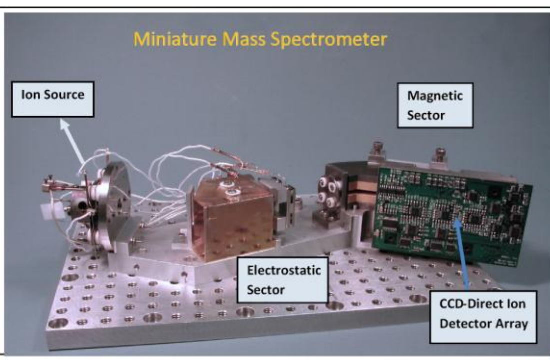


Figure 1: Photograph of Miniature Mass Spectrometer and modified CCD detector array

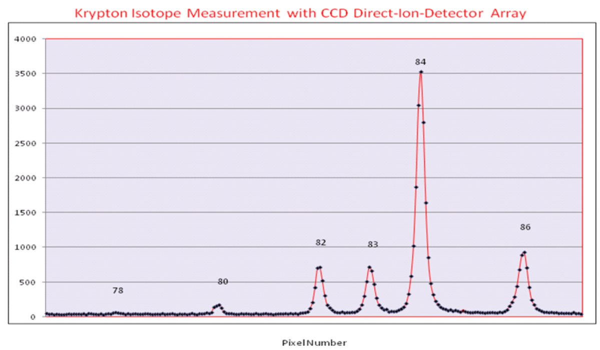


Figure 2: Mass spectrum of Krypton analyzed by the MMS

**Rb-Sr Jarosite Survey:** To further understand Martian jarosite and its potential as a geochronometer, terrestrial jarosite from various world wide localities have been analyzed for Rb-Sr isotopes by thermal ionization mass spectrometry (TIMS), and minor element chemistry by electron microprobe (EMP). This information is being used to evaluate the crystal chemical controls on the Rb/Sr ratio of jarosite [2, 3]. Analysis of samples revealed a large range of $^{87}$Rb/$^{86}$Sr ratios from 0.01 to 6.2 and Sr concentrations from 4 to 4000 ppm. Minor element analysis shows a possible relationship between P and Sr concentrations suggesting that the coupled charge substitution of $PO_4^{3-}$ for

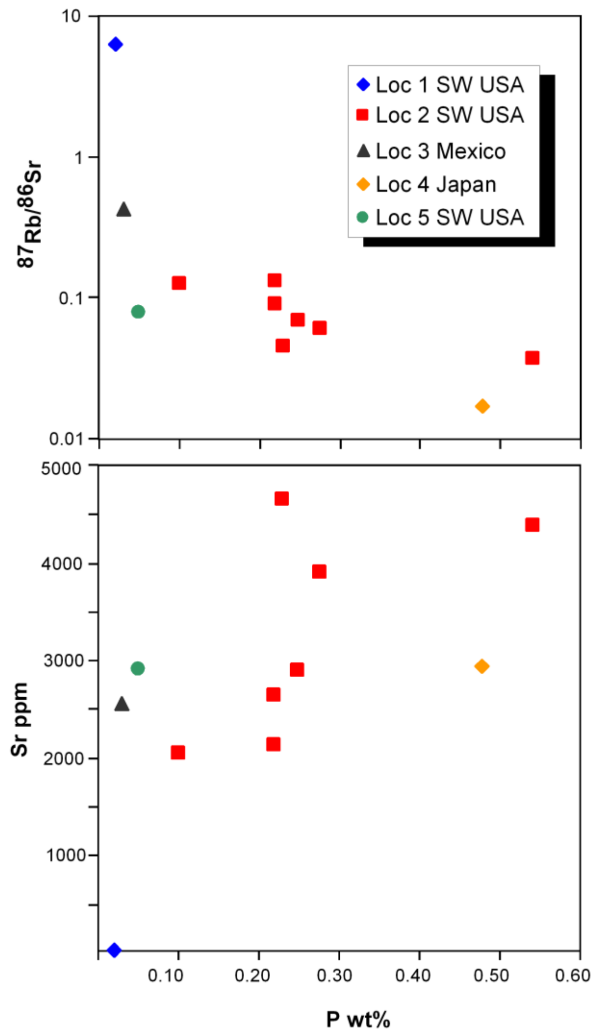


Figure 3: Plot of $^{87}Rb/^{86}Sr$ and Sr concentration determined by TIMS versus P concentration determined by EMP of jarosite minerals from worldwide localities. Each data point represents an individual sample from the color coated locality. Rb-Sr analyses are based on a bulk sample (20 milligrams) and P analyses are from the average of 10 or more EMP spot analyses. P contents for some samples are heterogenous at the micron scale by up to 0.1 wt% P.

$SO_4^{2-}$ and $Sr^{2+}$ for $K^+$ may control the Sr concentration in jarosite (Figure 3) [4]. The very high Rb/Sr ratio measured in P poor jarosite implies that it will be possible make robust model age determinations as shown in figure 4. For example, if we consider the possible Rb-Sr reservoirs on Mars, as inferred from SNC meteorites that have either very high or low Rb/Sr ratios; if the K-rich sulfate has a Rb/Sr ratio of ~2 the model ages will have a high precision (Figure 4). We note that in the case of old minerals the precision of the model age will be higher because the uncertainty of the $^{87}Sr/^{86}Sr$ of the reservoir will be smaller (Figure 4). Alternatively, it

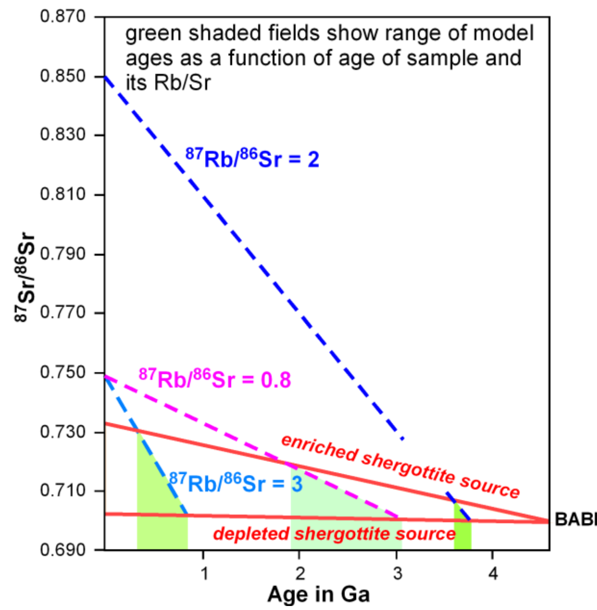


Figure 4: Plot of $^{87}Sr/^{86}Sr$ versus time of sulfates with different $^{87}Rb/^{86}Sr$ ratios. The intersection of these lines with possible Martian reservoirs defines the time that the minerals precipitated from aqueous solutions.

may be possible to constrain the initial $^{87}Sr/^{86}Sr$ of the reservoir by analysis of Ca or Mg sulfates which will have low Rb/Sr ratios. If the initial $^{87}Sr/^{86}Sr$ can be inferred the uncertainty in the possible source curves can be eliminated, which improves the precision of the model age.

**Future Work:** Our future work will include analyzing Sr isotopes in Sr rich minerals (celestite; $SrSO_4$ and strontianite; $SrCO_3$) and feldspars by laser ablation and standardizing these results relative to Rb-Sr analysis of these minerals via TIMS. An additional effort will be to fine tune the ability of the MMS to measure the major- and minor-element composition of minerals by using the 2-250amu mass range afforded by the modified CCD detector array. This capability will allow us to correlate spot Sr isotope analyses with bulk- or mineral chemical compositions. Additional work will include a continuation of the survey of Rb-Sr analyses on additional jarosite samples.

**References:** [1]Anderson et al. (2007) *LPS*, XXXVIII, 2153. [2]Leuth, V.W. et al. (2004) *Chemical Geology*, 215, 339-360. [3]Akai, J., et al. (1997), *30th International Geology Congress*, 9, 199-208. [4] Stoffregen, R.E. et al. (2000) *Sulfate Minerals, Reviews in Mineralogy and Geochemistry*, 40, 453-479.