

## CRITICAL ISSUES IN MARTIAN GEOCHEMISTRY INVOLVING MINOR AND TRACE ELEMENTS, AND THE APPLICABILITY OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS)

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**Introduction:** Mars missions to date have made almost no measurements of minor or trace elements. This will be true until 2007 with the exception of certain elements observable with the gamma-ray spectrometer on Odyssey, and elements such as S and Cl using x-ray spectrometry on MER and Beagle. Yet minor and trace elements hold important clues to understanding Mars' geochemistry. Laser-induced breakdown spectroscopy (LIBS) has been under development as a tool for rapid stand-off elemental composition measurements under both NASA in the US and CNES in France. Here we discuss a number of geochemistry issues for which minor and trace element detection are critical, and assess the applicability of LIBS to these issues.

**Some Critical Issues Affecting Minor and Trace Element Distributions:** *Source of sulfur-rich component in Mars dust:* The global martian dust appears to be a mixture of andesitic rocks as measured by Pathfinder APXS, basaltic rocks represented by the shergottites, and a third, salt-rich component. The source of this third component has been of great interest because of its geochemical significance. Hints of its composition come from the Viking X-ray fluorescence analyses [1], the Pathfinder APXS measurements [2], and Russian Phobos 2 gamma-ray detector [3]. Suggested origins of this salt component have included "acid-fog", or volcanic aerosol (VA) [4,5], hydrothermal fluids, or weathering of pre-existing ocean deposits [e.g. 6]. Typical terrestrial hydrothermal fluid systems consist of either the neutral-chloride (NC) type or the acid-sulfate (AS) type. NC systems occur at elevated temperatures in areas with abundant water, and produce chlorine enrichments, but low S/Cl ratios. AS systems involve condensation of subsurface vapor which enriches sulfur, but does not transport Cl to the surface, hence resulting in high S/Cl ratios. Newsom et al. [7] showed that a combination of NC and AS systems could account for the major elements found in the salt component, but due to the widespread variability of VA abundances in terrestrial systems, it is impossible to distinguish between hydrothermal (NC+AS) and VA systems based on major elements alone.

Minor and trace elements should distinguish between possible sources of the salt component of the

martian soil. In particular, lithium is significantly enriched in NC fluids relative to both AS and VA, with an expected abundance of ~100 ppm. On the other hand, volcanic aerosols are enriched in Ba, Br, Cd, Mo, W, and Zn relative to hydrothermal systems [7]. Ratios of these elements to lithium can clearly distinguish between the potential sources. Fig. 1 shows several predicted ratios for each of the three types of systems discussed above.

*Minor element correlations with oxygen fugacity in Martian rocks:* A recent study by Herd *et al.* [8] found correlations in martian meteorites between oxygen fugacity and trace element chemistry. This study, combined with earlier studies [9,10] on Rb-Sr and Nd-Sm systematics, strongly suggests that the crust-like reservoir is more oxidized, more LREE-enriched, and has heavier  $\delta^{18}\text{O}$  than the mantle-like reservoir. These correlations suggest that a wealth of information on the provenance of mars rocks is to be found in the mobile trace-element compositions.

*Other issues:* Certain minor or trace elements may prove essential as exobiology markers. A ubiquitous terrestrial example is the Mn coatings characteristic of terrestrial desert varnishes. Studies of Mn coatings on surfaces in terrestrial caves [e.g., 11] suggest that Mn may be useful as a potential biomarker in subsurface spaces on Mars as well.

Trace elements are also obvious distinguishers of sedimentary rocks in the absence of other distinguishing data.

**LIBS Overview:** The application of LIBS for planetary geochemistry has been discussed in numerous places over the past several years [12-18]. Very briefly, LIBS uses a pulsed laser beam to remotely analyze sample spots up to ~1 mm dia at distances up to ~20 m from the instrument by observing the characteristic spectral lines in the induced plasma "spark" to obtain elemental abundances. Advantages include very rapid, remote analysis, nearly complete elemental coverage, remote depth profiling capabilities, small analysis spot size and relatively low detection limits for most elements.

**LIBS Detection Limits** depend on instrumental characteristics, such as spectral resolution and optical

sensitivity, as well as on the composition of the sample. Samples with very high abundances of some transition elements (e.g., Fe, Mn, Ti) are likely to have reduced detection limits due to interferences from the numerous emission lines of these elements if the sample is observed with a relatively low-resolution instrument [e.g., 18]. For most samples a spectral resolution of  $\lambda/\Delta\lambda > 2500$  is sufficient. Table 1 gives rough LIBS detection limits for a number of minor and trace elements, assuming reasonable resolution, sensitivity, stand-off distances, and sample compositions [15].

Table 1 shows that LIBS detection limits are sufficient to address all of the issues mentioned above. In particular, the Ba/Li and Zn/Li ratios should be readily measurable in soils. For understanding the mobile-element and oxygen fugacity correlations, ratios such as Rb/Sr, Ba/Sr should prove very useful in cases where Rb is higher than in the shergottite basalts (e.g., if there is an analogue to terrestrial continental crust). LIBS also has sufficient detection limits for potential biomarkers such as Mn, which has been readily demonstrated by depth profiling through desert varnishes in field tests.

**Additional notes:** Minor and trace element detection, coupled with small analysis spot size, can prove far more useful than comparable detection limits in a larger-sample (e.g., whole-rock) analysis. For example, using LIBS it is possible to detect the presence of minor mineral phases such as zircons which may not be obvious from whole-rock analyses. In our 2001 field-work at the FIDO rover site [19], one analysis spot yielded a high Ba abundance, signaling the presence of a Ba-rich minor phase.

**References:** [1] Clark B.C. et al. (1976) *Science* 194, 1283-1288. [2] Rieder R.H. et al. (1997) *Science* 278, 1771-1774. [3] Trombka J.I. et al. (1992) *Proc. Lunar Planet Sci. XXII*, 23-29. [4] Banin A. et al. (1997) *JGR* 102, 13341-13356. [5] Clark B.C and Baird A.K. (1979) *GRL* 6, 811-814. [6] Forsythe R.D. and Zimbelman J.R. (1995) *JGR* 100, 5553-5563. [7] Newsom H.E. et al. (1999) *JGR* 104, 8717-8728. [8] Herd C.D.K. et al. (2001) *LPS XXXII*, 1150. [9] Shih C.-Y. et al. (1982) *GCA* 46, 2323-2344. [10] Jones J.H. (1986) *GCA* 50, 969-977. [11] Spilde M.N. et al. (2001) *LPS XXXII*, 1454. [12] Blacic J.D. et al. (1992) *Proc. Intl. Symp. On Spectral Sensing Res.*, 302-312, Maui, HI. [13] Wiens R.C. et al. (1998) *LPS XXXIX*, 1633. [14] Knight A.K. et al. (1999) *LPS XXX*, 1018. [15] Knight A.K. et al. (2000) *Appl. Spectrosc.* 54, 331. [16] Wiens R.C. et al. (2000) *LPS XXXI*, 1468. [17] Wiens R.C. et al. (2001) *LPS XXXII*, 1339. [18] Wiens R.C. et al. (2002) Combined remote mineralogical and elemental identification from rovers: Field and laboratory tests using reflectance and laser induced breakdown spectroscopy. *JGR-Planets*, in press. [19] Cremers D.A. et al. (2002) *LPS XXXIII* (this volume).

Li	3
Be	5
Cr	50
Ni	100
Cu	50
Zn	100
Ga	100
Rb	20
Sr	2
Ag	5
Cd	100
Sn	50
Cs	20
Ba	5
Pb	50

Table 1. Approximate detection limits, in ppm, for a number of minor and trace elements using LIBS.

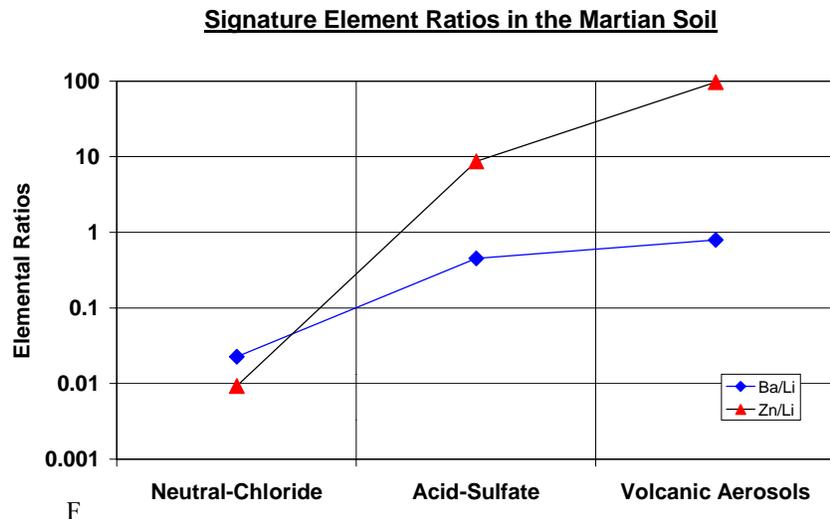


fig. 1. Predicted ratios for two types of hydrothermal fluids (neutral-chloride, and acid-sulfate) and for volcanic aerosols from data in Newsom et al. [7]. The volcanic aerosol data are limited to the Kudryavy, Merapi, and St. Augustine volcanoes.