

**LIMITS OF DETECTION FOR LIFE ON MARS: AN EXAMPLE USING IR SPECTROSCOPY OF SULFATE SALTS AND HALOPHILES FROM LAKES IN BRITISH COLUMBIA, CANADA.** B. C. Hyde, I. S. Foster, P. L. King, G. Southam and D. Nushaj, Department of Earth Sciences, The University of Western Ontario, London, Ontario, Canada.

**Introduction:** Recent investigations using the Mars Exploration Rovers [1, 2, 3] and OMEGA instrument aboard Mars Express [4, 5] have shown that sulfate minerals including Mg-sulfates are major contributors to martian mineralogy.

The southcentral region of British Columbia, Canada is host to a large number of evaporative salt lakes containing Mg-sulfate minerals [6]. These lakes offer a useful Mars analog site for sulfate formation because they are spring-fed, have low water volumes and many are fed by waters that interact with basaltic rocks. Also, these lakes can be used to examine halophilic organisms that flourish in this type of environment.

In this study we present mineralogical and biological data on two lakes and show infrared (IR) detection limits for halophiles in a salt matrix. The results of this study provide constraints on the minimum wt.% of organisms required to produce an IR signature for organic material on Mars.

**General Description of Lakes:** The lakes are predominantly spring fed by water that has traversed through basaltic rocks. The Basque Lakes, just south of the city of Ashcroft, are at least partially fed by a volcanic ash aquifer [7]. The lakes are composed of many separate brine pools all having their own subsurface spring (Fig. 1). Underlying and adjacent to each brine pool is a sequence of salt minerals that can be on the order of meters thick.



Figure 1. Brine pool at Basque No. 4. Photo width: 2m

**Lakes in this Study:** The two lakes studied here are part of the Basque Lakes: Basque No. 1 and Basque No. 4. The Basque Lakes all contain Mg-sulfate-rich brines (Table 1, [6, 7]). The mineral sequence just beneath the brine pools is primarily composed of an acicular epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) ( $\pm$  hexahydrite,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ; see below) layer at the surface followed by a mud layer and subsequent deposits of massive epsomite ( $\pm$  hexahydrite) at depth.

Lake Name	Molarity (M)			pH
	Mg	S	Na	
Basque 1	1.5904	0.9552	0.8076	8.31
Basque 4	1.3279	0.9235	1.0203	8.05

Table 1. Molarity of most abundant elements in brines (excluding  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  contributions) and pH.

At Basque No. 4, the natural biofilms were red colored suggesting that they contain photosynthetic halophiles (Archaea) [8].

At Basque No. 1, red crystals of epsomite were found in the subsurface deposit. This is possibly due to small amounts of red halophiles, similar to those found at Basque No. 4, entrained in the crystal structure. An attempt at culturing these organisms has not been carried out yet and the amount of any entrained organics appears to be too low to detect spectroscopically.

**Mineral Identification:** Care was taken to minimize changes in the hydration states of the minerals between sampling and analysis. During transport and storage, subsurface minerals were kept in their surrounding muds and surface minerals were kept moist in brine. The minerals were identified at the University of Western Ontario using X-Ray Diffraction (XRD). To prepare samples for XRD they were dried and powdered. The drying step was necessary to remove surface water and was performed directly before analysis, minimizing the amount of structural water loss. Previous work [9, 10] has shown that epsomite is the highest stable hydration state possible at the ambient sampling temperatures. Thus, any change in hydration state during analysis would produce a mineral with less than or equal to seven waters of hydration. Two of the samples analyzed were pure epsomite and five were epsomite with a small amount of hexahydrite. This suggests either an original composition of epsomite+hexahydrite, or pure epsomite that structurally dehydrated during sample preparation and/or analysis.

**Biological Culturing:** To examine halophiles in a salt matrix it was necessary to first enrich bacteria in a synthetic brine media. Inductively coupled plasma analysis provided the composition of the lake waters from which we produced a brine basal medium (BBM); the BBM was combined using the SMR2A method described by Shand [11] to enrich consortia of extremely halophilic Bacteria and Archaea from the

Basque lake samples. The samples were kept at room temperature, placed in sunlight, and allowed to grow for weeks to months depending on enrichment.

**Halophile Detection Limits:** IR emission spectroscopy has been used to identify martian minerals [e.g., 12]. The same instrumentation could be used to identify biologic signatures and in this study we examine biota in a salt matrix.

We used a Nicolet Nexus 670 FT-IR with a Pike Technologies Automated Diffuse Reflectance (DRIFTS) attachment to collect biconical reflectance IR data. To check the detection limit for halophiles in a salt matrix, we created mixtures of them with Mg-sulfate (epsomite  $\pm$  hexahydrite). A series of mixtures were made, with different ratios of halophiles to Mg-sulfate, to determine the concentration at which halophile spectral features were visible. Note that all spectra contain features due to atmospheric components.

The mixtures all contained 5 mg (dry wt.) of red halophiles. The Mg-sulfate amount was varied producing mixtures with 10, 15, 20, 25, 36 and 100 wt.% of halophiles. For DRIFTS analysis, 38 mg KBr was added to the mixtures to increase the reflected signal.

The Mg-sulfate (Fig. 2) and red halophiles (Fig. 3) both show molecular  $\text{H}_2\text{O}$  and  $\text{SO}_4^{2-}$  vibration features due to structural components in the salt and the halophile growth media. The red halophiles show distinct features at  $1443\text{ cm}^{-1}$  and  $1553\text{ cm}^{-1}$  (Fig.3) relative to pure Mg-sulfate (Fig. 2). The  $1553\text{ cm}^{-1}$  feature is likely due to C-N and N-H stretching vibrations [13]. The  $1443\text{ cm}^{-1}$  feature could be due to many bonds linked to the halophiles. These features were used to monitor the organics in the mixtures and are not affected by atmospheric components. Fingerprints are ruled out as a source of these features because they are dominated by C-H vibrations ( $\sim 2800\text{-}3000\text{ cm}^{-1}$ ).

A 25 wt.% halophile mixture shows the  $1443\text{ cm}^{-1}$  and  $1553\text{ cm}^{-1}$  features (Fig. 4) diagnostic of halophiles. The features weaken as dilution increases until they appear only as small distortions in the spectrum at 10 wt.% halophiles (Fig. 5). This places the lower limit of conclusive detection between 10 and 15 wt.%.

**Conclusions:** Detection of halophiles entrained in salts on Mars appears possible. If the organisms are similar to those here, the organic percentage must be high for positive identification using IR spectroscopy.

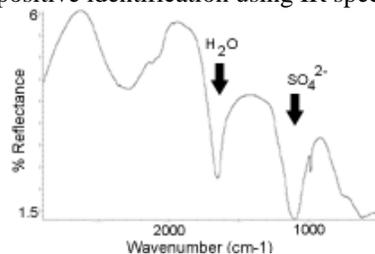


Figure 2. Pure Mg-sulfate.

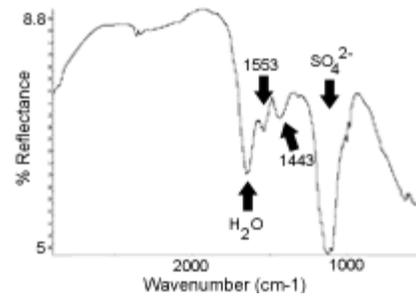


Figure 3. 100% red halophiles.

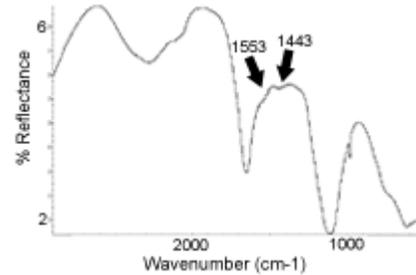


Figure 4. Mixture containing 25 wt.% red halophiles.

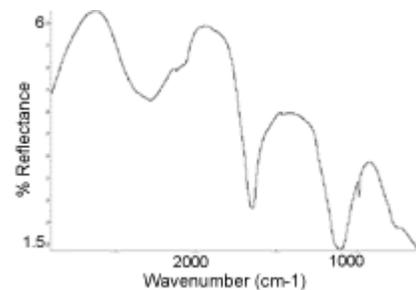


Figure 5. Mixture containing 10 wt.% red halophiles.

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**References:** [1] Rieder, R. et al. (2004) *Science*, 306, 1746-1749. [2] Squyres, S. W. et al. (2004) *Science*, 306, 1709-1714. [3] Squyres, S. W. et al. (2006) *JGR*, 111, 1-19. [4] Gendrin, A. et al. (2005) *Science*, 307, 1587-1591. [5] Langevin, Y. et al. (2005) *Science*, 307, 1584-1586. [6] Goudge, M. F. (1924) *Can. Dept. Mines No. 642*. [7] Nesbitt, H. W. (1990) *Fluid-Mineral Interactions*. Editors Spencer, R. J. and Chou, I-M, 355-371. [8] Dundas, I. D. and Larsen, H. (1962) *Archiv fur Mikrobiol.*, 44, 233-239. [9] Chou, I-M and Seal R. R. (2003) *Astrobio.*, 3, 619-630. [10] Peterson, R. C. (2006) *LPI Contrib. No. 1331*, 64. [11] Shand Lab (2006) <http://jan.ucc.nau.edu/~shand/protocol.htm>. [12] Christensen, P. R. et al. (2004) *Science*, 306, 1733-1739. [13] Marshal, C. P. et al. (2006) *Vibrational Spectroscopy*, 41, 182-189.