

**CHEMICAL EVIDENCE FOR SMECTITES AND ZEOLITES ON MARS: CRITERIA AND LIMITATIONS.**

B. C. Clark<sup>1</sup>, D. Ming<sup>2</sup>, D. Vaniman<sup>3</sup>, R. Wiens<sup>4</sup>, R. Gellert<sup>5</sup>, J. C. Bridges<sup>6</sup>, D. Morris<sup>2</sup>.  
<sup>1</sup>Space Science Institute (SSI), 4750 Walnut St., Boulder, CO 80401, [bclark@spacescience.org](mailto:bclark@spacescience.org); <sup>2</sup>NASA/JSC, Houston, TX; <sup>3</sup>PSI, Tucson, AZ; <sup>4</sup>LANL, Los Alamos, NM; <sup>5</sup>Univ. Guelph., Canada, <sup>6</sup>U. Leicester, UK.

**Introduction:** Aqueous alteration on Mars can produce a range of tell-tale secondary minerals [1]. Surface missions typically obtain detailed and highly localized element compositional information, but not always mineralogical information, whereas orbital missions deduce mineralogy from relatively high spatial resolution IR spectral mapping (decameters scale, for CRISM), but obtain element data only over much larger areas of martian terrain (~200 km). Surface missions have also discovered several occurrences of major geochemical alteration of igneous precursors, for many of which elemental composition is the only diagnostic information available. Many types of clays and zeolites have quasi-unique element profiles which may be used to implicate their presence. In some cases, one or more candidate minerals are sufficiently close in their component elements and their stoichiometry that ambiguity must remain, unless other constraints can be brought to bear. Geochemical characteristics of alteration products most likely on Mars can be compared to results from MER and MSL rover missions (e.g. Independence [4] and Esperance samples).

These considerations are needed for MER Opportunity rover now that Mini-TES is no longer operational. It also has importance for exploration by the MSL Curiosity rover because inferences and deductions available from ChemCam (CCAM) remote LIBS and/or in situ x-ray fluorescence (APXS) can be used as indicators for triage to select materials to sample for limited-resource instruments, SAM and Chemin.

**Identification Criteria:** Multiple criteria may be combined to pursue mineral identifications.

*Key Elements.* Many clay minerals, including the smectite montmorillonite, have key element profile signatures that are especially revealed by the Al/Si ratio. As shown in Table 1, the relative proportions of Al and Si for nominal stoichiometric compositions of the clay minerals produced by aqueous alteration can be significantly different from the nominal range of igneous minerals. This ratio is also particularly suited to x-ray fluorescence analysis (APXS) because the elements Al and Si are adjacent in the periodic table, and therefore their fluorescent x-rays are close in energy, minimizing certain potential matrix effects.

This should not be done without consideration of the other major elements in the sample, because there could be fortuitous combinations of minerals which on

the whole mimic the Al/Si ratio of an alteration product but are nonetheless igneous. In particular, the feldspars can combine to give net Al/Si ratios that cross the typical range for a given type of smectite. In addition, on Earth at least, soils can contain more than one type of clay mineral, sometimes in intimate combinations. For example, illite and kaolinite often associate with montmorillonite, thus altering the average Al/Si ratio. Illite contains a significant amount of potassium, whereas K is often low or virtually absent in many martian samples. Small amounts of kaolinites would be more difficult to detect.

Table 1. Example Al/Si Ratio's

Family	Sample	Al/Si (atom/atom)	Comments
<b>Basalts</b>			
	Adirondack	0.28	igneous
	Shergotites	0.16	igneous
<b>Smectites</b>			
	Montmorillonite	0.50	
	Nontronite	0.33	high Fe
	Saponite	0.33	high Mg
	Beidellite	0.71	high Al
	Griffithite	0.37	high Fe, Mg
<b>Other clay minerals</b>			
	Illite	0.37	high K
	Kaolinite/Halloysite	1.00	
	Hectorite	n/a	
	Palygorskite	0.13	high Mg
<b>Zeolites</b>			
	Natrolite	0.66	high Na
	Prehnite	0.66	high Ca
	Phillipsite	0.54	some Na, K, Ca
	Analcime	0.50	high Na
	Chabazite	0.50	significant Ca
	Stilbite	0.29	significant Ca
<b>Other alteration</b>			
	Allophane	1-1.53	
	Imogolite	2.00	
<b>Feldspars</b>			
	orthoclase	0.33	high K
	albite	0.33	high Na
	anorthite	1.00	high Ca

One method of taking into account all the major and minor elements is to construct models of overall composition based upon various sets of putative components [2]. Such analyses are greatly aided if there is a suite of measurements that encompasses a range of different proportions of the mineral constituents. Such results are often seen in CCAM LIBS analyses of multiple small spots across a specimen, and are even sometimes available if a series of APXS measurements can be taken at different locations on the same specimen. Observed trends in the data can be used to infer

which elements are associated with one another, and/or the degree to which they are not. This helps to identify the approximate abundances of constituents, reducing the range of plausible models.

Other methods can be graphical [3], considering various key elements or combinations thereof. Standard 2-D plots are often revealing. Ternary and even tetrahedral plots (4 apices) can be used to indicate whether a bulk composition is, within certain assumptions, indicative of alteration products enriched in Al beyond its igneous origins. To encompass even more elements, sums of elements or ratios can be used as plot parameters. One conventional plot is the A-CNK-MF ternary diagram, shown in Fig. 1. Here, points below the dotted line are indicative of feldspars, whereas points above the line could indicate excess Al. Montmorillonites and other alteration products plot above the dashed line. In this case, the deviation of points to the lower left is because of the presence of Ca-S rich veins, which drive the plot-points away from Mg, Fe and Al. Note that Si is not evaluated in this plot, except indirectly by difference.

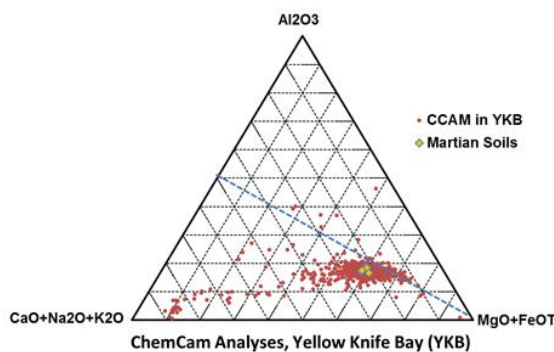


Fig. 1. Points above the line may indicate alteration. (molar concentrations)

**Trace Elements.** Because clays have affinities for soluble ions, with preferences depending on the cation and the specific mineral, they can take up or release various ions, depending on their concentration levels in solution and the strength of the affinities (the lyotropic series). The common exchangeable cations include  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Mg}^{2+}$ .  $\text{Ca}^{2+}$  also has strong affinity for ionic bonding, but may be less available in martian brines because of precipitation by abundant environmental sulfate. Many trace elements often are accentuated in alteration products relative to the igneous source material, including  $\text{Li}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ , as well as many transition metal elements. Other elements that may be present at enhanced levels include B, P, V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb and even rare earths. In addition, there is some capacity for

anion exchange, especially for  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ . When enriched over typical igneous abundances, these elements can provide additional evidence for alteration to clays and zeolites, as well as the previous presence of aqueous solutions to provide the medium for ion exchange [4].

**Practical Limitations:** Attention must be given to possible ambiguities and challenges in detections.

**Chemical Analogs.** Some minerals have element profiles that are not sufficiently different to implicate which member is present in the sample. For example, the zeolite known as phillipsite may mimic montmorillonite, in terms of Al, Si, and accessory elements, especially if there are additional components present. However, phillipsite typically has higher cation concentrations and forms best at higher pH.

**Mineral Mixtures** A practical limitation is that smectite may be a minor rather than major component of a rock or soil. Unless the other components can be conclusively identified, it may not be practical, within analytical uncertainties, to deduce the presence of clay or amorphous components.

**Other Alteration Phases:** Silica, in various forms, could be co-located with allophane, imogolite or other aluminous material to exhibit Al/Si in the range of 0.3 to 0.7, which encompasses many clays and zeolites.

**Quantity and Quality of Analyses:** Are there multiple analyses at diverse locations on the sample to seek trends? Are the error bars for the measurements too large for secure deconvolutions of components? These are the types of ancillary factors that must be considered when trying to predict mineralogical species from the chemical data alone.

**Conclusions:** Through a combination of element profile analyses, including tabulations, graphs and detailed modeling, it is possible in favorable cases to constrain and/or deduce mineralogical components adequate for inferring uniqueness of a sample as well as recognition of the signatures of aqueous alterations of various types [2-4]. Such analyses could be especially important for future rover analyses on Mt. Sharp and the rim of Endeavour crater.

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**References:** [1] Ming, D.W. et al. (2008) Chap. 23 in "The Martian Surface: Composition, Mineralogy, and Physical Properties", Ed by J. Bell III. [2] Clark, B.C. et al. (2005) *Earth Planet. Sci. Lett.*, 240, 73-94. [3] McLennan, S. M. et al. (2004) *Science*, DOI:10.1126/science.1244734. [4] Clark, B.C. et al. (2007) *J. Geophys. Res.*, 112, doi:10.1029/2006JE0