Seeking and Identifying Phyllosilicates on Mars – A simulation study,

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As a major mineral product of weathering and water-related alteration of igneous rocks, phyllosilicates are anticipated to occur widely on Mars. Water can gradually dissolve olivine, feldspar, and pyroxene, the major minerals of basalts and basaltic andesites. The less soluble products become clay minerals. Low T hydrothermal alteration can produce phyllosilicates such as serpentine, chlorite, and micaceous minerals. Weathering in an acid environment yields clay minerals such as kaolinite; weathering in alkaline environments forms montomorillonite [1]. No identifications of phyllosilicates were reported from the Mars Global Surveyor mission, perhaps because of the relatively low spatial resolution (~3x5km) of the TES instrument in orbit. Identification of these minerals may require on-surface observations, e.g., by the MER '03 or later missions.

Raman spectroscopy is a good method for on-surface mineral identification and characterization [2]. There are few reports in literature about Raman spectral features of phyllosilicates, however, mainly for two reasons. 1) Compared to silicates of other structural types (ortho-, chain-, and framework-silicates), phyllosilicates are more complex and structurally variable. The large, flexible sites in phyllosilicate structures permit frequent and irregular cation substitutions, complicating their mineral chemistry. 2) Naturally occurring phyllosilicates, especially clay minerals, are often extremely fine grained (grain size <10μm) and may occur as low density powders, which reduces the strength of Raman signal [3]. Also, many of them have high enough fluorescent backgrounds to reduce the Raman S/N. It appears, however, that much of the fluorescence of terrestrial clay minerals arises from organic residues incorporated during their formation or during sample preparation [2].

In this work, we report on a set of terrestrial ocean sediment samples (Fig.1) in which the Raman spectra of the phyllosilicates show little fluorescent background. These ocean sediments have been moderately metamorphosed; organic residues in the samples were transformed into disordered graphitic carbon (Fig. 2). Thus, high quality Raman spectra with low fluorescence backgrounds could be collected. Also, the samples were compacted, which further enhances the Raman signal strength. These samples show that phyllosilicates that no longer contain organic residues can yield definitive Raman spectra. Phyllosilicates on Mars may also be free of organic materials, and perhaps organic residues (if there were any!) would have been altered into graphitic carbon there, owing to the harsh environment (oxidizing atmosphere, temperature cycling, dryness, etc.).

Figure 1 shows a photo of part of a deep-ocean drilling core sample. Three core samples were examined: 801C-5R2-124, 801B-42R1-56, 801C-37R1-88. These samples represent variably altered alkalic and tholeiitic basalts (~170 Ma) from the Pigafetta Basin (tropical NW Pacific) recovered during the Ocean Drilling Program Legs 129 and 185 [4,5]. 801C-5R2-124 is a brecciated tholeiite basalt characterized by intense alteration. 801C-37R1-88 is less altered with secondary phases mainly residing in pore spaces and veins. 801B-42R1-56 is a moderately altered sample of alkali basalt with secondary minerals occurring as veins and replacing mesostasis and olivine phenocrysts.
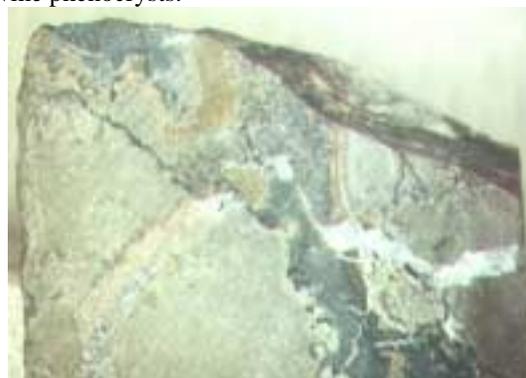

Figure 1. Part of 801C-5R2-124, a brecciated pillowrim.

Figure 2 shows typical Raman spectra of the phyllosilicates in these cores. In order to identify and characterize phyllosilicates, and to understand the geology behind them, we are developing a Raman spectral database of phyllosilicates. Although the standard Raman spectra of major type of phyllosilicates will be included, it is not reasonable to cover the entire range of compositions, especially those variations due to alteration. Instead, we seek to understand the structural and compositional information revealed in the spectra [6]. At this point in our study, we can generalize on interpretations of Raman spectral features of the major phyllosilicate structural types, and we can use this understanding to classify and in some cases to identify clay mineral samples. On the basis of the structural features that are the most useful from the spectroscopic point of view, we separate the major types of phyllosilicates in the following way: tri-octahedral phyllosilicates, in which bivalent cations (mainly Mg^{2+}, Fe^{2+}) occupy all of the octahedral sites; di-octahedral phyllosilicates in which only 2/3 of the octahedral sites are occupied by trivalent cations (mainly Al^{3+}). The differences in masses and electronegativities among these cations affect peak positions and relative peak intensities of $Si-O_{nb}$ and $Si-O_b-Si$ vibrational modes (O_{nb} = non-bridging oxygen, O_b = bridging oxygen) in

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Raman spectra. The major structure types of the basic layer units in these phyllosilicates are T-O, T-O-T, T-O-T – A, and T-O-T – O – T-O-T (T = tetrahedral layer, O = octahedral layer, A = interlayer large cation or water); these structures affect the Raman spectral patterns. Aluminum also enters the tetrahedral sites in many phyllosilicates. Li, K, Na, Ca, Mn, Ni, Ti, Ba, OH, and H_2O often substitute into the octahedral sites and interlayer spaces.
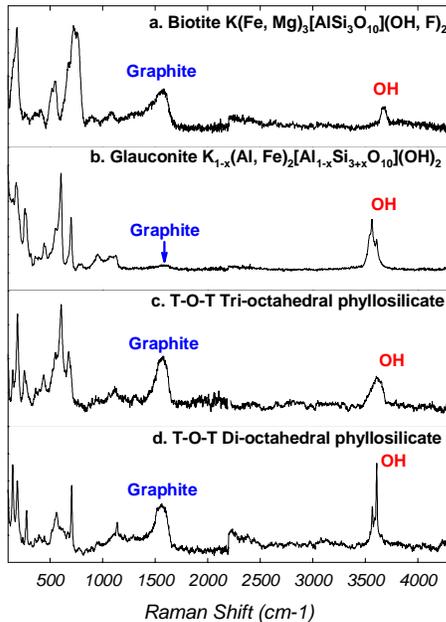

Figure 2. typical raman sp[ectra of phyllosilicate in ocean sediment sample.

In the Raman study of three deep-ocean drilling core samples, feldspar, pyroxene, were identified as the original igneous rock-forming minerals, although pyroxene is missing in one core and occurs sparsely in another. REE-apatite was present as igneous or altered. Calcite and ankerite occur in veins as products of hydrothermal alteration. Fe-oxides and Fe-hydroxides were identified in the veins mostly as hematite and goethite, with occasional magnetite. Graphitic carbon was found in every spectrum from the three cores and is presumed to be the residues of organic matter. All three polymorphs of TiO_2 (anatase, rutile, and brookite) were found, with anatase occurring more often.

Biotite, a T-O-T – A tri-octahedral phyllosilicate, was identified (Fig. 2a). The major phyllosilicate found in these samples, however, has the spectral pattern of an Fe-bearing T-O-T – A di-octahedral phyllosilicate (Fig. 2b). Compared to that of muscovite (not shown), the spectrum of this phyllosilicate has an additional doublet at 605 and 553 cm^{-1}, and a more distinctive multi-peak pattern in the OH stretching region that occurs at lower wavenumber than muscovite. This Raman spectrum matches the reference spectrum of glauconite, general formula $K_{1-x}(Al, Fe)_2[Al_{1-x}Si_{3+x}O_{10}](OH)_2$. Structurally, glauconite be-

longs to the muscovite subgroup, with Fe^{3+} replacing much of the Al^{3+} in the octahedral sites of muscovite, and some K^+ substituted by Na^+. The substitution of Al^{3+} by Fe^{3+} causes a downshift of the major Si-Ob-Si peak (from ~705 cm^{-1} of muscovite to 700 cm^{-1} of this sample), and the appearance of double peaks at 605 and 553 cm^{-1}. A peak at ~443 cm^{-1} suggests that part of Al^{3+} remains unsubstituted. The triplet in the OH stretching vibrational region suggests at least three possible types of cation occupancies around the OH site, e.g., Fe-Fe-Fe, Fe-Fe-Al, and Fe-Al-Al. Compared with the 3625 cm^{-1} OH peak of muscovite, the position at 3608 cm^{-1} of the highest frequency peak in the glauconite triplet suggests the absence (or extremely low probability) of Al-Al-Al occupancy, which is consistent with the high ratio of relative peak intensities of (605&553)-peak/443-peak. Glauconite is a common constituent of clastic sediment deposited under marine conditions [1].

Based on our general study of phyllosilicates [6], we can tentatively classify two unidentified phyllosilicates found in these cores. One is an Fe-bearing T-O-T – A tri-octahedral type (Fig. 2c). Based on its spectral pattern, it is neither chlorite nor saponite, which are common mineral products of hydrothermal alterations in marine environments. The major Raman peaks occur at about 677, 607, 554 cm^{-1} with variable peak patterns, often as a triplet. Fe-bearing hydrobiotite and vermiculite are possible candidates. These two minerals can form by hydrothermal alteration of biotite, which was detected in these samples (Fig.2a). Another unknown phase (Fig. 2d) is a T-O-T – A di-octahedral phyllosilicate with less Fe than glauconite. Part of its spectrum matches that of muscovite, but overall the spectrum does not match. In addition, the peak pattern in the OH stretching vibration region suggests more complicated cation occupancies around the OH site than found in muscovite, and different from that in glauconite. We tentatively assign this spectrum to illite, a hydration product of muscovite, although no muscovite was found in those cores.

In summary, the ocean sediments provide high quality Raman spectra of clay minerals, and appear to be a good simulation for planetary application. We are working toward a more refined classification and identification of these phyllosilicates.

References: [1] Grim, *Clay Mineralogy*, 2nd ed. 1968; [2] Wang et al. *JGR*, V104, p.8509, 1999; [3] Wang, #1644, LPSc XXX, 1999; [4] Lancelot et al., Proc. ODP, Init. Repts., 1990; [5] Plank et al., Proc. ODP, Init. Repts., 185, 2000; [6] Wang et al., this volume, 2002;