RELEVANCE TO MARS OF CATION EXCHANGE BETWEEN NONTRONITE AND Mg-SULFATE BRINE.

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Introduction: Much current interpretation of martian phyllosilicate and sulfate minerals focuses on separation of the two, as distinct assemblages marking a transition in time from an earlier wet, phyllosilicate-forming environment to a later, acidic and relatively water-poor evaporitic system dominated by sulfate deposition [1]. In a broad sense, this epochal transition appears valid, but in detail there is evidence that phyllosilicate and evaporite systems intermeshed [2]. In terrestrial evaporite systems, associated clay minerals are common and provide significant information on evaporate origin and evolution. Most evaporative basins have some terrigenous component as products of sedimentary transport or eolian input. Evaporite salt assemblages may also acquire phyllosilicates through fluid reaction with aluminosilicate detritus, often involving Mg-rich brines as expected on Mars and leading to varied clay mineral associations including not just smectites but illite, kaolinite, corrensite (mixed-layer chlorite-smectite), and chlorite.

In addition to possible transitions in clay mineralogy via brine interaction, brines contain high concentrations of cations in solution that may exchange with interlayer cations in smectites. This mode of interaction is often rapid and has much lower energetic barriers than transformations that affect octahedral and tetrahedral sites in clay minerals. Cation exchange is likely to be far more prevalent than recrystallization in clay minerals on Mars. This may especially be the case where clay minerals that formed in an earlier and wetter environment were subsequently exposed to brines as the global environment became drier. The widespread distribution of Mg-sulfates on Mars indicates that brines with significant concentrations of $MgSO_4$ in solution may be implicated. A range of clay mineral compositions has been identified on Mars, many of which are Fe-rich, such as nontronite. To better understand cation-exchange effects between Mg-sulfate solutions and nontronite, we purified a sample of the Clay Minerals Society source Australian nontronite NAu-1 to remove minor amounts of quartz. The purified NAu-1 was then exposed to $MgSO_4$ solutions and both solid and solution products were studied to determine the nature of interaction, including cation exchange.

Methods: A sample of nontronite NAu-1 was pulverized in a W-carbide mortar and disaggregated in deionized water with a sonic probe. Sequential settling in deionized water was used to separate size fractions, followed by centrifugation in two stages (5,000 rpm for 5 minutes and 8,000 rpm for 40 minutes; ref. [3]). The last and finest fraction produced the purest nontronite and was used for brine exposure experiments.

Brines with molalities of 0.05, 0.5, and 1.0 were prepared by dissolving ultrapure $MgSO_4$ reagent in deionized water. Brines of the three molalities were sealed in Teflon containers with splits of the purified nontronite in a brine:nontronite weight ratio of 10 g brine to 1 g nontronite. The containers were agitated at room temperature (293 K) for 19 days on an arm shaker. The clay mineral fraction was then segregated from the brine by centrifuging twice at 8,000 rpm for 60 minutes, first to collect the reacted brine (solution S1) and then after sonic probe dispersal of the sedimented solids in 110 g of deionized (DI) water to collect the residual salt (solution S2). The S1 and S2 solutions were both analyzed for cations in solution.

Collected clay mineral sediments were dried and analyzed by X-ray diffraction (XRD), using a Siemens D500 diffractometer. Analysis was conducted on bulk samples and on oriented mounts (including glycolation and analysis after heat treatment at 450 °C). In addition, XRD analysis of salts prepared from dried portions of solutions S1 and S2 confirmed the nature of salt phases formed. Solution compositions were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (using a PE-SCIEX ELAN 6100), inductively coupled plasma-optical emission spectroscopy (ICP-OES) (using a Perkin-Elmer Optima 2100DV), and ion chromatography (IC) (Dionex-Summit). Cation data are discussed in this abstract.

Results: XRD analyses of nontronite starting material and of the nontronite products after Mg-sulfate brine exposure indicate little difference in crystal structure, other than a decrease by ~4% in interlayer spacing (decrease in 001 spacing from 14.7 Å to 14.1 Å; Fig. 1). This shift is attributable to smaller Mg hydrated species exchanged for larger Ca hydrated species in the nontronite interlayers, based on observation of Ca released from nontronite into the brine solutions.

Both unexposed nontronite and brine-exposed nontronites expanded to an 001 spacing of 16.9 Å on glycolation. Analysis of S1 and S2 solutions showed significant release of interlayer Ca into the brine (unreacted NAu-1 nontronite contains ~3.4 wt% CaO [4] in interlayer sites available for exchange with Mg).

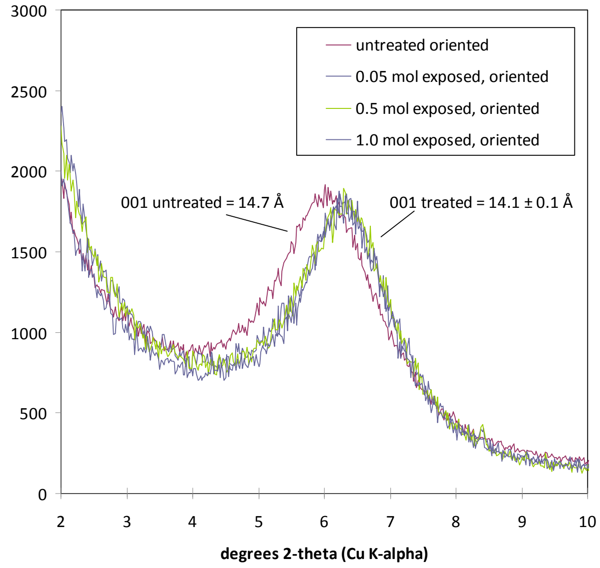

Figure 1: XRD analysis of nontronites, showing 001 diffraction peak. Samples were oriented on an off-axis-cut, zero-background quartz plate.

Cation contents of solutions S1 and S2 for each of the three brine molalites are summarized in Table 1. As noted above, the primary consequence of $MgSO_4$ brine exposure was release of interlayer Ca from nontronite to solution (accompanied by exchange for Mg from solution). Exchange was most complete at the two higher brine molalities, where total amounts of 10.28 to 11.95 mg of Ca were released to solutions S1 plus S2. This amount of Ca accounts for ~50% of available interlayer Ca in NAu-1 [4]. At the lowest brine molality (0.05) only ~25% of interlayer Ca was exchanged. Less Na and K (minor interlayer cations in NAu-1) were lost to solution. Some Si (1.009 to 1.325 mg) was also lost to solution at all brine molalities; it is uncertain whether the Si is from nontronite tetrahedral sites or from colloidal or dissolved silica (quartz is an impurity in NAu-1). Detectable Al and Fe at the lowest brine concentration suggests that minor amounts of cations from octahedral and tetrahedral sites may be released in more dilute brines (note also that significantly more Si was released to the DI wash, S2, than to the concentrated brines, S1). The Al and Fe found in the most dilute brine could be attributed to greater clay particle dispersion (higher effective surface area for dissolution), as smectite particles will aggregate at high brine concentrations [5]. Some of the Si, Al, and Fe detected in the least concentrated brine might represent colloidal nontronite.

Table 1: Cation Abundances (mg) in Solutions S1 and S2 After Treating 1 g Samples of Nontronite NAu-1with $MgSO_4$ Brines of Three Different Molalities (0.05, 0.5, 1.0)

mol.	sol.	Si	Al	Fe	Ca	Na	K
0.05	S1	0.158	0.007	0.024	3.64	0.580	0.187
0.05	S2	1.167	0.001	0.008	1.71	0.434	0.342
0.05	total	1.325	0.008	0.032	5.35	1.014	0.529
0.5	S1	0.189	-	-	3.34	0.572	0.336
0.5	S2	1.126	-	-	6.94	0.285	0.537
0.5	total	1.315	-	-	10.28	0.857	0.873
1.0	S1	0.130	-	-	3.29	0.661	0.526
1.0	S2	0.879	-	-	8.66	0.192	0.566
1.0	total	1.009	-	-	11.95	0.853	1.092

mol. = molality; sol. = solution (S1 = brine after exposure, S2 = subsequent wash of solids with deionized water)

Discussion: With these experiments we have begun to constrain products of smectite interaction with brine composed of a salt component widely distributed on Mars. Results show that in $MgSO_4$ brines at moderate temperature (293 K), brine interaction with nontronite is largely limited to cation exchange. No evidence of newly formed Mg-chloritic interstratification was observed. However, extensive exchange of interlayer Ca for Mg from solution was confirmed. Evaporation of the brine after exchange produced gypsum as well as Mg-sulfates. This supports results reported in [6], where Mg-sulfate brines were reacted with zeolites, various smectites, and palagonite JSC-1. In those experiments (with evaporation at ~Mars P_{H_2O}) release of Ca to the brine was only a trace effect with zeolites, minor with palagonite, but very significant with all smectites. The relative facility of cation exchange with smectites compared to other potential cation sources when exposed to Mg-rich brines indicates that brine evolution on Mars can be greatly influenced by clay minerals. This in turn suggests that analyses of clay minerals from martian sediments might constrain the extent of sediment interaction with such brines, using interlayer Mg content as a measure of interaction.

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References: [1] Bibring J.-P. et al. (2006) *Science* 312, 400-404, [2] Milliken R.E. et al. (2010) *Geophys. Res. Lett.* 37, doi:10.1029/2009GL041870. [3] Chipera S.J. et al. (1993), *MSA Rev. Min.* 28, 235-249, [4] Keeling J.L. et al. (2000) *Clays and Clay Min.* 48, 537-548. [5] Hoffman H. et al. (2004) *Clays and Clay Min.* 52, 14-24. [6] Vaniman D.T. and Chipera S.J. (2006) *Amer. Min.* 91, 1628-1642.