SALT-HYDRATE STABILITIES AND MARS SAMPLE RETURN MISSIONS. D. T. Vaniman[1], D. L. Bish[2], and S. J. Chipera[3], [1]Group EES-6, MS D462, Los Alamos National Laboratory, Los Alamos, NM 87545 (vaniman@lanl.gov), [2]Department of Geological Sciences, Indiana University, 1001 E 10th St., Bloomington, IN 47405, [3]Chesapeake Energy Corp., 6100 N. Western Ave., Oklahoma City, OK 73118.

Salts on Mars: Early evidence from Viking for salts on Mars [1] has been reinforced by subsequent orbital [2] and landed [3] missions. Clark [4] first laid out the role of hygroscopic salts in martian hydrogeology. Salt hydrates on Mars can include structural OH (e.g., K-jarosite $KFe^{3+}_3(OH)_6(SO_4)_2$ with OH at corners shared between FeO_6 octahedra), structural H_2O (e.g., hexahydrite $MgSO_4 \cdot 6H_2O$ with H_2O oxygens in octahedral coordination with Mg), and H_2O in independent sites (e.g., epsomite $MgSO_4 \cdot 7H_2O$ with the 7th H_2O extrapolyhedral). In general, only salt hydrates with H_2O in independent sites may dehydrate and rehydrate reversibly. The other structures are usually destroyed by dehydration, with loss of mineral information concerning formation environment and with release of H_2O that may react with other phases, possibly condensing on and dissolving soluble constituents. Recent work on several sulfate hydrates is summarized here.

Ca-sulfates. $CaSO_4 \cdot nH_2O$ occurs as gypsum (n=2) anhydrite (n=0), and bassanite ($n \cong 0.5$). Gypsum has H_2O molecules in 25% of the apices of 8-fold polyhedra containing Ca, the other 75% shared by oxygens of SO_4 tetrahedra. Bassanite, in contrast, has chains of SO_4 tetrahedra around channels containing H_2O. With slow dehydration of bassanite, H_2O can be removed almost entirely, producing "soluble" anhydrite. Aggressive complete dehydration with heating produces "insoluble" anhydrite with Ca-SO_4-Ca chains in an orthorhombic structure. All three Ca-sulfate forms might occur on Mars. Gypsum and insoluble anhydrite should be stable under most conditions of collection and sample return; in the presence of H_2O ice, bassanite can regain water and may fully rehydrate to gypsum but the process is slow (e.g., $\sim 10^3$ hours at -2 °C).

Mg-sulfates. The Mg-sulfate system has highly variable values of n in the formula $MgSO_4 \cdot nH_2O$, with common values of 7 (epsomite), 6 (hexahydrite), and 1 (kieserite). Chipera and Vaniman [5] point out the propensity for multiple metastable forms under dehydration. In addition, at low pH_2O, amorphous forms appear with low values of n dependent at least in part on temperature of dehydration [6].

Recent work in the Mg-sulfate system has led to the recognition that a phase long suspected to have 12 waters of hydration is in fact an 11-hydrate [7]; discovery of this phase on Earth and suggestions that it may occur in cold, icy environments on Mars are re-flected in the new mineral name "meridianiite" [8]. This new mineral has SO_4 tetrahedra and Mg in octahedral coordination with H_2O oxygens, between sheets of H_2O, and it can not survive above 275 K. Clearly, only a very ambitious refrigerated sample system could return such a sample to Earth. A mission to return such material would probably be a component of one designed to collect and return H_2O ice, not likely in the near term.

Fe-sulfates. Acid systems on Mars can produce ferric sulfate salts [9]. Jarosite is the only confirmed Fe-sulfate mineral on Mars, determined by Mössbauer. Jarosite is quite resilient because of the lack of H_2O molecules and strong linkage by OH of corner-sharing octahedra. Other Fe-sulfates are not so durable [10]. Coquimbite ($Fe_2(SO_4)_3 \cdot 9H_2O$) has independent H_2O and dehydration on heating to 30 °C produces an amorphous product that does not rehydrate. Kornelite ($Fe_2(SO_4)_3 \cdot 7H_2O$) behaves similarly. Botryogen ($MgFe(SO_4)_2(OH) \cdot 7H_2O$) becomes amorphous at comparably low temperatures and also will not reversibly rehydrate, but changes into a solid crust. Even modest heating of these H_2O-bearing ferric sulfates can be destructive, and degradation products can produce both cemented solids and viscous liquids [11].

Mixed-cation sulfates. Experiments [12] with the mixed-cation sulfates blödite ($Na_2Mg(SO_4)_2 \cdot 4H_2O$), kainite ($MgSO_4 \cdot KCl \cdot 2.75H_2O$), and polyhalite ($K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$) show that all are likely stable at Mars surface conditions. The least stable is kainite, which above ~60 ºC at low pH_2O may form a yet uncharacterized phase [12]. These three mixed-cation salts should be stable under conditions of sample collection and return if maintained at ≤50 ºC.

Other salts. Sulfate salts dominate in both orbital and surface data from Mars. However, APXS data leave little doubt that halides are also present. Chloride hydrates could include antarcticite ($CaCl_2 \cdot 6H_2O$), bischofite ($MgCl_2 \cdot 6H_2O$) [see ref. 13], and tachyhydrite ($CaMg_2Cl_6 \cdot 12H_2O$). Thus the sulfates described above only hint at the salt hydrate complexity that may be present on Mars.

Case Histories of Stability Problems in Extraterrestrial Samples: Lunar and meteorite samples have been subject to concern over which features are native and which may be products of terrestrial alteration. This is particularly the case for meteorite finds where the sample is known to have been subjected to

terrestrial weathering, but even strict sample collection, transmittal, and storage protocols can lead to alteration.

Lunar experience. Goethite (FeO(OH)) "rust" observed in Apollo 16 rocks stimulated great interest but was eventually found to have formed by hydration-oxidation of lawrencite ($FeCl_2$) after collection [14]. This is but one example of problems unstable salts can cause. Such problems may be exacerbated if samples from different depths, or collected at different seasons, are stored together. For hydrous silicates (e.g., smectites) water release may be nondestructive, but salts can dissolve or alter with exchange of very little water.

Meteorite experience. Epsomite is observed as a hydrous phase in primitive CI1 chondrites and has been cited as evidence of late-stage oxidation of the CI1 parent body [15]. However, there is strong evidence that epsomite formed in these meteorites after they were placed in humid terrestrial museums [16].

Implications for Mars sample return: Many salt hydrates might not be returned to Earth unmodified unless efforts are made to preserve Mars conditions of temperature and pH_2O [17]. Freezing samples from point of collection to processing for analysis on Earth would help maintain unstable hydrates but would be difficult, costly, and not foolproof – exchange of H_2O vapor between samples may still occur. Some samples collected at equatorial to mid latitudes may be desiccated and for these samples exceptional preservation may be unnecessary. Much is uncertain and a sequential approach to sample return is warranted.

Start easy, with equatorial sample return. Shallow regolith and rock surfaces from equatorial regions are likely to be desiccated, for mineral water loss under summer midday temperatures is more effective and rapid than rehydration at nighttime or winter conditions when frost is present. Sample return from higher latitudes where ground ice is present will not only present challenges with possible unstable salt hydrates but also with rover or lander operations at very cold temperatures, as well as the logistics of landing and departure at high latitude.

Analyze in situ. Sample analysis *in situ* will provide baseline determination of mineralogy, composition, and fabric against which later observations on Earth can be compared. This is recognized by MEPAG [18] in recommendations allowing for a sample analysis system of ~50 kg on the lander or rover. Active analysis systems have their own challenges and the analytical tools should avoid or minimize heating samples above maximum site temperature.

Plan ahead for on-planet sample holding. Temperatures on the lander or rover may affect salt hydrate preservation. For example, the heat of an equatorial summer plus heat produced by the RTG on the 2009 MSL rover can raise the sample cache to 50 °C. Insulation or shading of the sample container might prevent temperature from rising so high, but thermal design constraints and consequences need careful evaluation.

Store separately. Samples collected at summer from an exposed rock surface may, if contained with samples collected from frost-coated regolith at winter, undergo H_2O vapor exchange with deleterious effects (*e.g.*, loss of interlayer H_2O from smectite leading to chloride salt deliquescence). Separate containerization of each collected sample can minimize such effects.

Chill while in transit. Current sample return considerations do not anticipate active refrigeration on the return spacecraft, with an upper temperature constraint of 50 °C [18]. Design to keep temperature as low as possible should be considered, and active refrigeration should be evaluated in trade studies.

Process in an appropriate environment. Avoidance of elevated temperature as samples are processed, allocated, and analyzed will be important for at least some splits of the returned material. It may sufficient to first examine a chilled split for physical alteration (deliquescence, solution, etc.) and get a baseline as-received mineral analysis before other splits are processed and allocated.

Analyze with vigilance. Analytical results that produce unexpected evidence of H_2O exchange between minerals, suspicious mineral morphologies, and dissolution/precipitation features should be scrutinized to determine whether such features may be artifacts.

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