CHEMICAL MODELS OF SALTS IN THE MARTIAN REGOLITH  A. H. Treiman, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058. (treiman@lpi.jsc.nasa.gov).

The martian regolith is rich in ionic salts, which affect its chemical and physical properties, and will affect its resource potential and toxicity. Sulphate, halide, and carbonate salts are expected from theory, chemical analyses, and martian meteorites. A new inference here is that chromate salts may be present and abundant in the regolith. The origin of these salts is not known; they have been ascribed to hydrothermal action, meteoritic contributions, and volcanic aerosols/gases. Low temperature alteration (diagenesis) is a potentially important contributor to regolith salts.

Introduction: Ionic salt minerals in the martian regolith are important tracers of global and local chemical processes on Mars, appear to be important in setting the physical properties (i.e. trafficability) of the martian surface, will likely be important resources for human exploitation, and could possibly present hazards to human health. MECA and other instruments on the MARS 2001 lander are designed to investigate the regolith, so it is appropriate to examine the current knowledge of likely salt mineral in the martian regolith.

Earlier Results: Current understanding of salt minerals at/near Mars surface comes from geochemical theory, and data from telescopic, orbital, and landed instruments (e.g., [1-3]). Lander data provide the strongest evidence for salts. The Viking XRF (VXRF) experiments found that the regolith is rich in Cl and S, and that duricrust is richer – SO3 to 9.2%wt, and Cl to 0.7%wt [1]. Mars Pathfinder APX (MPAPX) analyses confirmed these enrichments and showed that they did not derive from local rocks [3,4].

The abundance of S and its enrichment in duricrust suggested that the regolith contains soluble sulfate salts, probably of Mg (e.g. kieserite) or Na and Mg (e.g. loeweite) [1]. Definitive spectroscopic signatures of sulfate have not been found [2,5].

Halide salts are also likely. VXRF and MPAPX all found regolith with 0.5-0.7%wt Cl. A likely host mineral is halite, NaCl [1], and the correlation of Mg and Cl in VXRF analyses suggests the presence of a magnesium-bearing chloride [6]. Bromine was detected in a few VXRF analyses, suggesting widespread enrichment in halogens.

Carbonates, especially of Ca, Mg, and Fe, have been suggested on theoretical grounds, but direct evidence is limited. Viking GCMS data are consistent with up to ~10% Ca-Mg-Fe carbonate minerals in the regolith, but LR data seem inconsistent with more than 1% Ca-Mg carbonates; the remainder could be (Ca-) Fe carbonate [2]. MPAPX data limit the abundance of carbon in regolith to < 0.5% atom [7,8]. Spectroscopic evidence for carbonates is limited and ambiguous [2].

Chromium salts have never been considered but appear in geochemical models (see below) and are hinted at in MPAPX data. Published MPAPX spectra of soils show a strong CrKα peak, while comparable rocks lack such a peak [7]; unpublished spectra in a poster gave ~0.06% Cr2O3 for rocks and ~0.35% Cr2O3 for soil [9]. Unfortunately, VXRF data did not yield Cr abundances, and MPAPX analyses are still being calibrated [7,8]. As noted below, a martian chromate mineral has been found in a martian meteorite [10,11].

Martian Meteorites: The martian meteorites all contain salt minerals (or remnants of them) that have been attributed to martian weathering or hydrothermal activity [12]. Most abundant are carbonate minerals, especially of Mg-Fe ALH84001 [13] and Fe in the nakhlites [14]. Ca- and Mg- carbonates and sulphates are also present in the nakhlites and the shergottites [10-15]. Meteorite EETA79001 contains a complex suite of salt minerals, including carbonates, sulphates, a lead chromate-sulphate [10,11], and an Mg phosphate [12]. Halite of preterrestrial origin is present in the nakhlites [14], and is probably present in the other martian meteorites. These salts commonly occur with other signs of low-temperature aqueous activity: clays, ferrihydrite, and/or marcasite or pyrite.

Source of Salts: From the high abundances of S and Cl (and Br) at the Viking 1, Viking 2, and Mars Pathfinder landing sites, its seems reasonable that salt components have been added to the regolith on a global (or northern hemisphere) scale. But the sources of salt-forming elements are not clear. Several models have been proposed, and each has implications for the abundances of water in the regolith and for enrichments of specific trace elements in the regolith. Lacking analyses of water and trace element abundances in the regolith, it is difficult now to reject or confirm the influence of any of these mechanisms.

Volcanic Emanations. It was suggested early on that the excess S and Cl in the regolith might derive from volcanic gases and aerosols [16], and this idea found support in the similarity between the composition of the Shergotty martian meteorite and that of the regolith minus S and Cl [17]. This concept has seen a
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On Earth, low-temperature reaction of igneous rock with water tends to produce Mg-SO₄-Na-Cl brines, from which Mg and Na sulfate minerals can precipitate (e.g., [25]). Under oxidizing conditions on Mars (buffered by 6 mbar CO₂), water equilibrated with Shergotty composition rock would also be a sulfate brine (vis. [26]); on evaporation, it would precipitate NaCl and Mg and Na sulfates (epsonite, MgSO₄•7H₂O; mirabilite, Na₂SO₄•10H₂O). Near the martian surface, these would dehydrate to kieserite MgSO₄•H₂O, and possibly thenardite, Na₂SO₄ (Figure 1). Thorium is immobile in these fluids (except as colloids [27]). If chromite does not alter, significant Pb can be transported. If chromite does alter, most of the Pb is immobilized as crocoite PbCrO₄.

If reaction is isolated from Mars' atmosphere, the system becomes highly reducing (H₂~15 bars) and Mg remains in silicate minerals, leaving an alkaline Na-Ca-OH-Cl brine (e.g., [28]). On exposure to atmospheric CO₂ and evaporation, it will produce calcite, silica, and eventually replace the calcite with alkali-bearing carbonates (e.g., gaylussite, Na₂Ca(CO₃)₂•5H₂O). The original reduced, alkaline brines cannot carry significant Cr, Pb, or Th.

Conclusions: With available data, the source(s) of the salt minerals in the martian regolith cannot be defined. The regolith contains chondritic material, but the bulk of regolith salts are likely indigenous, martian. Newsom and Hagerty [17] compiled data on fluid compositions in terrestrial alteration regimes, and their list of critical elements forms a starting point for interpretation of MECA chemical analyses. However, volcanoes on Earth and Mars may produce gases of different compositions, in part because martian basalts...
are significantly drier than terrestrial. Similarly, hydrothermal systems on Mars may not carry the same solutes as Earth systems because their source rocks may be different. The putative Th content of the martian regolith [19] is an embarrassment for most models. The excess abundance of Cr in martian regolith is unexpected, and could be reflect the presence of chromate salts.

Low-temperature alteration and weathering of local rock is an unappreciated potential contributor to regolith salts, and should be explored in more detail. In particular, it will be informative to compare trace element abundances of Mg-Na-SO4-Cl brines developed from igneous rocks with those of the source rocks.