BAD WATER: ORIGIN OF PHOENICOCHROITE-LANARKITE SOLID SOLUTION, $PB_2O(CRO_4,SO_4)$, IN MARTIAN METEORITE EETA79001.

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In martian meteorite EETA79001, Gooding & Muenow [1] found a secondary mineral grain with elemental abundances Pb:Cr:S ~ 6:2:1. These ratios are consistent with solid solution between phoenicochroite, $Pb_2O(CrO_4)$, and lanarkite, $Pb_2O(SO_4)$ [2]. The groundwater from which this mineral formed was alkaline (pH>8), rich in sulfate, low in carbonate, moderately oxidized, and may have had [Pb] $\sim 10^{-5}$ M and [Cr] ~ 10^{-4} M. This water would have been a resource and a health hazard; its Pb and Cr contents exceed current EPA limits for potability.

Introduction: There is abundant evidence and theory suggesting the actions of groundwater in Mars [3-6]. The compositions of Martian groundwaters are poorly constrained [7-9], but are crucial to understanding the history of water on Mars, its global geochemical cycles, the potential toxicity of Martian materials [10,11], and potential resources for human exploitation.

Martian meteorite EETA79001, a basalt [12], contains secondary minerals deposited by water on Mars [1,13]: calcite, Ca-Mg carbonate, Ca-sulfate, Mg-phosphate, silica, S- and Cl-aluminosilicates (clays?), and a Pb-Cr-S mineral ("Phase X" [1]). These minerals are younger than 180 m.a. (basalt crystallization age) and older than 0.5 m.a. (cosmic ray exposure age).

What is Phase X? Phase X was found as crusts in a vesicle in the shock-melt of EETA 79001 [1], and interpreted as Martian. SEM-EDX spectra implied elemental ratios Pb:Cr:S = 3.1:1:0.4 unlike the common mineral crocoite ($PbCrO_4$), and [1] suggested it might be a new mineral. The analysis is close to Pb:(Cr+S) = 2:1, as in phoenicochroite, $Pb_2O(CrO_4)$, and lanarkite, $Pb_2O(SO_4)$. I infer that Phase X is a solid solution between them: $Pb_2O[(CrO_4)_{0.7}(SO_4)_{0.3}]$.

On Earth, crocoite ($PbCrO_4$) and anglesite ($PbSO_4$) are more common than phoenicochroite and lanarkite. These minerals form in oxidized zones above Pb deposits and veins [2]; phoenicochroite is also found in Cr-contaminated soil. In the lab, both compounds melt congruently near 950°C [14]. Sulfate-chromate solid solutions are known, as both anions have the same charge, shape, and size; i.e., There is complete solid solution between sulphate alum and chrome alum, $KAl(SO_4,CrO_4)_2 \cdot 12H_2O$ [15]. Phoenicochroite and lanarkite form a complete solid solution at high T [14], but have not been studied at low T.

Stability of Phase X : In the absence of thermochemical data for phoenicochroite, the stability of Phase X is best constrained through its lanarkite component. Equilibria and water compositions were calculated using Geochemist's Workbench® [16] with additional data from [17]. Lanarkite is stable at moderate & high $f(O_2)$ and intermediate $f(S_2)$, Fig. 1, and at 8<pH<11, Fig. 2.

The stability of phoenicochroite is constrained by other equilibria in Pb-Cr-O. Crocoite ($PbCrO_4$) is stable in all but the most alkaline solutions, where lead oxides and metal prevail. The stability field of phoenicochroite must straddle these (metastable) boundaries, and so it is restricted to alkaline waters (like lanarkite).

Water Composition : The composition of the water that deposited Phase X cannot be defined exactly, but can be constrained by assuming that the secondary minerals are cogenetic and contemporaneous. The assemblage calcite + gypsum buffers $a(CO_3^{2-})/a(SO_4^{2-})$, and appears to constrain $a(SO_4^{2-})$ to ~ 0.015 and $[SO_4^{2-}]$ ~ 0.5 M for alkaline Na-Cl bearing brines (Harvie-Møller-Weare activity model [16], vis. [8, 13]). These imply $f(CO_2) \sim 10^{-7}$ bar, i.e. not communicating with the Martian atmosphere.

With this composition and solution pH=9, lanarkite stability would require $a(Pb^{2+}) > 10^{-8.5}$. Under these conditions, $a(CrO_4^{2-})$ was likely $> \sim 10^{-4.5}$ M, the limit for crocoite stability. Calculation of Pb and Cr concentrations is impossible without knowing the overall solution chemistry and strength, because of the potential importance of ion complexation. For example, if the depositing water were ~ 3M NaCl, Phase X would require [Pb] $\sim 10^{-5.2}$ M and [Cr] ~ 10^{-4} M (Debye-Hückel activity models), or ~1 ppm Pb and ~6 ppm Cr.

Origin : The water that deposited Phase X was alkaline, sulfatic, and oxidized [18], and rich in Pb^{2+} and CrO_4^{2-}. Most authors have suggested that Martian groundwaters were acidic from oxidation of sulfides and Fe^{2+} [19]. Magmatic vapors and hydrothermal fluids would also have been acidic, could reasonably have been enriched in Pb, but likely carried little Cr [11]. Water that reacts extensively at low T with mafic silicates is alkaline and reduced [9], and could carry significant Pb and Cr. The geologic setting for deposition of Phase X and the other secondary minerals in EETA 79001 remains unclear, but has great potential for elucidating groundwater processes and geochemical cycles on Mars.

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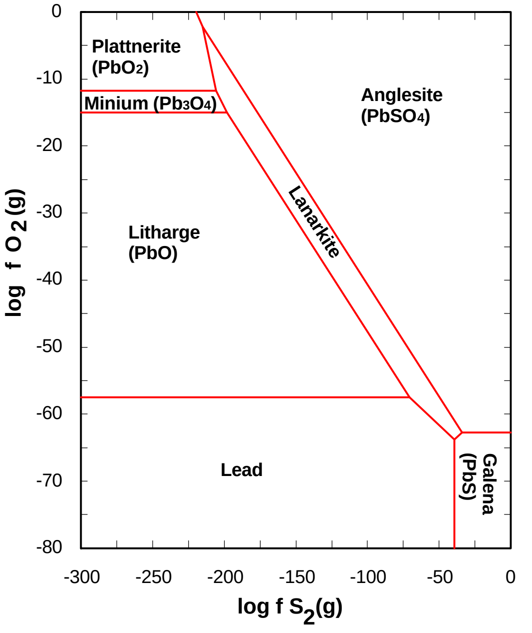

Figure 1. Mineral stabilities in Pb-S-O, 25°C. The commonest Pb minerals are galena and anglesite.

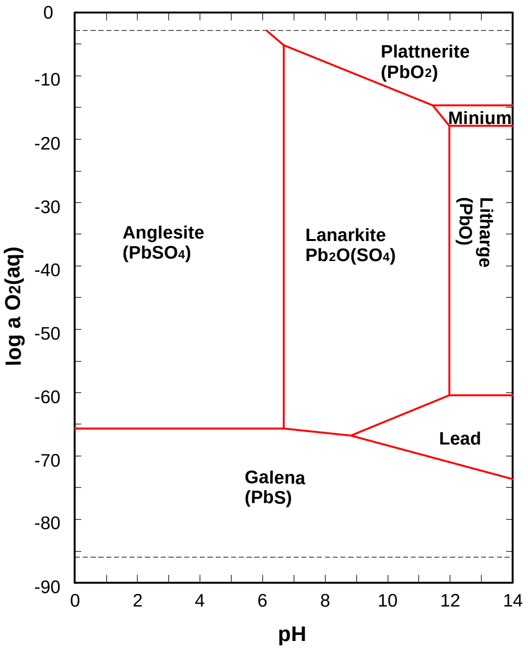

Figure 2. Mineral stabilities in Pb-S-O, 25°C, as a function of pH, for $a(SO_4^{2-}) = 0.016$, $a(Pb^{2+}) = 10^{-6}$. Dashed lines are stability range of H_2O. Anglesite dissolves at $a(Pb^{2+}) < 10^{-7}$. Lanarkite solubility is a function of pH but it is not stable at any pH for $a(Pb^{2+}) < 10^{-11}$.