**A CASE FOR HYDROTHERMAL GRAY HEMATITE IN ARAM CHAOS.** D. C. Catling[1] and J. M. Moore[2], [1]Dept. Atmospheric Sciences & Astrobiology Program, Box 351640, University of Washington, Seattle, WA 98195-1640 (davidc@atmos.washginton.edu) [2]M/S 245-3, Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035-1000 (jmoore@mail.arc.nasa.gov).

**Introduction:**

The Thermal Emission Spectrometer (TES) on Mars Global Surveyor has detected deposits of coarse-grained, gray crystalline hematite in Sinus Meridiani, Aram Chaos, and Vallis Marineris [1]. Detailed features in the hematite spectral signature of the Sinus Meridiani region show that the spectrum is consistent with emission dominated by crystal c-faces of hematite, implying that the hematite is specular [2]. Gray specular hematite (also known as "specularite") is a particular gray crystalline form that has intergrown, hexagonal plates with a silvery metallic luster. We believe that the key to the origin of specularite is that it requires crystallization at temperatures in excess of about 100°C. In reviewing the occurrence of gray hematite on Earth, we find no exceptions to this warm temperature requirement [3]. Thermal crystallization on Mars could occur (1) as diagenesis at a depth of a few kilometers of sediments originally formed in low-temperature waters, or (2) as direct precipitation from hydrothermal solution. Aram Chaos has unique chaotic terrain that offers more clues to the formation of the hematite than the relatively featureless flat terrain (as seen from orbit) of Sinus Meridiani. Aram Chaos provides the opportunity to look at a combination of TES data, Mars Orbiter Camera images, and Mars Orbiter Laser Altimeter (MOLA) topography. This combination of data suggests that high concentrations of hematite were formed in planar strata and have since been exposed by erosion of an overlying light-toned, caprock. Lesser concentrations of hematite are found adjacent to these strata at lower elevations, which we interpret as perhaps a lag deposit. The topography and the collapsed nature of the chaotic terrain favor a hydrothermally charged aquifer as the original setting where the hematite formed. An alternative sedimentary origin requires post-depositional burial to a depth of ~3-5 km to induce thermally driven recrystallization of fine-grained iron oxides to coarse-grained hematite.

**How does gray hematite form on Earth?:** We can consider formation in (a) igneous (b) sedimentary and (c) hydrothermal environments.

(a) *Igneou environments*. Gray hematite cannot be a directly ascended, igneous rock (a "lava") because the magmatic oxygen fugacity on Mars is unlikely to ever lie in the hematite stability field. Hematite is not plausible because the oxygen fugacity ( $f_{O2}$) is vastly lower (~4 to 8 orders of magnitude) than the magnetite-hematite buffer, based on redox-sensitive geochemical indicators in Martian meteorites [4,5]. Where hematite occurs in so-called "igneous" environments on Earth, such as Kiruna-type ores (e.g., El Laco in Chile), fluid inclusions containing chlorides and anhydrite and field observations suggest hydrothermal alteration of the host rock [6,7]. For example, specular hematite in volcanic rocks of Pilot Knob in the St. Francois Mountains (Missouri) is clearly hydrothermal, given the occurrence of hematite veins (some as much as 3 m in width), cavity fills, and mineral like tourmaline that are indicative of warm temperatures [8]. High temperature oxidation of basalt in $O_2$-rich terrestrial air can produce thin coatings of gray hematite [9], but it is doubtful if the early Martian atmosphere has sufficient $O_2$ to make this a realistic scenario; also if atmospheric oxidation were all that were required for specular hematite, it would be ubiquitous on Earth and Mars rather than occuring in unique geological predicaments.

(b) *Sedimentary formation*. Gray hematite does not form directly from a low-temperature aqueous solution. Instead, fine reddish-colored iron oxides form, usually goethite (FeOOH). So-called "sedimentary" deposits of specularite require diagenesis where sediments have been heated at depth to greater than ~100°C., causing recrystallization of fine-grained iron oxides to coarse-grained gray hematite. For buried sediments at moderate depths, water is either bound in chemical compounds or adsorbed onto the iron oxide grains. Porosity and permeability are small and fluids "fight" their way out, which yields the approximate assumption that the pore-fluid pressure approaches the lithostatic pressure. Thus iron oxide dehydration and hematite recrystallization will occur at a depth where the geotherm intersects the dehydration line for bound water. Fig. 1 shows a thermodynamic calculation using the data of [10]. Assuming a typical megaregolith conductivity of 2.5 W $m^{-1}$ $K^{-1}$ and an early Mars geothermal gradient gives the depth of intersection (dashed line assumes a geothermal heat flux of 50 mW $m^{-2}$; solid line, assumes a geothermal heat flux of ~80 mW $m^{-2}$). The depth of burial is 3-5 km of overburden matieral, which is difficult to reconcile with commonly inferred Martian geological processes.

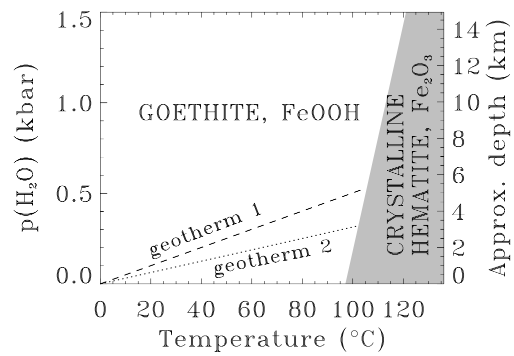


**Fig. 1**: Stability fields of goethite (FeOOH) and hematite ($Fe_2O_3$) as a function of temperature and $H_2O$ pressure. The latter can be taken as being approximately equal to the lithostatic pressure, giving the equivalent subsurface depth. At depth, hydrous iron oxides (typified by goethite) recrystallize to coarsely crystalline hematite due to heating (see text).

That thermal transformation is needed is borne out by all terrestrial field observations [3]. As an example, specularite (with 50-100 μm-sized platy crystals) in the the Brockman Formation, part of the Hamersley Range in Western Australia, formed at temperatures ~140°C on the basis of oxygen isotopes [11]. This temperature is consistent with the estimated maximum temperature of 205-325°C from an estimate of the burial depth. If the origin of the coarsely crystalline hematite on Mars started with aqueous deposition in a standing body of water, this must have been followed by either deep burial up the geothermal gradient or some other large-scale thermal perturbation due to igneous activity.

(c) *Hydrothermal formation*.

Gray, platy hematite can form directly in hydrothermal solution. Small crystals have larger vapor pressures and greater solubility than larger crystals. Thus, the response to heating is grain growth because at higher temperatures bigger crystals are more stable. Also, when a $Fe(OH)_3$ gel is formed from aqueous oxidation at warm temperatures (i.e., closer to 100°C rather than room temperature), it is found that there tend to be more hematite nuclei present, which leads to large hematite platelets (several microns or tens of microns) in subsequent aging to coarse hematite crystals. This is borne out by several laboratory studies that show a temperatures >100°C is required, with the exact temperature depending on pH and pressure [12,13]. In the field, specularite occurs hydrothermally, around fumaroles, for example, the Valley of Ten Thousand Smokes in Alaska. Here fumaroles developed on hot ash-flow tuff that fell on top of the water and ice of preexisting rivers, lakes and glaciers. It has been suggested that specularite froms from $FeCl_3$ vapor upon contact with water vapor to form fumarolic specular hematite deposits. Ferric chloride has a high vapor pressure is readily transported in the vapor phase above 200°C where it can react with water vapor and form hematite:

$$2FeCl_3(g) + 3H_2O(g) = Fe_2O_3(s) + 6HCl(g)$$

Fig. 2 shows a summary of pathways to gray hematite.

**Aram Chaos: geomorphology of thehematite**

[1] report the presence of a gray hematite zone in the north-east quadrant of Aram Chaos. Aram Chaos (21°W, 2°N) is an isolated area of chaotic terrain contained completely within an eroded and largely infilled crater. It forms part of the larger occurrence of chaotic terrain to the east of Vallis Marineris between 10 to 50°W and 20°S to 10°N. Chaos regions on Mars are areas where jumbled arrays of blocks have apparently been produced by collapsed ground. Chaotic terrain (and several box canyons) serve as the source regions for large out-flow channels that generally flow northwards and converge in the northern lowlands, principally Chryse Planitia. We now examine the geology and topography of Aram Chaos in some detail.

We examined the topography of Aram Chaos from Mars Orbiter Laser Altimeter (MOLA) data. MOLA tracks across the hematite-rich region in Aram Chaos show that the crystalline hematite is typically confined between about -3000 m and -2500 m elevation relative to the Martian geoid defined by the MOLA team. The TES spectral signature is weak at elevations close to -3000 m. The maximum signal occurs around -2600 m, equivalent to topographic benches in the MOLA topography. We interpret the lesser concentrations of hematite found at elevations up to a few hundred meters below this level as most likely a lag deposit from physical weathering. The individual tracks show that hematite does not occur above about -2500 m elevation. Thus, where the topography rises above this evevation, a break occurs in the hematite signal.

Correlation of the TES gray hematite location in Aram Chaos with MOLA topographic mapping and imaging by MOC allows us to characterize the morphology and local stratigraphy of this material. Wide angle MOC images show that much of Aram Chaos' interior is surfaced by a prominent light-toned caprock.

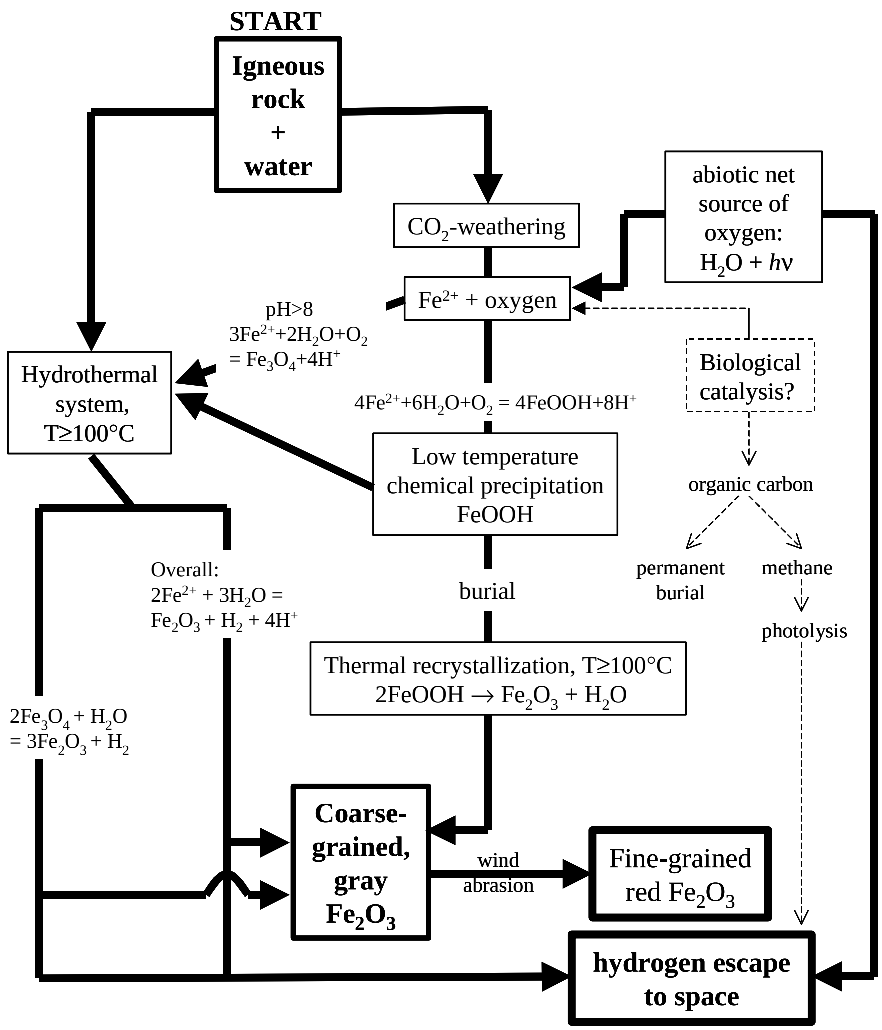


**Fig. 2**. Chemical pathways for the formation of gray crystalline hematite. Two main routes are shown: (1) low-temperature precipitation followed by hydrothermal processing (2) direct hydrothermal formation. Redox balance requires that the production of an oxidized species, hematite, be balanced by stoichiometric reductant, such as hydrogen. A dashed sub-pathway shows the likely effect of microbial biology, if it ever existed on early Mars.

Fig 3. shows that scarp-bounded outliers of the caprock (labeled 'C') occur to the east of a main outcrop (not shown, left of the image), which suggests that caprock was once more extensive. Bounding scarps of caprock material exhibit step benches in MOC NA images, which we interpret to be due to the differential erosion of horizontal discrete layers. Locally, the upper caprock surface immediately above the hematite deposit is relatively smooth at the scale resolvable in MOC NA images (Fig. 3). The main gray hematite-bearing material emerges from beneath the caprock. The hematite deposit itself also shows alternating benches and steps, inferred to be an erosional expression of layering. The hematite-bearing outcrops always appear to be heavily etched and pitted on decameter scales, with some fluting in MOC NA images. These outcrops generally do not extend beyond 10-15 km of the last occurrence of the caprock, from which we speculate that it is more susceptible to erosion than is the caprock. It is reasonable to infer that the hematite-bearing rock is much more extensive than its exposures, where protected by caprock. Laterally beyond and topographically below the bounding scarps of the hematite-bearing rock outcrop is a surface ubiquitously covered by duneforms (Fig. 3). There is a detectable weak presence of hematite in this "duneform" material. If the duneform material is composed of relatively recently formed sand dunes whose sands were derived from the erosion of the hematite-bearing material, then the hematite-bearing deposit is probably not well consolidated and composed of individual sand-sized grains of predominantly basaltic composition. Presumably, the abrasion of sands in the dunes of the duneform material fairly quickly mutes or destroys the hematite signature. However, the evidence for the duneform deposit being stratigraphically superposed is not absolutely unequivocal. These "dunes," if in fact that is what they are, could be "fossils" exhumed from beneath the hematite material.

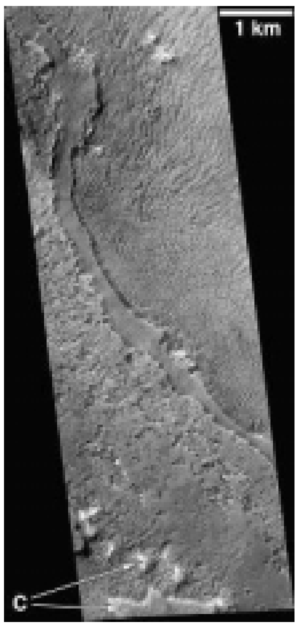


**Fig. 3**. Portion of MOC narrow angle image M19-01361, centered at ~3.5°N, 20.6°W.

Groundwater release and structural failure is a plausible explanation for how the apparently collapsed ground of Martian chaotic terrain formed [14]. Presumably, such release would be triggered by tectonic or geothermal activity. Thus the geology and topography of Aram Chaos is consistent with the formation of gray hematite due to the confinement and subsequent release of a hydrothermal aquifer. Possible terrestrial analogs are the Proterozoic brecciated zones in northern Yukon, Canada [15]. Here, breccia was generated by explosions of volatile-rich fluids within the crust, most probably caused by igneous intrusions at depth. Hydrothermal fluids shattered large volumes of rock. The Yukon breccia zones, collectively called Wernecke Breccia, cover an area 48,000 $km^2$ and are characterized by disseminated specular hematite [15]. Massive specularite zones are present in some Wernecke breccias. The gray hematite in Aram Chaos may have similarly had such a hydrothermal origin.

**Conclusion:** We conclude that the gray crystalline hematite in Aram Chaos most likely resulted from hydrothermal activity, given that:

(1) Thermal processing at temperatures > ~100°C is necessary to produce gray crystalline hematite based on thermodynamic calculations and bearing in mind the warm temperature constraint associated with all known occurrences of gray crystalline hematite on Earth.

(2) The chaotic terrain of Aram Chaos is thought to have formed by the geothermal melting of ground ice or the expulsion of groundwater, causing a loss of support and collapse of overlying material. Such a geological context would have been accompanied and probably preceded by hydrothermal activity.

(3) The topography of the gray hematite region in Aram Chaos indicates its occurrence in geologic strata within a specific topographic range. This is consistent with an ancient aquifer, which at one point, we postulate, was hydrothermally charged.

The observed caprock may be mechanically homogeneous and perhaps relatively impermeable, such that it confined an aquifer. Also, the erosional pitting and etching of the hematite-bearing outcrops could be the consequence of a form of cavernous weathering, in which fluids passing though such rock differentially cement (or uncement) the rock.

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