A LIKELY FORMATION MECHANISM FOR THE HEMATITE-RICH SPHERULES IN THE EQUATORIAL REGION OF WESTERN MARS. Chaojun Fan[1], Hongjie Xie[1], Dirk Schulze-Makuch[2] and Steve Ackley[1], [1] LRSG at University of Texas at San Antonio, San Antonio, TX 78249, USA (chaojunfan.fan@gmail.com, Hongjie.Xie@utsa.edu and Stephen.Ackley@utsa.edu), [2] SEES at Washington State University, Pullman, WA 99164, USA (dirksm@wsu.edu)

Introduction: The gray crystalline hematite on Mars was detected in three regions, Sinus Meridiani, Aram Chaos and Valles Marineris by the thermal emission spectrometer (TES) onboard the Mars Global Surveyor (MGS) orbiter [e.g.1, 2]. The Mars Exploration Rover (MER) Opportunity confirmed that hematite-rich spherules (~ 4.2 mm) are embedded in sulfur-rich layered outcrops and accumulated on the surface as lag deposits of whole and broken spherules at Sinus Meridiani [e.g. 3-5]. The formation mechanism of hematite-rich spherules has been discussed in a wide range of possible processes since then. Here, we argue for an alternative mechanism that the spherules were originally formed in Valles Marineris and transported to Meridiani Planum (named Sinus Meridiani as well) accompanied with accretion of finer volcanic materials, abrasion of basaltic fragments and break down of whole crystalline spherules during the wash-out flows from Valles Marineris to Meridiani Planum. This is consistent with the hypothesis of the origin and redistribution of sulfates in the equatorial region of western Mars [6].

The proposed formation of the sulphates and associated hematite-rich spherules in the Equatorial Region of Western Mars: Sulfates were detected *in situ* by the lander Opportunity in surface sands and underlying sulfate-rich sedimentary deposits in Meridiani Planum. The OMEGA/MEX identified massive sulfate outcrops alternating with layered volcanic deposits in Valles Marineris. It was proposed [6] that sulfates formed as evaporites in enclosed standing bodies of water in the Valles Marineris area following the early alteration of Martian basaltic crust, were then elevated by the Tharsis uplift, and transported together with rock materials to Meridiani Planum by periodic outbursts of water, where they were deposited as sediments. The model comprehensively addresses all forms of sulfate occurrences near the equator in the western Martian hemisphere and relates it to physiographic processes (volcanic, tectonic and sedimentary) affecting the Martian surface and reasonably explains the occurrences of sulfates, and the fate and source of sulfates in the region.

During the precipitation of massive sulfate evaporites, volcanic materials erupted and were deposited alternately to form the dark layers in Valles Marineris before Tharsis was uplifted. The oxidation and crystallization of volcanic materials in the dark layers due to hydrothermal fluids produced crystalline hematite-rich spherules and microcrystalline hematite in Valles Marineris. The crystalline hematite-rich spherules were transported to Meridiani Planum along with sulfates by the outbursts of water and deposited in the layered sulfate-rich alluvial/fluvial sedimentary deposits there. The spherules were also possibly (partially) formed by accretion of hematite particles and abrasion of basaltic clasts during the transportation of sulfates and volcanic materials from Valles Marineris to Meridiani Planum. Some original spherules might have broken down into small pieces during the fast turbulent flows. Diagenesis likely took place within the hematite-rich spherules after they were deposited in the sulphate-rich sedimentary rocks as indicated by the stalks of spherules and the combinations of two or three spherules in a line.

Discussion: Several formation modes for gray hematite detected by TES occurred, either by chemical precipitation or thermal oxidation [7]. The deposits of gray hematite are likely formed by chemical precipitation from Fe-rich aqueous fluids. Based on recent studies, the spherules at Meridiani Planum could be formed by 1) deposition from shallow water bodies [e.g., 7]; 2) oxidation and compaction of volcanic ash [8, 9]; 3) oxidation and crystallization in a hydrothermal environment [10, 11]; 4) oxidation and crystallization of iron in sedimentary deposits [12]; 5) precipitation of jarosite by groundwater dissolution [13]; 6) accretionary lapilli of impact surge [14]; 7) as products of organic compounds in a thermal system [15]; 8) impact melt spherules [16, 17]; 9) fine-intimate hematite coatings [18]. None of these hypotheses is unreasonable, but the region rich in the crystalline hematite-rich spherules is not the topographically lowest area, so it was unlikely for the spherules to form in a late-stage ponding event associated with the most recent channel formation [7]. Meanwhile, Pathfinder APXS showed that the soils are significantly enhanced in Fe and Mg relative to the rocks, which suggests that soils might not be the weathering products of local rocks.

The crystalline hematite was proposed to be produced by oxidation and compaction of volcanic ash or from volcanism directly based on the overwhelmingly abundant volcanic rocks on Mars [8]. There is no evidence for lava flow features, vents, or constructs on the hematite-bearing unit in Meridiani Planum [19]. Hematite lava was doubted by Catling and Moore [10] because the oxygen fugacity (fO_2) of magmas is too low to support hematite thermodynamically and the density of hematite lava is not consistent with the 10^5 km^2 aerial extent of the Sinus Meridiani deposit. The oxidation of pyroclastic materials during emplacement may be a possible formation of crystalline hematite. It was suggested that oxidation of volcanic ash or rocks in hydrothermal fluids rather than in air is more likely based on analogue sites on Earth such as in the St. Francois Mountains of Missouri [10]

There are likely two main chemical pathways to form the crystalline hematite on the basis of its terrestrial analogues and its laboratory synthesis [10]; 1) oxidation of iron at the lower temperature and precipitation of iron oxides in a standing body of water, and thermal recrystallization to gray hematite with subsequent burial [12] and 2) formation of the coarse-grained hematite directly in hydrothermal fluids. Catling and Moore [10] argued that temperatures of about 100 °C or above are needed to form platy hematite crystals of several micrometers in size. If the origin of the crystalline hematite on Mars started with aqueous deposition in a standing body of water, this must have been followed by either deep burial required by the geothermal gradient or some other large-scale thermal perturbation such as igneous activity or contact metamorphism. The formation of hematite crystals of several micrometers in size or larger is not favored at room temperatures or below.

The crystalline hematite may form by thermal processing from microcrystalline or amorphous iron oxide [e.g. 20]. But the hematite-rich spherules on Mars unlikely formed at a high temperature, thus such formation mechanisms can be ruled out as impact melt spherules, volcanic lapilli, or other mechanisms do not create hematite dominated by [001] emission based on Fresnel modeling of hematite crystal surfaces [21].

It was argued for a unique formation of the hematite-rich spherules in Meridiani Planum, that is, they formed as condensation spherules and accretionary lapilli through ground-hugging turbulent flows of rock fragments and ice produced by meteorite impact [14]. But the proposed process needs reasonable explanations for the sulfate cementation of two types of basaltic fragments, lack of ballistic impact ejectas, and up to 40% finer-grained sulfates if the impact is not fortuitous to hit at the sites of massive sulfate deposits (no massive sulfate deposits were identified at Meridiani Planum [22]). Meanwhile, more meteorite impacts might be needed to produce the thick multi-strata cross-bedding at Meridiani Planum because impact surge is unlike volcanic surge, which would likely have multiple impulses with out-bursting of volcanic materials.

It was also reported that numerous areas in Vallis Marineris exhibit the spectral signature of gray hematite, with the most extensive outcrops being within Candor and Ophir Chasma, and concluded that the hematite-bearing materials are associated with dark materials [7]. The gray hematite is apparently absent in some regions of Vallis Marineris that do not exhibit interior layered deposits, so that gray hematite formation appears associated with dark layers. The dark layers are supposed to be volcanic material deposits which alternate with layered sulfate evaporites.

The processes we propose are consistent with all available information and evidences about the hematite-rich spherules to date: 1) the spherules were only detected in the equatorial region of western Mars (at least so far) and no spherules were found in other sulfate-rich deposit areas; 2) the extensive occurrences of gray crystalline hematite were detected in Ophir and Candor Chasmas at Valles Marineris; 3) a good correlation of Ni and Fe in spherule-rich areas and non-spherule-rich areas [23]; 4) the spherules are well-sorted and exhibit the coexistence of original spherules and their broken pieces; 5) basaltic clasts of variable angularity and vesiculation are interspersed among the spherules [24]; 6) Bounce rock found at Meridiani Planum has a unique composition compared with its surroundings [25]; 7) the soils, significantly enhanced in Fe and Mg relative to the rocks, might not be the weathering products of local rocks [26]; 8) the spherules were likely formed at a temperature of over 100 °C but not high enough to implicate direct volcanic activities or deep burial.

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