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Hematitic concretions at Meridiani Planum, Mars: Their growth timescale and possible relationship with iron sulfates

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Abstract

Using diffusion-based models for concretion growth, we calculate growth times of hematitic concretions that have been found in the Burns formation at Meridiani Planum, Mars, by NASA's Opportunity Mars Exploration Rover. Growth times of ~350–1900 terrestrial years are obtained for the observed size range of the concretions over a range of parameters representing likely diagenetic conditions and allowing for an iron source from diagenetic redistribution. This time scale is consistent with radiometric age constraints for the growth time of iron oxide concretions in sandy sediments of the acid-saline Lake Brown in Western Australia (<3000 yr) reported elsewhere. We consider the source of the iron for Meridiani concretions by calculating the constraints on the supply of Fe^{3+} to growing concretions from the dissolution and oxidation rates of iron minerals on early Mars. Mass balance arguments suggest that acid dissolution of jarosite ($(H_3O,K)(Fe^{3+}3(OH)_6(SO_4)_2)$ and minor ferric sulfates is probably the most plausible dominant contributor to Fe^{3+} in the concretions. Ferrous iron released from melanterite ($Fe^{2+}SO_4 \cdot 7H_2O$) that is subsequently oxidized could also have been an important iron source if melanterite existed prior to diagenesis. Our conclusion that the iron is sourced from iron sulfates may explain the global observation from orbiters that grey crystalline hematite occurs in association with sulfate deposits.

Keywords: Mars; concretions; sulfates; Meridiani; hematite

1. Introduction

Since 2004, NASA's Mars Exploration Rovers have yielded unprecedented data on Martian surface geology and chemistry. In Meridiani Planum, the Opportunity rover has examined a series of outcrops that form a stratigraphic unit, which was named the Burns Formation. The Burns formation is at least 800 m thick (Edgett, 2005) and its analysis reveals a sulfate-rich dune–interdune-playa sedimentary sequence (Grotzinger et al., 2005; McLennan et al., 2005) populated by 2–5 mm hematitic (Fe_2O_3) spherules (Squyres and Athena Science, 2004). In a wider context, massive accumulations of sulfates have also been remotely detected from the OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité) instrument on ESA's Mars Express (Gendrin et al., 2005) and the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) instrument on NASA's Mars Reconnaissance Orbiter (Knudson et al., 2007). Some of these sulfates are associated with hematite, such as in Aram Chaos (Bibring et al., 2007; Glotch and Christensen, 2005), so determining the genetic relationship between sulfates and hematite is an important issue for understanding some of the most interesting geology of Mars.

Several origins have been suggested for the hematite spherules, but there is strong sedimentological evidence that they are concretions, which form when water carries dissolved minerals through sediments or porous rocks and minerals precipitate concentrically and incorporate or replace surrounding sediments (although the Meridiani concretions do not show morphological or compositional nuclei). Knauth et al. (2005) suggested that the spherules are volcanic or impact-induced lapilli. However, the sedimentology clearly favours a concretionary origin: 1) laminae

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are not deflected around the spherules by burial or compaction, so they likely crystallized on the spot, unlike the case of drops of molten lava (glass spherules) or pellets of congealed ash (lapilli) 2) spherules show banding or grooves that parallel the surrounding laminations, as expected for concretions 3) spherules are distributed uniformly throughout the unit rather than in bedding planes, 4) a distinct Fe-rich mineralogy is inconsistent with volcanic lapilli or impact glasses and 5) doublets are present, which are statistically unlikely for lapilli but expected for concretions (Squyres et al., 2004; McLennan et al., 2005). Thus, the consensus view is that hematite spherules formed as concretions when iron-rich groundwater penetrated the stratigraphic column.

Different terrestrial analogues have been proposed for the hematite spherules. Morris et al. (2005) suggested a hydrothermal origin through acid-sulfate alteration of basaltic tephra, using the analogy of spherules observed at the Mauna Kea volcano, Hawaii. These 10–100 micron-sized spherules are compositionally zoned. However, the Meridiani spherules are larger and apparently of homogeneous composition, suggesting they were formed in less fluids and over longer timescales. Chan et al. (2004) compare concretions in Utah's Navajo Sandstone, which formed in porous quartz arenite from the dissolution of iron oxides by reducing fluids and subsequent Fe-precipitation. The variety of concretions illustrated in the Navajo sandstone establishes important geometries and distribution relationships. However, there are notable chemical differences between these and Meridiani concretions. Unlike Meridiani concretions (which are almost pure hematite), Navajo concretions show significant incorporated siliciclastic material, indicative of high pore-fluid velocities. Episodic elevation of the regional water table at Meridiani Planum (McLennan et al., 2005; Andrews-Hanna et al., 2007) would provide stationary pore-waters, consistent with small, incorporated siliciclastic fractions (McLennan et al., 2005; Squyres et al., 2006) and low sphericities (±6%) of Meridiani concretions (Grotzinger et al., 2005). More similar to the Meridiani spherules, semi-soft iron oxide concretions up to a few centimeters in diameter in sandy sediments of acid-saline Lake Brown in Western Australia are in intermediate stages of formation and actively lithify when removed from the lake bed (Bowen et al., 2008). The Yilgarn Craton is Archean continental crust that constitutes the bulk of the Western Australian land mass. It is host to Lake Brown and many other acid-hypersaline, lacustrine environments, which exhibit several depositional and mineralogical similarities to Meridiani Planum including precipitation of evaporites, iron oxides and sulfates during wet episodes and reworking during dry periods (Benison et al., 2007). Furthermore, dating of the surrounding organic-rich sediments of Lake Brown places age limits of between 1410 (±100) and 2913 (±48) years on these concretions (Bowen et al., 2008).

The observed size range of spherules at Meridiani Planum, shown in Table 1, is the result of varying diagenetic conditions during formation and Aeolian reworking. Weathered out loose spherules that litter the soils and gather in topographic depressions can be similar in size to those in neighboring outcrops, which implies their origin. Conversely, some loose spherules can be smaller than spherules embedded in sulfate-rich sediments (Squyres and Athena Science, 2004; McLennan et al., 2005; Weitz et al., 2006). The mean diameter of weathered out spherules is 1.44 mm, while spherules embedded in host rock maintain a larger average diameter of 4.2 mm. Size differences are likely due to differences in source material fluxes during diagenesis or the erosive capabilities of aeolian processes, which leave lags (Chan et al., 2004).

Table 1
Size and abundance of spherules at Meridiani Planum as measured by McLennan et al. (2005) and Weitz et al. (2006)

Locality	McLennan et al. (2005)			Weitz et al. (2006)	
	Vol.% of host unit occupied	Standard deviation	Spherule-bearing rocks considered	Mean radius (mm)	No of spherules measured
Eagle Crater	1.2	0.4	4	1.98	21
Fram Crater	4.3	0.8	6	–	–
Endurance Crater	4.0	2.0	6	2.24	20
Average for outcrops	3.2	2.0	–	2.11	–
Average for soils	–	–	–	1.44	–

Episodic aqueous recharge is thought to have created the sulfate-rich mineralogy of the Burns formation, which has been interpreted as re-worked evaporite minerals by Squyres et al. (2006). During recharge, iron could have been supplied to form the hematitic spherules in various ways. Fe^{2+} from dissolution of basaltic phases and ferrous sulfates would have been subject to low-temperature oxidation. Ferric sulfates may have occupied 15–40 vol.% of the Burns formation in the form of vugs and crystal moulds (Clark et al., 2005; McLennan et al., 2005). It is possible that some dissolution of iron sulfates to form secondary porosity may have been contemporaneous with the formation of the hematite (McLennan et al., 2005), in which case the iron could have been supplied locally. Once ferric ions appear in solution they are highly susceptible to form Fe-hydroxides, such as ferrihydrite, a reddish-brown insoluble gel (Cornell and Schwertmann, 1996). Once emplaced as a proto-concretion, this precipitate would subsequently dehydrate to goethite and then to hematite over time (Nordstrom and Munoz, 1994; Catling and Moore, 2003; Chan et al., 2007).

Through application of diffusion-based diagenetic models, we here provide insight into the likely formation timescales of the hematitic concretions in the Burns formation and deduce the sources of iron from the modeled supply rates.

2. Diffusion-based diagenetic models

We consider a variety of diffusion-based models that concern only the transport of Fe ions to the growth surface of a concretion. These models were originally developed for growth of calcite concretions (Berner, 1968; Lasaga, 1979; Wilkinson and Dampier, 1990; Wilkinson, 1991; Lasaga, 1998). In our study, the models are applied to a steady-state replenishment of Fe^{2+} or Fe^{3+} to the surface of the concretion. We calculate growth times based on parameters such as concretion size, diffusion coefficients, etc. and their plausible ranges based on