Hematitic concretions at Meridiani Planum, Mars: Their growth timescale and probable sourcing of iron from iron sulfates.

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Introduction: The Mars Exploration Rover, Opportunity, at Meridiani Planum has examined in detail a series of outcrops that form a stratigraphic unit, which was named the Burns Formation. Analysis revealed a sulfate rich dune-interdune-playa sedimentary sequence [1, 2] populated by 2 - 5mm hematitic (Fe_2O_3) spherules [3]. Episodic aqueous recharge is thought to have created the sulfate-rich mineralogy, which has been interpreted as re-worked evaporite minerals [4]. During recharge, iron could have been supplied to form the hematitic spherules, which are widely accepted as being concretions, in various ways. Fe^{2+} from dissolution of basaltic phases and ferrous sulfates would have been subject to slow, low-temperature oxidation. Ferric sulfates may have occupied 15 – 40%vol. of the Burns formation in the form of vugs and crystal moulds [1, 5] and are therefore a primary candidate for iron sourcing. It is possible that some dissolution of iron sulfates to form secondary porosity may have been contemporaneous with the formation of the hematite [1], in which case the iron could have been supplied locally and diagenetically redistributed during aqueous recharge. Once ferric ions appear in solution they are highly susceptible to form Fe-hydroxides, such as ferrihydrite, a reddish-brown insoluble gel [6]. Once emplaced as a proto-concretion, this precipitate would subsequently dehydrate to goethite and then to hematite over time [7-9].

Using diffusion-based models for concretion growth, we calculate plausible growth times of these concretions. We also consider the source of the iron 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. Broadly speaking, this work helps explain the spatial relationship between sulfates and hematite that is observed in many regions on Mars (e.g. Iani and Aram Chaos).

Diffusion-based diagenetic models: We consider five 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 [10-14]. In our study, the models are applied to a steady-state replenishment of Fe^{2+} or Fe^{3+} to the concretion surface. We calculate growth times based on parameters such as concretion size, diffusion coefficients, etc. and their plausible ranges based on our current knowledge of the Burns formation and the early Martian surface environment (see [15] for details of parameters). Source iron may be supplied from external reservoirs, such as slow dissolution of basaltic material, or from pre-emplaced evaporite minerals that are dissolved so that their iron is diagenetically redistrib-

uted during aqueous recharge. Two of the models (figure 1a) apply to simple growth situations where the pore fluid is stationary and concretion-forming iron is sourced externally i.e. there is no diagenetic redistribution. That of [10] assumes a linear concretion gradient between the concretion surface and the edge of the depleted zone, while the model of [12] assumes a non-linear concentration gradient. The model of [13] (figure 1b) allows for diagenetic redistribution of iron in pre-emplaced evaporite minerals.
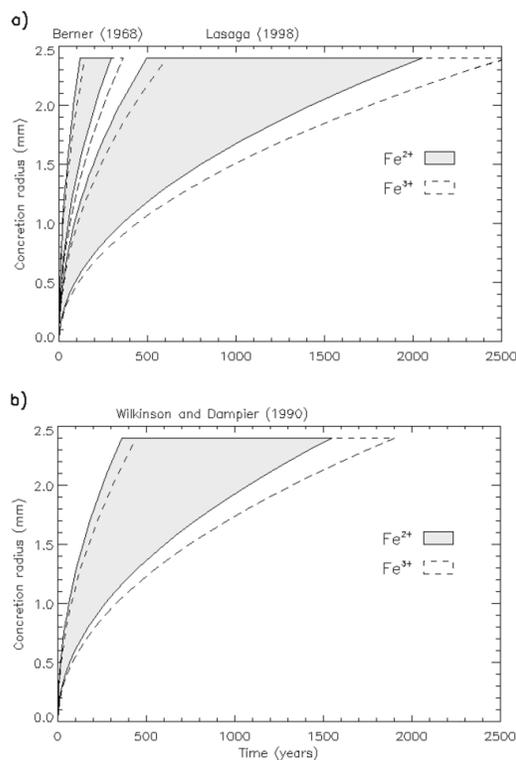

Figure 1. Concretion growth times from: a) The simple models of [10] and [11, 12], the latter of which corrects for a non-linear concentration gradient in the depleted zone. b) The diagenetic redistribution model of [13].

Two of the models allow consideration of a mobile-pore fluid (figure 2), which would increase bulk transport of source material and reduce growth times. Using pore-fluid velocities of 10^{-3} to 10^{3} m year^{-1} (which covers the range for terrestrial groundwater) the mobile pore-fluid model of [10] shows growth times of roughly one terrestrial week, while that of [13], which also accounts for diagenetic redistribution, produces times no longer than two weeks. Shorter growth times would imply larger iron fluxes, which would need to be predominantly trivalent, since the system would be

surface-reaction limited by the slow oxidation of Fe^{2+} on the surface of Mars (which we later discuss). A cryogenic, hypersaline and acidic pore-fluid could carry such high iron concentrations of ferric iron [16], though this would probably be subject to lower diffusion coefficients and increased viscosity, which would work to lengthen growth times.
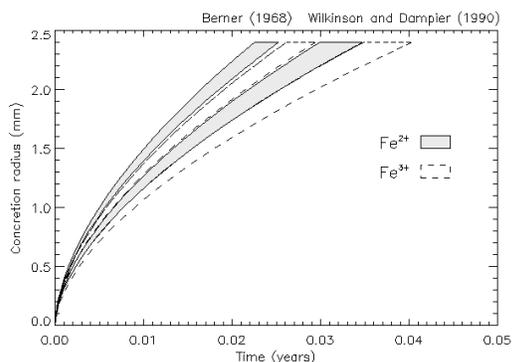

Figure 2. The range of concretion growth times calculated by the mobile pore-fluid models of [13] and [10].

Nevertheless, we cannot completely discount the possibility that a mobile pore-fluid was involved because iron-rich cryogenic hypersaline acidic brines may be capable of delivering the high ionic fluxes required for such short growth times. But our favoured scenario is that of a stationary (or near-stationary) pore-fluid and diagenetic redistribution (figure 1b). This is consistent with the highly spherical shape of concretions, which otherwise become ellipsoidal in strong flow. Upper limit growth times of ~350 – 1900 terrestrial years are obtained for the observed size range of the concretions. 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 W. Australia ($\leq$1500 years) [17].

Iron sources: The Fe^{3+} contained in the concretions in one cubic meter of the Burns formation ranges from 394 – 2822 moles Fe^{3+} m^{-3} based on observed properties of the Burns Formation at Eagle and Fram Crater respectively. The required ferric iron could be produced via oxidation of dissolved Fe^{2+} (from dissolution of ferrous sulfates or basaltic phases) or supplied via dissolution of ferric sulfates. We conduct mass balance calculations, which 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 $(Fe^{2+}SO_4 \cdot 7H_2O)$ and subsequently oxidized could also have been an important iron source if melanterite existed prior to diagenesis [1].

From the rate data of [18] we find that dissolution of Fe^{2+} from basaltic phases on Mars is comparatively slow and probably provided a negligible contribution to the concretion-forming iron unless the available mineral surface area per m^3 of basaltic material was very high (as in an ash pile) and conditions were warm ($\geq$0°C) and highly acidic (~pH 2). Once ferrous iron is in solution, it would need to be oxidized to Fe^{3+} in order to precipitate. Therefore, the rate of precipitation must be controlled by the oxidation rate of Fe^{2+} in a pore-fluid interacting with the early Martian atmosphere. We calculate the amount of moles of Fe^{3+} created per cubic meter of fluid in 500 and 1000 years according to a relationship by [19] between oxidation rate of Fe^{2+}(aq), its concentration $[Fe^{2+}]$, pH, partial pressure of oxygen, (pO_2), temperature T (K), and ionic strength I, of the solution. We find that by assuming an atmospheric oxygen pressure similar to todays value, a temperature of 0°C and near-neutral acidity can the necessary Fe^{3+} be created from oxidation of Fe^{2+}. However, atmospheric oxygen pressure was probably much lower in the past [7, 20], which would have significantly reduced oxidation rates of Fe^{2+}. Therefore, it is probable that a significant fraction of the Fe^{3+} was supplied from dissolution of ferric sulfates. We suggest that the supply of iron from iron sulfates to form hematite likely explains the orbital observation that grey crystalline hematite occurs globally in association with sulfate deposits.

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