IRON PRECIPITATION PATTERNS IN GELS: IMPLICATIONS FOR THE FORMATION OF HEMATITE CONCRETIONS AT MERIDIANI PLANUM, MARS.

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Introduction: Precipitation experiments in gels can produce many different morphologies that may be analogous to natural situations involving self-organization; namely the formation of hematite concretions by diffusion-mediated processes in the Jurassic Navajo Sandstone, Utah and at Meridiani Planum, Mars. Our experiment consists of an outer electrolyte (A) diffusing into a gel containing a dilute solution of the inner electrolyte (B). In days to weeks, the moving reaction front forms precipitation patterns of the insoluble compound (AB), such as tree-like crystals, thread-like crystals, Liesegang banding, or any combination of these. In this work we focus on patterns formed by iron precipitates (iron phosphate, carbonate, hydroxide) and their subsequent oxidation to iron oxide after the patterns are formed.

This process of diffusion-controlled pattern formation has been found to occur in natural environments; one of the most well-studied terrestrial examples is the Navajo Sandstone formation in Utah. The interior morphology of the Utah hematite concretions varies from a homogenous interior to concentric banding, sometimes exhibiting a cement “rind” [1, 2]. The concretions are thought to have formed by the reducing and mobilizing of iron (probably by hydrocarbon-containing fluids [3]) originally derived from hematite grain coatings [4]; then reduced Fe-containing fluid met more oxidizing groundwater and precipitated as iron oxide or hydroxide [1, 2]. The concretions are more resistant to weathering than the surrounding rock which lets them become exposed on the surface [3, 1]. The hematite “blueberries” discovered at Meridiani Planum [5] could have been formed by similar processes except that on Mars, iron was already reduced and contained in sulfide-rich deposits, and was likely mobilized by the dissolution of pyrite [6]. The Martian spherules examined to date all show a homogenous interior structure (i.e. no concentric banding), but varying morphologies have been observed [7].

Understanding the conditions under which various types of concretions are formed and why diffusion-controlled processes sometimes lead to banding patterns instead of homogenous precipitation or crystal formation can help us interpret the interior structure of hematite spherules. This can, in turn, reveal information about the environment in which they were formed.

Results: Experimental results thus far indicate that the formation of concentric bands is dependent on both the impurities present in the diffusion medium and on the iron compounds that are present at the time of formation. When two nucleating species compete in the diffusion medium, they will precipitate in turn, and the opposing concentration gradients and particle nucleation only in localized areas lead to the formation of Liesegang bands. Using different gels as diffusion media produces very different results. Gels that should have fewer impurities (i.e. silica gel or purified agarose) tend to produce tree-like or thread-like crystals (although this also depends on the specific chemical reaction occurring) whereas gels with large amounts of interfering organic compounds are more likely to produce bands.

The presence or absence of banding can also be affected by which iron compounds are precipitating out of solution. One approach is to assume that in a natural situation iron hydroxide would precipitate at a redox reaction front first, and would later react with oxygen to form hematite [2]. However it is also possible that iron could have precipitated with other compounds such as phosphate or sulfide and could later have been replaced with hydroxide. In this case, as we also observe in laboratory experiments, the original precipitation pattern is preserved as one iron compound is replaced with another and as it eventually oxidizes. Theories of formation of the Martian spherules as iron sulfide later oxidizing to hematite, or as iron oxide formation directly, are both consistent [8]. Sulfide could have been an aqueous component in the early Martian oceans [6], as could phosphate (as evidenced by the positive correlation of P, Cl, and S in Martian soil analyses [9]). The formation of concretions through precipitation of Fe(III) compounds other than hydroxide could lead to distinctive interior morphologies, as we observe in iron diffusion experiments in the laboratory. Understanding the conditions under which specific precipitation patterns form will provide a more accurate interpretation of the interior of the “blueberries”.

Conclusions: We have performed diffusion experiments in gels with iron and other compounds that are likely to have been present on early Mars, and the process of self-organized precipitation and subsequent oxidation to iron oxide is similar to the processes thought to have been responsible for the formation of hematite concretions in the Navajo Sandstone and at Meridiani Planum. Our observations thus far indicate that the precipitation pattern produced is dependent on which ion the iron precipitates with first, as well as the amount of impurities present in the gel. This could have implications for the interpretation of the Martian "blueberries" if the interior morphology can indeed be an indicator of which iron compound was originally present. There is also the possibility that concentric banding in the interior of a hematite concretion could be an indicator of the amount of organic compounds present at the time, since in gel diffusion experiments the organic "impurities" appear to have an effect on band formation. Further studies of Liesegang banding and other pattern formation in gels, to simulate various chemical reactions and environmental conditions that may have been present on early Mars, will broaden our understanding of concretion formation.

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