PROCESSES OF FORMATION OF SPHEROIDAL CONCRETIONS AND INFERENCES FOR "BLUEBERRIES" IN MERIDIANI PLANUM SEDIMENTS.

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Introduction: The MER Opportunity Athena Science team has described spheroidal hematite nodules in sediments at Meridiani Planum on Mars [1]. They were informally referred to as "Blueberries" in the initial press releases and for brevity that is the name to be used in this abstract. Not all spheroidal objects in sediments are nodular concretions, but this paper will discuss the diagenetic processes possibly relevant to understanding the origin of the Blueberries. There are many occurrences of spheroidal diagenetic concretions in terrestrial sediments and detailed work has been done to understand the processes of their formation. In particular, it is possible to reconstruct the controls on their shapes and compositions, both mineral and chemical. Although there may not be good analogs for the Meridiani Planum hematite spherules on Earth, it may be possible to deduce the former environmental conditions that led to their formation and whether they might retain (or even be) biosignatures.

Processes of concretion formation: Sediments become sedimentary rocks by precipitation of mineral cements in the pore spaces between detrital grains. Concretions usually are distinguished from the surrounding rock by the presence of much larger amounts of cement producing a more strongly lithified part of the rock that can become very clearly apparent during subsequent weathering. The formation of concretions is part of the process of reduction of potential energy of the sedimentary system. The cement may be produced by dissolution of less stable mineral phases such as aragonite and precipitation of the more stable calcite. This process occurs extensively in limestones and only forms nodular concretions when the cement precipitation is focused into a different environment within the sediment, for example a burrow. Such concretions are usually not spheroidal. However, these and other concretions may be distinctive if they are formed early in the burial process and the surrounding sediments suffer greater subsequent compaction.

The most distinctive concretions are formed in clastic sediments where they stand out because their mineral composition is different from that of the bulk rock. These authigenic minerals are produced by chemical reactions that reduce the potential energy of the system. The main chemical disequilibrium in terrestrial sediments results from the redox contrast between the detrital grains and organic matter. Weathering and transport occur in oxygenated conditions and result in oxidized detrital grains. Sedimentation with a reducing agent, organic matter, present is chemically unstable. Various processes oxidize organic matter and the byproducts of these reactions form the mineral cements. However, if there is energy to be gained from a process and if microbes can perform it more efficiently than abiological processes, then biotic processes will prevail. This is inferred from the isotopic compositions of ancient concretions [2] and also by microbiological analysis of concretions that are forming now [3].

Diagenetic Reactions that produce concretions: There are successive**,** microbially mediated processes that oxidize organic mater in sediment during burial after oxygen dissolved in porewater has been consumed by aerobic bacteria [4]. Those most relevant to this discussion are ferric iron reduction and sulfate reduction, both of which are significant in forming concretions on Earth and may have been relevant on Mars (but may not have been microbial there).

Controls on shape of concretions: The processes described above may produce iron sulfide and/or a variety of carbonate minerals. For the carbonates, carbon comes predominantly from the organic matter as identified by its isotopic composition [2] and may produce calcite, if there is insufficient available iron, or siderite (iron carbonate). Availability of iron may control not only the mineral composition of the concretion but also its shape. Iron reduction produces alkaline conditions that favor precipitation of carbonate, while sulfate reduction may lead to formation of small amounts of acidity. The balance of these two reactions and their localization are significant in concretion formation [4,5]. For carbonate concretions, predominance of iron reduction can be considered as a positive feedback mechanism for precipitation and may lead to laterally extensive cementation forming ledges rather than spheroidal nodules [5]. However, sulfate reduction may have a negative feedback effect and result not only in locally focused carbonate precipitation, but also sterilization of the surrounding volume of sediment leading to a discrete nodular concretion not coalesced with neighbors. Iron sulfide concretions also may be constrained by similar processes. This is exemplified in the case of the pyrite (iron sulfide) and calcite concretions found in the organic rich Jurassic sediments of Yorkshire, England. A typical example is shown in Figure 1, which shows the pyrite rim and the calcite center. Because it has been exposed in the cliff face the pyrite has partially oxidized to hydrated iron oxide, limonite. The concretions show radial zonation of trace chemical and isotopic compositions [6].

Figure 1: A pyrite-rimmed calcium carbonate concretion form the Early Jurassic Jet Rock formation (Whitby, Yorkshire, England).

The model for concretion formation here depends on self-organization of an initially fairly homogenous sediment. Oxidation of organic matter occurs by reduction of sulfate present in marine porewaters. In the absence of sufficient iron to produce pyrite, the sulfide in solution diffuses outwards in all directions until it can react with inwardly diffusing reduced iron. In a completely homogenous sediment this would result in a spherical concretion. In this case where there is a considerable clay mineral content, there is greater horizontal than vertical permeability leading to the oblate shape seen in Figure 1. The diffusion gradients are maintained by the reaction of the sulfide and dissolved iron producing low concentrations of both components at the site of precipitation of pyrite, which forms as a spheroidal shell [6]. A similar process can operate to form purely sulfide spheroidal concretions and even at a much smaller scale, the microscopic, spherical pyrite framboids [7]. The negative feedback mechanism controls spacing and forms the sharp boundary to the concretion. The control on initiation of concretionary growth may be a higher concentration of organic matter and may be amplified by the growth of the microbial community. Similar processes have operated for at least 2Gy on Earth [8].

Preservation of original mineral compositions: As described for the concretion shown in the Figure, the original mineralogy may be altered by subsequent process; e.g. oxidation of reduced iron minerals. In the case of the very large pyrite rimmed concretions of the Middle Jurassic of the UK [9], all that is left of the pyrite is now gypsum. In summary, simple nucleation controlled growth will form clumps or bands of cement not spheroids. Spheroidal nodular concretions on Earth result from spherical diffusion of products of diagenetic reactions involving organic matter.

Blueberries: The Blueberries are formed of hematite and are described as having precipitated from water in the pores of the sediment [10]. However, from the above discussion of processes needed to form spheroidal concretions on Earth, it is hard to see what is the driving mechanism for in situ production of oxidized iron in solution and its spherical diffusion. However, it is possible to speculate on another plausible mechanism. If organic matter had been present in the acidic and oxidized sediment then it could have acted as a focus for a redox reaction that could have produced a reduced iron mineral phase, for example an iron sulfide or carbonate. This does not imply a microbial process, but such reactions are very much slower in the absence of microbial mediation. On Earth, sulfate reduction processes in sulfate evaporites have formed sulfide concretions [11] but in that case do not always produce spheroidal shaped nodules. Where the original mineralogy has been changed, it may still be possible to deduce the process of formation if the trace element or iron isotope compositions are retained and their spatial distributions will indicate the concentric zonation typical of the original material. Maybe a similar approach will be applied eventually to the Blueberries.

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