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Hematite spherules in basaltic tephra altered under aqueous, acid-sulfate conditions on Mauna Kea volcano, Hawaii: Possible clues for the occurrence of hematite-rich spherules in the Burns formation at Meridiani Planum, Mars

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Abstract

Iron-rich spherules (>90% Fe_2O_3 from electron microprobe analyses) ~10–100 μm in diameter are found within sulfate-rich rocks formed by aqueous, acid-sulfate alteration of basaltic tephra on Mauna Kea volcano, Hawaii. Although some spherules are nearly pure Fe, most have two concentric compositional zones, with the core having a higher Fe/Al ratio than the rim. Oxide totals less than 100% (93–99%) suggest structural H_2O and/or OH^{-1}. The transmission Mössbauer spectrum of a spherule-rich separate is dominated by a hematite (α-Fe_2O_3) sextet whose peaks are skewed toward zero velocity. Skewing is consistent with Al^{3+} for Fe^{3+} substitution and structural H_2O and/or OH^{-1}. The grey color of the spherules implies specular hematite. Whole-rock powder X-ray diffraction spectra are dominated by peaks from smectite and the hydroxy sulfate mineral natroalunite as alteration products and plagioclase feldspar that was present in the precursor basaltic tephra. Whether spherule formation proceeded directly from basaltic material in one event (dissolution of basaltic material and precipitation of hematite spherules) or whether spherule formation required more than one event (formation of Fe-bearing sulfate rock and subsequent hydrolysis to hematite) is not currently constrained. By analogy, a formation pathway for the hematite spherules in sulfate-rich outcrops at Meridiani Planum on Mars (the Burns formation) is aqueous alteration of basaltic precursor material under acid-sulfate conditions. Although hydrothermal conditions are present on Mauna Kea, such conditions may not be required for spherule formation on Mars if the time interval for hydrolysis at lower temperatures is sufficiently long.

Keywords: Mars; Meridiani Planum; Mars Exploration Rover; Spherule; hematite; concretions; sulfate

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1. Introduction and background

The scientific basis for selection of Meridiani Planum as the landing site for the Mars Exploration Rover (MER) Opportunity centered on detection of the mineral hematite (α-Fe_2O_3) by the Thermal Emission Spectrometer instrument on the Mars Global Surveyor spacecraft [1–4]. High hematite concentrations are plausible though not definitive mineralogical markers for aqueous processes, making Meridiani Planum a viable location to land and attempt to study the products of aqueous processes in situ. Hematite was also detected in Aram Chaos and several isolated locations in Valles Marineris, but only the Meridiani Planum site was considered safe for landing [4].

The Miniature Thermal Emission Spectrometer (Mini-TES) and Mössbauer Spectrometer (MB) instruments on Opportunity confirmed the presence of hematite at Meridiani Planum. Specifically, Mini-TES detected hematite in an accumulation of spherical particles (spherules) on a sulfate-rich outcrop surface and in lag deposits elsewhere [5]. As shown by observations with the Panoramic Camera (Pancam) and Microscopic Imager (MI), the hematite-rich lag deposits correspond to spherules that were originally imbedded within outcrops and have weathered out from surrounding and softer sulfate-rich rock and accumulated as whole and broken spherules ~1–8 mm in diameter [6–10]. Spherules currently imbedded in the outcrop have a mean diameter of 4.2 ± 0.8 mm [11]. MB found high concentrations of hematite in sulfate-rich outcrops (the Burns formation), in the same accumulation of spherules analyzed by Mini-TES, and in ripple crest soils that are accumulations of whole and broken spherules (lag deposits) [12]. The high Hm concentration in deposits with broken spherules [12] and Pancam spectra of spherules sectioned by the MER Rock Abrasion Tool (RAT) [10] both show that hematite is present throughout the spherule volume and not just present as a coating.

Two populations of hematite are present in the outcrop, because MB spectra of outcrop rock for which the instrument's field of view was free of spherules show that ~40% of the Fe in the sulfate-rich rock is present as hematite [12]. Although analyses of spherule-rich targets by the Opportunity Alpha Particle X-ray Spectrometer (APXS) show high concentrations of total iron (>30% calculated as Fe_2O_3) and low concentrations of SiO_2 (<38%) [13], the nominal chemical composition of spherules is currently not known.

There is substantial evidence that the hematite-rich spherules in the Meridiani outcrop are concretions [10]. These concretions may have formed rapidly from breakdown of pre-existing jarosite or other iron sulfates during diagenesis when a "chemically distinct groundwater recharge event" occurred [11]. Formation of the spherules represented one of the latter phases of formation and alteration of the layered rocks encountered by Opportunity. The question addressed in this paper is whether or not there are mineralogical and elemental terrestrial analogues for these spherules whose formation pathways are consistent with formation by aqueous processes and that might provide insight into the overall system that produced the layered sulfate-rich deposits observed by Opportunity.

According to [14], diagenetic, hematite-cemented concretions found in the Jurassic Navajo Formation (quartz arenite in southern Utah) are possible terrestrial analogues for Meridiani spherules. The Navajo Formation (NF) concretions form in porous, relative insoluble quartz arenite by dissolution of iron oxides by reducing fluids and subsequent Fe precipitation to form spherical Fe- and Si-rich concretions (SiO_2>60%) when the Fe-rich fluids encounter oxidizing groundwater [14]. Compared to Meridiani Planum (MP) spherules, however, NF spherules have a higher value for the SiO_2/Fe_2O_3 ratio (>1.5 and <1.3 and for NF and MP spherules, respectively) and are therefore not good compositional analogues for Meridiani spherules. However, the formation process for NF spherules may be broadly applicable to Meridiani Planum. Simplistically, the process would involve percolation of reducing, Fe^{2+}-rich, and perhaps sulfate-rich fluids through porous material with basaltic bulk composition and precipitation of Fe^{3+}-rich concretions when oxidizing conditions are encountered. An important consideration for this model applied to Meridiani Planum is whether fluid transport can be maintained in a material that is likely to be considerably more soluble with respect to the Fe^{2+}-rich fluid than quartz.

In this paper, we report a terrestrial mineralogical and morphological analogue for the Meridiani Hm- and Fe-rich spherules. The terrestrial spherules were formed in association with aqueous, acid-sulfate alteration of basaltic material on Mauna Kea volcano (Hawaii). The Mauna Kea (MK) spherules are mineralogically hematite and have SiO_2/Fe_2O_3<0.04.

2. Samples and methods

Sample HWMK745R is a clastic volcanic breccia rock (~10 cm in diameter) collected at ~13,000 ft on the Puu Poliahu cone of Mauna Kea volcano on the island of Hawaii. Puu Poliahu is a subaerial cinder cone that