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Research paper

Pedogenic hematitic concretions from the Triassic New Haven Arkose, Connecticut: Implications for understanding Martian diagenetic processes

J.H. Wilson^{a,*}, S.M. McLennan^a, T.D. Glotch^a, E.T. Rasbury^a, E.H. Gierlowski-Kordesch^b, R.V. Tappero^c

^a Department of Geosciences, SUNY at Stony Brook, Stony Brook, NY, 11794-2100, USA

^b Department of Geological Sciences, Ohio University, Athens, Ohio 45701-2979, USA

^c National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY 11973, USA

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ABSTRACT

The Triassic New Haven Arkose locally contains mm-scaled pedogenic hematitic concretions, within red arkosic sandy mudstones, that provide insights into concretion-forming processes on Earth and Mars. Concretions represent ~8% of the sediment by mass (~7% by volume), are irregularly distributed and have a near-normal size distribution with a mean diameter of 1.53 mm and graphic standard deviation of 0.64 mm. X-ray diffraction (XRD) and attenuated total reflectance (ATR) spectroscopy indicate that the concretions are composed of ambient sediments: quartz, montmorillonite, and feldspar, and a minor phosphatic phase that is also implied by geochemistry; however, the concretions preferentially exclude coarser grain sizes, and are cemented by hematite and goethite. Optical observations and synchrotron X-ray fluorescence (XRF) chemical mapping indicate that concretions are massive to weakly zoned with respect to hematitic cements. Compared to the surrounding sediments, concretion rare earth elements (REE) are elevated in total abundances, exhibit light rare earth element (LREE)-enrichment, and possess negative Ce-anomalies; Th/U ratios are lower due to elevated U. Mass balance calculations indicate that ~20% of the concretions are composed of iron oxides and that ~30 mm³ of ambient sediment is required to provide the hematitic cement in a single 1.5 mm diameter concretion. Element mobility during concretion formation was tested assuming different immobile elements (Al, Ti, Zr). Assuming Zr immobility provides intermediate results, and indicates the following gains in concretions: Pb (572%), Fe (322%), Mn (142%), REE (438-116%), V (138%), U (124%), Ni (84%), and Nb (58%); other elements show either gains or losses of less than \pm 50%. Ce-anomalies, low Th/U, and elevated V and U abundances point to a significant redox influence on element distributions in the concretions. High iron content, crude internal concentric banding, and redox controls suggest that the concretions are formed in seasonally variable, but generally moist, soil conditions with annual precipitation >130 cm. Trace element enrichment patterns are broadly consistent with derivation from downward percolating weathering fluids. Although the New Haven Arkose pedogenic concretions have significant differences and were clearly formed by different mechanisms than hematitic spherules discovered on Mars, they nevertheless exhibit a number of textural (e.g., sphericity, size distributions) and geochemical (e.g., Ni enrichments) similarities that support models suggesting that the Martian spherules are formed as sedimentary concretions.

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1. Introduction

1.1. Purpose of study

An exciting discovery made by the Mars Exploration Rover (MER) Opportunity at Meridiani Planum, Mars was the presence of millimeterscaled spherules, informally called "blueberries" (Squyres et al., 2004). These "blueberries," in fact, are likely to be hematite-rich sedimentary concretions. Accordingly, the spherules are interpreted to have formed

E-mail address: janette_wilson@brown.edu (J.H. Wilson).

within eolian sulfate-rich sandstones by diagenetic processes involving groundwater interaction (Squyres et al., 2004; Grotzinger et al., 2005; McLennan et al., 2005). Physical erosion of the soft host sandstone then resulted in the more resistant concretions forming a lag deposit on the surface of Mars (Fig. 1), thus explaining the hematite anomaly observed from orbit by the Mars Global Surveyor Thermal Emission Spectrometer (TES) (Christensen et al., 2000). Although the general diagenetic history of these concretions is now reasonably well understood (McLennan et al., 2005; Calvin et al., 2008; Sefton-Nash and Catling, 2008), many of the important details of their formation, such as growth mechanisms (e.g., replacive versus displacive), detailed mineralogy, mineralogic paragenesis, and trace element behavior are not well constrained. There also remains some dispute about the groundwater diagenetic origin of these spherules (see Section 1.3 below).

^{*} Corresponding author at: Department of Geological Sciences, Brown University, Box 1846, Providence, RI, 02912, USA.

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Fig. 1. Images taken by the Mars Rover Opportunity characterizing the distribution of spherules on at Meridiani Planum, Mars. Scale bars are 5 mm across. (a) Microscopic Imager (MI) photograph taken on Sol 144 with arrows showing non-disrupted bedding planes by concretions. (b) MI image taken on Sol 28 with an arrow showing a band around a concretion that possibly traces bedding. (c) Surface lag deposit of spherules is shown in this 2 meter wide false color (750 nm, 530 nm, and 430 nm filters) photo taken by Pancam on Sol 188. (d) MI image taken on Sol 122 showing a "doublet" in a surface lag deposit. Note the similar size of conjoined concretions. (e) MI image taken on Sol 48 showing a "triplet" in a surface lag deposit. Note the middle spherule is larger than the other two and the linear conjunction. (f) MI image taken on Sol 84 showing spherule that has been broken in two by natural processes and that shows no internal structure at MI resolution (30 μ m/pixel).

The recognition of sedimentary concretions on Mars has greatly rejuvenated interest in terrestrial concretions, nodules, and spherules as possible analogs (e.g., Chan et al., 2004, 2005; Morris et al., 2005; Benison, 2006; Chan et al., 2006; Haggerty and Fung, 2006; Souza-Egipsy et al., 2006; Burt et al., 2007; Busigny and Dauphas, 2007; Chan et al., 2007; Tripathi and Rajamani, 2007; Bowen et al., 2008; Golden et al., 2008; Potter and Chan, 2011; Potter et al., 2011). By studying similar materials on Earth, we may be able to gain some insights into the formation of the hematitic concretions on Mars and thus constrain paleoenvironmental conditions on the planet's surface. Although there are a number of geologic settings on Earth that contain hematite- or goethite-rich nodules and concretions (e.g., Alagha et al., 1995; Chan et al., 2004; Morris et al., 2005; Tripathi and Rajamani, 2007; Bowen et al., 2008; Potter and Chan, 2011; Potter et al., 2011), none is a perfect analog – in all cases (including those reported in this study), there are both similarities and significant differences. Geochemical modeling and experiments suggest that Meridiani concretions are formed in a highly distinctive geochemical environment of geographically extensive acidic, high ionic strength, and Mg–Fe-rich groundwaters (McLennan et al., 2005; Tosca et al., 2005; Tosca and McLennan, 2006; Tosca et al., 2008; Hurowitz et al., 2010). This type of environment that produces hematite and jarosite naturally on present-day Earth is most closely associated with the saline acidic lakes of Australia (Benison et al., 2007; Long et al., 2009). Nevertheless, each occurrence of hematitic concretions and nodules, while being an imperfect analog, may provide additional insights into one or more of the processes that operated on Mars. Thus, Calvin et al. (2008) suggested that pedogenic concretions may indeed provide the best physical analog to the Meridiani spherules.

Characterizing the chemical composition of concretions and nodules also provides fundamental constraints on the conditions under which they form. The geochemistry of iron- and manganese-rich pedogenic concretions, in particular, have received a great deal of attention because such data help constrain the composition and history of weathering fluids and thus the paleoenvironmental conditions (Gallaher et al., 1973; Rankin and Childs, 1976, 1987; Zhang and Karathanasis, 1997; Sundby et al., 1998; Palumbo et al., 2000; Stiles et al., 2001; Aide, 2005; Cornu et al., 2005; Rasbury et al., 2006; Tripathi and Rajamani, 2007; Feng, 2010; Potter and Chan, 2011).

The occurrence of soil-forming processes within the Triassic New Haven Arkose in Connecticut has long been recognized (e.g., Krynine, 1950) although their paleoclimatological significance has been more controversial. On the basis of petrography (including recognition of ferruginous concretions in the overlying Portland Formation) Krynine (1950) concluded that warm, humid conditions prevailed during deposition of the New Haven Arkose. Hubert (1977, 1978) identified widespread calcrete horizons that he interpreted as pedogenic features formed during arid conditions. However, more recent detailed petrographic and stratigraphic examinations of these calcretes (Rasbury et al., 2006) indicates diagenetic formation by precipitation from groundwater at several meters depths and accordingly could be consistent with wetter conditions.

Locally the New Haven Arkose (and overlying formations) contains millimeter-scale hematitic concretions that have long been interpreted to form within paleosol horizons (e.g., Krynine, 1950; Gierlowski-Kordesch and Gibling, 2002; Gierlowski-Kordesch and Stiles, 2010).

In general appearance, notably size, shape, and volumetric abundance, coupled with the presence of hematite, these pedogenic concretions¹ bear a striking superficial resemblance to the Meridiani concretions. On the other hand, it is very clear that the geologic setting and mode of formation is not the same as on Mars. Nevertheless, through geochemical and mass balance studies, we may be able to draw some inferences and conclusions that are relevant to understanding the formation of the concretions on Mars. In addition, the geochemistry of these concretions will provide important constraints on pedogenic processes operating within the Hartford Basin during the early Mesozoic. Accordingly, the goals of this study are (1) to evaluate the physical characteristics, petrography, and major and trace element geochemistry of this particular occurrence of terrestrial hematitic concretions in order to place possible constraints on concretion formation on Mars and (2) provide insight into the general process of pedogenic hematitic concretion formation on Earth.

1.2. Geologic setting

The Upper Triassic New Haven Arkose is part of the Newark Supergroup and is preserved as the lowermost sedimentary unit within the Hartford Basin of Connecticut. The paleoenvironmental setting is generally interpreted as a half-graben rift basin characterized by sheetflood to

¹ In the terrestrial literature, the terms "nodules" and "concretions" are both commonly used in pedogenic environments. We adopt the term "concretion" since the objects described are highly spherical (see AGI Glossary of Geology) and this term is used to describe Martian spherules.



Fig. 2. Map showing the basic stratigraphic relations in the Hartford Basin (left). The outcrop locality where the sediment containing concretions was collected is marked with a star. The area shown on the left is located within the bounds of the dotted box on the upper right. The Upper Triassic–Lower Jurassic boundary is currently marked at the contact between the New Have Arkose and the Talcott Basalt formations. Map adapted from Rasbury et al. (2006).

braided fluvial facies (Blevins-Walker et al., 2001; Gierlowski-Kordesch and Gibling, 2002; Wolela and Gierlowski-Kordesch, 2007). The New Haven Arkose is estimated at 2400 m thick (Fig. 2) and contains mudstones, siltstones, sandstones, and conglomerates. During deposition, no lake deposits are formed due to the open hydrologic environment of an incipient rift valley (Bohacs et al., 2003; Wolela and Gierlowski-Kordesch, 2007). Based on single-grain laser fusion ⁴⁰Ar/³⁹Ar age dating of mica grains, Blevins-Walker et al. (2001) concluded that most of the sediments were derived from the Alleghenian Orogen to the east. Sediments were also derived from igneous and metamorphic rocks of the western highlands. Varying amounts of multiple sediment types contributed to the basin fill depending on drainage patterns and hydrology at the time of deposition (Wolela and Gierlowski-Kordesch, 2007).

Sedimentary packages generally fine upward over a few meters from sandstone to mudrock. The mudrock is interpreted as overbank sheetflood deposits upon which soils developed, such as the sample described herein (Gierlowski-Kordesch and Gibling, 2002). There is some dispute about the hydrology during the time of deposition, but according to Krynine (1950) and Gierlowski-Kordesch and Gibling (2002), climate modeling combined with preserved hydrodynamic features and soil development suggest seasonally humid conditions that may have approached a tropical monsoonal environment.

1.3. Mars spherules

1.3.1. Origin

Predominantly dark gray spherules on Mars were discovered by the Mars Exploration Rover (MER) Opportunity both on the surface as an erosional lag and within the mildly indurated rock below the surface at Meridiani Planum, occurring in large-scale, layered sedimentary deposits spanning continuous areas of 150,000 km² (Calvin et al., 2008). Although there are several interpretations of these spherules, the broad consensus is that they represent sedimentary concretions (Chan

et al., 2004; Squyres et al., 2004; Chan et al., 2005; McLennan et al., 2005; Calvin et al., 2008; Sefton-Nash and Catling, 2008). Alternative models involve processes such as hydrothermal activity, accretionary lapilli deposition, carbonatite magmatism, and oxidation of meteorite impact metallic spherules (e.g., Knauth et al., 2005; McCollom and Hynek, 2005; Morris et al., 2005; Haggerty and Fung, 2006; Golden et al., 2008; Niles and Michalski, 2009; Fan et al., 2010).

One alternative model of special interest to this study is that of Knauth et al. (2005), who presented arguments against a concretionary origin for the hematite spherules on Mars. In their model, the Meridiani sedimentary rocks represent an impact base-surge deposit that is formed during an impact of an iron meteorite. The hematitic spherules are thus interpreted as oxidized iron metal impact spherules, an interpretation supported by elevated concentrations of nickel in the Meridiani spherules (see below). Burt et al. (2007) suggested that because Ni²⁺ cannot be oxidized in aqueous solutions (the source for concretions), Ni²⁺ should not have substituted for Fe³⁺ in hematite concretions on account of charge balance differences.

1.3.2. Characteristics

The Rock Abrasion Tool (RAT), panoramic multispectral stereoscopic camera (Pancam), alpha-particle X-ray spectrometer (APXS), and the Mössbauer spectrometer, carried aboard the MER rovers detected the presence of spherules, coarse gray hematite, strong elemental lines of iron, and the Fe³⁺ sextet associated with hematite, respectively (Bell et al., 2004; Klingelhöfer et al., 2004; Rieder et al., 2004; Soderblom et al., 2004; Morris, 2006; Weitz et al., 2006; Calvin et al., 2008). Mini-TES (miniature thermal emission spectrometer), which is sensitive to the top ~100 µm of a surface, did not detect a silicate component to the spherules (Glotch and Bandfield, 2006; Calvin et al., 2008) although geochemical mass balance is consistent with a significant (up to ~50%) silicate component (Jolliff and the Athena Science Team, 2005; McLennan et al., 2005). Calvin et al. (2008) characterized these spherules

as having a dominant, highly uniform, highly crystalline α -Fe₂O₃ composition. Accordingly, there remains an uncertainty about the exact amount of hematite in the spherules.

The same mass balance approach can be used to constrain trace element abundances in Martian spherules. Of the trace elements reported in this paper, the Mars rovers' APXS instrument analyzes only for Cr, Ni, and Zn (it also routinely measures Br and when abundances are high enough, Ge). Of these, it is clear that the Ni is enriched in the spherules by about a factor of 2 over the enclosing sediment, whereas Zn shows no enrichment or depletion. The distribution of chromium is less clear. In some field experiments (e.g., "Berry Bowl" experiment; see Jolliff and the Athena Science Team, 2005) Cr appears enriched at levels similar to Ni but when hematitic (spherule-bearing) soils are compared to normal soils, no such enrichment is apparent.

Calvin et al. (2008) observed two size distributions, where the "normal-sized" spherules have an average diameter of 3.6 mm and the small spherule distribution has an average diameter of 0.8 mm with ranges of 1 mm–6.7 mm and 0.68 mm–1.12 mm, respectively. These values compare to an average diameter of 4.2 mm (s.d. = 0.8 mm) for 454 measured spherules that were embedded within the outcrops at Eagle and Endurance craters (McLennan et al., 2005). Some spherules possess overgrowths or recrystallized rims of sulfate-rich cement where the average total diameter of spherule plus overgrowth is ~0.4 mm larger than that of "normal" spherules (McLennan et al., 2005; Calvin et al., 2008).

The volumetric abundance of spherules within the outcrop was measured at several outcrops near the landing site (McLennan et al., 2005). The overall average is 3.2% (s.d. = 2.0% for n = 17) with values ranging from 1.2% at Eagle crater (s.d. = 0.4%; n = 4) to 4.3% at Fram crater (s.d. = 0.8%; n = 6) and 4.0% at Endurance crater (s.d. = 2.0%; n = 6).

The high sphericity of the spherules (average aspect ratio of 1.06; s.d. = 0.04; McLennan et al., 2005) indicates uniform growth from a central point and non-directional fluid flow in the generally homogeneous sediment (McLennan et al., 2005; Calvin, et al., 2008). The lack of an absorption feature at 390 cm⁻¹ in TES and Mini-TES spectra is consistent with a concentric or radial internal spherule structure (Glotch et al., 2006; Golden et al., 2008); however, the microscopic imager (MI) cannot confirm this with any degree of confidence because of spatial resolution limitations (Calvin et al., 2008). The lack of the absorption feature also indicates that the hematite is dominated by a single crystal axis orientation parallel to the c-axis, like that of laminated or platy crystal grains (Lane, et al., 2002; Glotch and Bandfield, 2006; Glotch et al., 2006; Calvin, et al., 2008).

Further characterization of the spherules by McLennan et al. (2005) revealed rarely developed latitudinal ridges or furrows marking the spherule surfaces (Fig. 1b), occurrence of joined spherules into "doublets" (Fig. 1d) and rarely "triplets" (Fig. 1e), a three-dimensional distribution with uniform inter-spherule distances (i.e., non-random), the lack of occurrence of concentrations along bedding planes within the outcrop rock, and the lack of internal structure at the MI resolution of about 30 µm per pixel (Fig. 1f).

2. Methods

2.1. Samples and sample preparation

This study is based on a single five-kilogram sample of New Haven Arkose mudrock taken from an exposure of the Triassic New Haven Arkose near the town of Meriden, Connecticut on Interstate 691, which was collected by Gierlowski-Kordesch in the summer of 2003 (Fig. 2). In this area, the sequence contains sandstones in channels that generally fine upward, and in turn are overlain by mudrock alluvial deposits, upon which ancient soils developed (Hubert, 1977, 1978; Fig. 3a). The sample was selected to be representative of hematitic concretion-bearing pedogenic mudstones within the New Haven Arkose. The sample is a highly friable, reddish-brown, texturally immature arkose and contains numerous small, dark gray, nearly spherical concretions. Once sampled and stored in a container, the friable nature resulted in partial disaggregation into fragments ranging from about several centimeters to less than 1 mm. One hundred grams of representative material was separated from the whole sample and divided into ten aliquots of approximately 10 g each. All visible concretions were hand-picked from each separate aliquot using a light microscope and tweezers, weighed, and stored in separate vials.

2.2. Sieve analysis of concretions

Prior to sieving, concretions were cleaned using ultrasonication techniques to remove fine particles and dried at ~85 °C overnight. They were then separated into size populations using sieves ranging from 180 µm to 4 mm with 0.5 ϕ intervals and weighed. Sieve sizes included (with the corresponding phi scale in parentheses): 180 µm (2.5 ϕ), 250 µm (2 ϕ), 355 µm (1.5 ϕ), 500 µm (1 ϕ), 710 µm (0.5 ϕ), 1.00 mm (0 ϕ), 1.41 mm (-0.5 ϕ), 2.00 mm (-1 ϕ), 2.83 mm (-1.5 ϕ), and 4.00 mm (-2 ϕ).

2.3. Thin section analysis

The three largest fragments of soil were impregnated with blue epoxy to facilitate thin sectioning and to highlight porosity. A total of six standard thin sections were made, such that successive sections were cut from each of the three pieces of soil. Thus, section UOP1 is paired with UOP2, UOP3 with UOP4, and UOP5 with UOP6.

2.4. X-ray diffraction (XRD)

Approximately 0.03 g of representative concretions from each size class was ground in ethanol by hand using an agate mortar and pestle. Once material was fine enough (no visible grains), it was placed on a clean microscope slide, covered, and air-dried. The process was repeated for a sample containing no spherules. The two samples were analyzed by XRD using a Scintag PAD X diffractometer with Cu K α_1 radiation at 40 kV and 25 mA. Data were collected between 2 θ angles of 5° and 90° with 0.02° scan steps. Although there was some expectation that clay minerals might be detected, analyses were performed on untreated samples. The 'Match!' program and database (version 1.9c) were used to identify mineralogy.

2.5. Attenuated total reflectance (ATR) spectroscopy

Infrared spectra of the concretions were obtained using a Nicolet 6700 FTIR spectrometer equipped with a SmartOrbit ATR accessory, KBr beamsplitter, and a deuterated L-alanine doped triglycine sulfate (DLaTGS) detector with a KBr window. Portions of previously cleaned concretions of sizes 355–500 μ m, 500–710 μ m, 710–1000 μ m, 1–2 mm, and 2–4 mm were scanned. The 5 minute data acquisition period consisted of 256 scans per spectrum. Between scans, the type IIa diamond ATR element was cleaned with ethanol.

2.6. X-ray fluorescence (XRF) microprobe mapping

In order to evaluate the detailed distribution and redistribution of major and trace elements between bulk sediment and concretions, a portion of one of the thin sections was selected for elemental mapping using the X-ray microprobe at the National Synchrotron Light Source at Brookhaven National Laboratory. Due to the brighter X-rays, this technique has higher sensitivity than standard electron microprobe elemental mapping. However, because beamline X26A analyzes samples in ambient conditions, only elements with Z > 20 can be mapped. Major and trace element maps were produced with 5 s dwell times and 10 µm step sizes.



Fig. 3. Field view and corresponding photographs illustrating pedogenic features within the New Haven Arkose. Note that there are no defined soil horizons, which is a typical characteristic of soils in wet climates. (a) Representative concretions separated from sediment ranging from 1.41 to 2 mm in size. (b) Pieces of the friable bulk sediment showing embedded concretions. (c) Small concretions growing close together between larger grains. Note that none of the larger grains is incorporated within the concretions. (d) Rare concretion formed around a piece of plant matter. Note the smaller concretions inside the larger one (upper right interior of rind) and possible incipient concentric layering, both common occurrences in these concretions. (e) Concretion exhibiting concentric growth. (f) Ambient sediment surrounding small concretions under cross-polarized light. Quartz, feldspar, and some rock fragments can be seen.

Synchrotron-based X-ray microfluorescence (μ SXRF) analysis of a thin section of sediment containing concretions from the New Haven Arkose was performed at Beamline X26A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY). Briefly, this beamline uses Kirkpatrick–Baez (K–B) mirrors to produce a focused spot (5 by 9 µm) of hard X-rays with tunable energy achieved via Si(111) or Si(311) channel-cut monochromator crystals. For μ SXRF imaging, the incident energy was fixed at 17 keV to excite all target elements simultaneously. Samples were rastered in the path of the beam by an XY stage oriented in a plane 45° to the beam, and X-ray fluorescence was detected by a 9-element Canberra Ge array detector positioned 90° to the incident beam. Elemental maps were typically collected from a 1 to 3 mm² sample area using a step size

of 10 μ m and a dwell time of 5 s. The fluorescence yields were normalized to the changes in intensity of the X-ray beam (I₀) and the dwell time. Data acquisition and processing were performed using IDL-based beamline software designed by CARS (U. Chicago, Consortium for Advanced Radiation Sources) and NSLS Beamline X26A (data analysis software available at http://www.bnl.gov/ x26a/comp_download.shtml).

2.7. Chemical analyses

About 1 g of each of the concretion size classes that contained sufficient material (Sample 3A, 0ϕ ; Sample 3B, -0.5ϕ ; Sample 3C, -1ϕ) was weighed out. A fourth sample comprised a mix of the 0.5ϕ , 1ϕ ,

and 1.5ϕ (Sample 3D) size classes, summing to 1 g. Each of the four 1gram samples was crushed in ethanol using an agate mortar and pestle into a very fine powder. Four additional samples were assembled by weighing out 10 g each of (a) two aliquots of the original sample containing spherules (Samples 1A and 1B) and (b) two aliquots of the sample with spherules removed (Samples 2A and 2B). Each 10gram sample was crushed in an agate lined shatter box swing mill.

Major and trace element analyses were performed at the Washington State University GeoAnalytical Lab. The laboratory employs a ThermoARL Advant'XP + sequential X-ray fluorescence spectrometer and an Agilent 4500 + inductively-coupled argon plasma quadrupole mass spectrometer (ICP-MS), respectively. The XRF techniques used in the laboratory are described in Johnson et al. (1999). The ICP-MS techniques are described on the Washington State University GeoAnalytical Lab website (www. sees.wsu.edu/Geolab/note/icpms.html). XRF results for international standards and duplicate ICP-MS analyses for sample 1A are given in the Supplemental material (Table S1). Estimates of analytical uncertainty for trace elements by these techniques are estimated as follows: ± 2 ppm for XRF, $\pm 5\%$ for REE by ICP-MS, and $\pm 10\%$ for other trace elements by ICP-MS. Trace elements Sc, Rb, Ba, Sr, Zr, Y, Nb, Pb, La, Ce, Th, Nd and U were determined by both XRF and ICP-MS, and comparison of the two methods is in good agreement. For this study, ICP-MS data are used due to the generally better precision of this method.

3. Results

3.1. Petrography and textural analysis

The bulk sample is a reddish, extremely friable, arkosic, sandy mudstone. Excluding concretions, most of the sediments is composed of mud- and sand-sized particles with less common larger grains. Concretions appear to hold together larger clumps of sediments about \leq 3 cm in size. Smaller concretions in some cases were clustered together, whereas larger concretions were spaced further apart. Point counts of four thin sections (>1150 points total) indicate that the sediment is composed of approximately 65% red mud, 25% quartz, 6.8% concretions, with the remainder being subequal amounts of feldspar (mainly K-feldspar) and rock fragments (mainly granitic and metamorphic) and trace amounts of mica, plant matter, and other material. Outside the concretions, guartz is about 50/50 monocrystalline/polycrystalline. Feldspar and rock fragments typically show signs of substantial in situ alteration suggesting that there could be an unknown amount of pseudomatrix within the sediment. Grains are generally angular to sub-angular and the sediment is very poorly sorted. Secondary cracks in the rock are filled with vein calcite or are vacant. The sediment shows iron bands or bleached areas (Fig. 3e, upper right corner).

Concretions vary in size from 180 μ m to just under 4 mm, a range of over 4 ϕ units. They contain very small detrital grains of mostly monocrystalline and subordinate polycrystalline quartzes, in comparison to the size of the concretion itself. Some concretions also contain small grains of muscovite. Concretions rarely include grains other than quartz and feldspar, although one concretion is formed around a piece of organic matter (Fig. 3d). Concretions of about the same intermediate size tend to touch or be very close to each other. A large concretion is most commonly surrounded by many other smaller concretions. Some concretions exhibit a greater opacity around the rim, with lessening opacity inward in a concentric fashion. Others are darker in the center and exhibit poorly developed concentric layering. Still others appear to be solid masses of the same opacity.

Although the sediment within the concretions is broadly similar to the sediment outside of the concretions, there are differences related to the detrital grain size distributions. Thus, the concretions do not contain any large quartz grains ($>\sim$ 150 µm, excluding grains forming a nucleus to the concretions that can be slightly larger) comparable to the sizes that occur outside of the concretions, although, small quartz grains are also present outside of the concretions. The concretions do not encompass large grains except for one concretion observed to form around a piece of plant matter and another where a coarser quartz grain (~400 μ m) appeared to form a nucleus. The opaque nature of the concretions made it difficult to evaluate textural relationship but no evidence was observed for differences in sand/silt grain shapes within the concretions compared to those outside.

Concretions taken from the ten aliquots of sediment were individually weighed and represent 8.2% (2.2% s.d.) of the sediment by mass. Given that the concretions are likely denser than the ambient sediment, this is consistent with the 6.8% by volume observed in thin sections. Length to width ratios, measured on 104 concretions from the 6 coarsest grain size fractions, average 1.18 with a standard deviation of 0.13.

The results of the grain size analysis of the concretions are given in Table 1 and Fig. 4. The size distribution is near-normal for the size range greater than about 0.35 mm (<1.5 ϕ). The bulk of the concretions lies in the range between 0.71 mm and 2.83 mm (0.5 ϕ and -1.5ϕ). Using the graphic approaches described by Folk (1968), this grain size distribution has the following characteristics: Median (M_d) = 1.47 mm (-0.56ϕ); Graphic Mean (M_z) = 1.53 mm (-0.61ϕ); Inclusive Graphic Standard Deviation (σ_I) = 0.64 mm (0.65 ϕ); Inclusive Graphic Skewness (Sk₁) = -0.09 (near symmetrical); and Graphic Kurtosis (K_G) = 0.98 (mesokurtic).

3.2. X-Ray diffraction (XRD)

The XRD analysis of separated concretions revealed a strong intensity peak for quartz with weaker intensity peaks for hematite, goethite, and possibly montmorillonite (Supplementary Figure S1). Because the samples were not suitably prepared, individual clay minerals could not be identified with any confidence. Some weak peaks may be attributed to a phosphorus-bearing phase; however, the mineral cannot be accurately characterized. Chlorapatite and phosphosiderite were the closest matches, but other expected peaks were not observed.

The XRD patterns of the bulk concretion-free sediment are similar to those of the concretions apart from the absence of goethite and hematite. Other tentatively identified species of chlorapatite, phosphosiderite, and some other phosphorus-bearing phases were also observed but, like the concretions, could not be identified with any confidence.

3.3. Attenuated total reflectance (ATR) spectroscopy

ATR spectroscopy of the concretions also corroborated the presence of clay, hematite, and quartz within the concretions. Spectra were obtained for each of the individual grain size fractions of the concretions but no significant differences were observed (Supplementary material Figure S2). The results for the representative

Table 1

Size distribution of concretions taken from the New Haven Arkose showing weight percentages of each size class compared to the total.

Sieve size	Weight of concretions in sieve pan	Cumulative %	
4 mm (−2Φ)	0 g	0	0
$2.83 \text{ mm} (-1.5 \Phi)$	0.7748 g	9.56	9.56
$2 \text{ mm} (-1\Phi)$	1.5709 g	19.39	28.95
1.41 mm (−0.5Φ)	1.9411 g	23.96	52.91
1 mm (0Φ)	2.5103 g	30.99	83.90
710 μm (0.5Φ)	0.9555 g	11.79	95.69
500 μm (1Φ)	0.3041 g	3.75	99.44
355 μm (1.5Φ)	0.0393 g	0.49	99.93
250 μm (2Φ)	0.0024 g	0.030	99.96
180 μm (2.5Φ)	0.0003 g	0.004	99.964
Totals	8.101 g	99.96	-

Table 2			
Major and trace element data for	sediment and concretions	from the New Haven	Arkose.

	MCL 1A	MCL 1B	MCL 2A	MCL 2B	MCL 3A	MCL 3B	MCL 3C	MCL 3D
	Major elements (wt.%)							
SiO ₂	62.87	62.67	63.55	63.47	46.23	48.81	46.99	42.06
TiO ₂	0.762	0.721	0.695	0.688	1.068	0.983	1.045	1.089
Al_2O_3	15.86	15.36	15.29	15.24	13.31	13.13	13.03	13.15
Fe ₂ O ₃	6.91	6.81	5.72	5.79	26.15	24.91	26.97	25.38
MnO	0.125	0.117	0.111	0.108	0.310	0.302	0.300	0.311
MgO	2.17	2.09	2.06	2.06	1.69	1.73	1.72	1.74
CaO	0.87	0.88	0.87	0.88	0.63	0.69	0.63	0.62
Na ₂ O	0.91	0.92	0.90	0.90	0.65	0.67	0.67	0.64
K ₂ O	4.19	4.07	4.07	4.06	3.39	3.35	3.34	3.43
P_2O_5	0.082	0.077	0.073	0.094	0.056	0.053	0.053	0.052
Sum	94.74	93.70	93.34	93.29	93.48	94.628	94.76	88.48
LOI (%)	5.74	5.63	5.65	5.66	-	-	-	-
	Trace element	s (ppm)						
La	51.2	51.2	41.8	62.7	272.3	236.6	251.1	277.9
Ce	117.2	93.5	84.2	198.0	370.4	273.2	314.4	355.1
Pr	11.4	12.0	9.85	29.8	58.4	41.8	48.2	53.8
Nd	42.8	45.4	37.4	130.4	214.8	143.6	170.5	190.8
Sm	9.17	9.29	7.83	28.0	39.1	24.7	30.1	34.0
Eu	1.92	1.93	1.65	5.73	7.09	4.43	5.34	6.23
Gd	8.43	8.11	6.93	21.6	30.6	20.4	24.2	27.1
Tb	1.40	1.30	1.13	2.91	4.74	3.47	3.93	4.33
Dy	8.53	7.79	6.86	14.8	27.0	20.9	23.2	25.3
Но	1.69	1.53	1.36	2.46	5.07	4.11	4.46	4.82
Er	4.58	4.08	3.69	5.58	12.7	11.0	11.7	12.4
Tm	0.65	0.59	0.54	0.69	1.68	1.53	1.57	1.68
Yb	3.94	3.59	3.37	3.89	9.48	8.89	9.04	9.55
Lu	0.61	0.56	0.53	0.59	1.35	1.28	1.28	1.33
Ba	749	741	727	720	1087	1103	1068	1124
Th	21.7	18.2	17.3	18.1	31.5	28.0	28.7	36.0
Nb	15.1	14.6	14.1	14.1	24.1	24.5	24.9	26.9
Y	41.1	36.5	33.8	60.3	103.4	87.4	94.8	102.4
Hf	6.41	6.22	6.14	6.33	6.22	6.68	6.53	6.15
Та	1.16	1.13	1.08	1.09	1.46	1.49	1.51	1.54
U	3.13	3.09	2.83	3.05	7.71	7.13	7.08	6.89
Pb	57.2	57.2	44.1	43.9	361.5	315.7	330.8	349.7
Rb	168.9	166.1	166.0	164.1	153.0	162.1	157.6	166.4
Cs	7.56	7.47	7.24	7.32	7.71	8.18	7.81	7.98
Ni	39	40	39	39	90	79	80	67
Cr	72	67	69	69	86	71	81	92
Sc	17	17	16	16	16	16	16	17
V	86	86	78	177	254	164	207	229
Sr	71	73	72	72	100	107	102	103
Zr	225	219	215	219	220	239	240	228
Ga	20	20	20	20	21	24	21	18
Cu	20	21	21	19	27	28	26	28
Zn	74	70	68	70	71	69	70	73



Fig. 4. Cumulative percent (by mass) of concretions as a function of grain size. Note that the range $-2\,\varphi$ to $+1\,\varphi$ approximates a normal distribution.

2 mm fraction are compared to laboratory SWY-2 montmorillonite, hematite, and quartz spectra in Fig. 5. The best match for the clay is montmorillonite, which is consistent with the XRD data, but the existing spectral library in use does not include enough clay mineral spectra to accurately discriminate among various montmorillonite types. The spectrum also shows an absorption feature near 3 µm due to the presence of water/OH in the structure, which is most likely associated with the montmorillonite.

3.4. Synchrotron XRF mapping (S-XRF)

 μ S-XRF mapping (Fig. 6) of iron clearly shows zoning within one of the mapped concretions (lower left concretion) while it is much less pronounced in the other. Among the other major and minor elements, Mn and Ti are the only ones mapped that are enriched in the concretions compared to surrounding sediments. In the case of Mn, there is a clear correlation with Fe within the concretions but such a detailed correlation is far less clear for Ti. It appears that K is concentrated around the edges of the concretions and dispersed mainly in the matrix of the sediment, consistent with concentrations within



Fig. 5. IR spectra of concretions from the 2 mm size fraction. (a) Compared to montmorillonite (SWY-2), which appears to be the main contributor to the concretion spectrum. Note that any small features between approximately 1900 and 2400 wavenumbers are artifacts due to diamond that is used in the FTIR spectrometer. (b) Compared to spectra for hematite, quartz, and montmorillonite. A mixture of these three minerals can account for the features between 400 and 1200 wavenumbers in the concretion spectrum.

clay minerals and feldspar. The black (low count) regions on all of the major element maps are locations of quartz grains. Calcium is broadly depleted within the concretions compared to the surrounding finegrained matrix material. However, there are two bright regions within the concretions indicating highly elevated Ca, which are consistent with a trace Ca-phosphate phase also weakly defined in the XRD patterns.

Mapped trace elements show two basic patterns that, compared to the major elements, mirror either the patterns of Fe and Mn or that of Ti. In the case of rare earth elements (REE), using La, Ce, and Y as examples (Fig. 6), it is clear that there is a strong enrichment within the concretions that is correlated to iron oxide (i.e., hematite/goethite) abundances. On the other hand, the ferromagnesian trace elements V and Ni show more muted elemental enrichment in the concretions (the V map is not shown in Fig. 6 because concentrations were so low that at those levels, the V counts are difficult to separate from the Ti (Kb) counts, which have overlapping energy dispersive spectra). Within the concretions, there is no clear correlation of V and Ni with Fe enrichment, nor is there any evidence that these elements are being excluded from the iron-rich regions. Arsenic, an element known to concentrate in Fe concretions (e.g., Partey et al., 2009; Potter and Chan, 2011), was monitored in the synchrotron XRF mapping. However, we cannot accurately quantify the As concentration in the concretions because the standard microscope slides used to mount the sample also contain substantial As. For this reason, As was detected in greater amounts in the background and, therefore, the apparent As concentrations are not considered reliable.

3.5. Major and trace element geochemistry

Samples 1A and 1B, two aliquots of the bulk sediment (i.e., including concretions), are geochemically typical of immature sandstones (e.g., Taylor and McLennan, 1985) based on the major and trace element data (Table 2) and chondrite-normalized REE patterns (Fig. 7). The chemical index of alteration (CIA) is 62 suggesting only modest effects from weathering. Incompatible trace element abundances are somewhat high for sandstones (e.g., Th~20 ppm; Pb~57 ppm; Zr~220 ppm) but ferromagnesian elements are at modest levels (e.g., Cr~70 ppm; V~86 ppm; Ni~40 ppm) and key trace element ratios are unremarkable (e.g., Th/U~6.7; Rb/Sr~2.3) (Table 2). Chondrite-normalized REE patterns (Fig. 7) are similar to typical post-Archean sedimentary rocks, such as post-Archean average Australian shale (PAAS), but with higher overall abundances (Taylor and McLennan, 1985; McLennan, 1989).

Of the two concretion-free samples, 2A is generally similar to the bulk sediments 1A and 1B, apart from lower iron content and lower abundances of selected trace elements (REE, Pb). Both features are consistent with the removal of the concretions (see below). On the other hand, sample 2B is clearly anomalous. This sample was prepared exactly the same way as sample 2A but in spite of this, the REE pattern differs greatly with 2B having highly elevated total REE and a concave down pattern compared to 2A (Fig. 8). The only other differences between 2A and 2B are that 2B is slightly enriched in P_2O_5 (0.094 versus 0.073%) and enriched in V by a factor greater than two (177 versus 78 ppm).

Mass balance calculations indicate that it is not possible that the differences between 2A and 2B are due to simple contamination by concretions. For example, concretions have a negative Ce-anomaly (see below) and have elevated heavy REE abundances (Fig. 7). In addition, although the concretions are enriched in V, they are not enriched in P₂O₅, but are greatly enriched in Pb; neither of these features is observed in sample 2B. Instead, we attribute this anomaly to a trace REE-rich phosphate phase that is less than or equal to about 0.02% of the total sediment mineralogy and that by chance happened to be present in sample 2B, possibly related to biological activity associated with pedogenesis. This interpretation is consistent with the observed V enrichment since V may substitute for P in the phosphate structure. The presence of phosphates is generally consistent with the XRD patterns, although the suggested enrichment is far too low to be detected by XRD. Normalizing the REE pattern of 2B with that of 2A produces a concave-down sediment-normalized REE pattern with peak enrichment in the vicinity of the middle-light REE (Fig. 8). Such a pattern is typical of sedimentary phosphatic phases (e.g., Byrne et al., 1996; Hannigan and Sholkovitz, 2001).

The major element compositions of the concretions are characterized by elevated Fe, Mn and Ti compared to the bulk sediment and concretion-free sediment. Other major elements are depleted to varying degrees. The major element chemistry is also consistent with the



Fig. 6. Synchrotron-based X-ray microfluorescence (μ SXRF) images showing the distribution of Fe, Mn, Ti, Ca, K, Ni, La, Ce, and Y in concretions from the New Haven Arkose. The color scale below the images represents increasing concentration from black to white, lowest to highest, respectively and the scale bar for size is 500 µm.



Fig. 7. Chondrite-normalized REE diagram for sediments and concretions from the New Haven Arkose. Also shown for comparison is the REE pattern for average shale represented by post-Archean Average Australian Shale in (PAAS). Note the general similarity but higher total REE abundances of the sediment samples with the exception of the highly anomalous sample 2B. Also note the high REE abundances and negative Ce-anomaly in the concretion samples.

concretions preferentially excluding coarser grained detritus dominated by quartz and preferentially forming within the clay-rich portions of the sediment. Thus, the SiO₂/Al₂O₃ ratios of the concretions, averaging 3.5 (s.d. = 0.2), is significantly lower than that of bulk sediments (SiO₂/Al₂O₃ = 4.0) or concretion-free sediment (SiO₂/Al₂O₃ = 4.2).

Rare earth element patterns (Fig. 7) are characterized by high abundances and significant negative Ce- and Eu-anomalies. Compared to the surrounding sediments (Fig. 8), the REE patterns are LREE-enriched with significant negative Ce-anomalies but only slight negative Eu-anomalies. Among the other trace elements, compared to surrounding sediments the concretions have higher abundances of Ba, Th, Nb, Ta, U, Pb, Ni, Sc, V and Sr; whereas Zr, Hf, Rb, Cs, Cr, Ga, Cu and Zn are at comparable levels. The implications of these observations for element transport associated with concretion formation will be discussed below.



Fig. 8. REE diagram showing anomalous sample 2B and concretion sample 3C normalized to concretion-free sediment 2A.

Another difference between the concretions and surrounding sediments is that the concretions exhibit lower Th/U ratios. The range of Th/U in the four concretion analyses is 3.9–5.2. In the bulk sediment aliquots (1A, 1B) the ratios are 5.9 and 6.9 and in the concretionfree aliquots (2A, 2B) the ratios are 5.9 and 6.1.

4. Discussion

4.1. Iron mass balance

If the concretions were formed by hematitic cementation of average bulk sediments, then the hematite concentration within them could be determined from simple mass balance calculations (note that our calculations are for total iron oxide calculated as hematite, but include goethite, which was also identified by XRD). However, petrographic evidence indicates that the concretions form almost exclusively within the finest grained fraction of the sediment with particles larger than about 150 µm (fine sand) being mostly excluded. Accordingly, mass balance between the iron contents of the concretions (3C) and concretion-free sediment (2A) suggests that 22.5% hematite and this represents an upper limit. The sand fraction comprises approximately 35% of the volume of the rock and is composed mainly of quartz with lesser feldspar, rock fragments, and mica. If it is assumed that this fraction contains no iron then a lower limit to the hematite content in the concretions, of about 19.9%, can be determined. From these calculations, we conclude that the concretions are composed of approximately 20% hematite (plus goethite).

Assuming that the iron in the concretions is derived exclusively from surrounding sediments, a second question is what region around the concretion would be required to produce the iron for the hematite and goethite? This can also be estimated from mass balance among the concretions, bulk sediment, and concretion-free sediment from the relationship:

$$r_{sed}^3 = r_{conc}^3 * \frac{(Fe_2O_3)_{conc}}{(Fe_2O_3)_{sed}}$$
(1)

where r_{sed} and r_{conc} are the radii of depleted sediment and concretions, respectively, $(Fe_2O_3)_{sed}$ is the weight percent iron oxide extracted from the sediment, and $(Fe_2O_3)_{conc}$ is the weight percent iron oxide added to the concretion. Comparison of the bulk sediment to the concretion-free sediment indicates that 1.10% Fe_2O_3 has been removed to form the concretions. For concretions with 20% Fe_2O_3 as cement, the volume of sediment required to produce a 1.5 mm diameter concretion is 32.1 mm³ or a spherical volume with a diameter of about 3.94 mm.

4.2. Element mobility during concretion formation

The strong enrichment of a variety of trace elements in the concretions compared to surrounding sediments (Table 2, Figs. 7, 8) indicates significant transport of trace elements into the concretions. In order to better quantify this effect, it is instructive to calculate the mass gain/loss of various elements relative to an immobile element ($\Delta C^j/C^i$) between a typical concretion (3A) and surrounding sediment (2A) using the following relationship:

$$\Delta C^{j}/C^{i}(\%) = 100 * \left[\frac{C_{s}^{j}/C_{s}^{i}}{C_{p}^{j}/C_{p}^{i}} - 1 \right]$$
(2)

where *C* is concentration in weight percent, superscripts j and i are element of interest and "immobile" element, respectively, and subscripts s and p are sample of interest (concretion) and reference sample (ambient sediment), respectively.

A critical issue in such a formulation is choosing an appropriate "immobile" element in order to account for possible bulk mass differences. We performed the calculations using three commonly assumed "immobile" elements: Al (Table 3), Ti, and Zr (Supplementary material Table S2). Results differ significantly depending on the element chosen. For Al as the immobile element, the concretions gained Fe (453%), Mn (217%) and Ti (76%) and lost all other major elements to varying degrees. All trace elements show gains in the concretions by amounts varying from as low as 21% (Zn) to as high as 780% (Pb). In the case of Ti being "immobile", all major elements, apart from Fe (214% gain) and Mn (80% gain), were lost from the concretions. Among the trace elements, Pb, REE, U, V, and Ni show significant gains whereas other elements show variable but relatively minor gains and losses. When Zr is chosen, all elements display an intermediate pattern of gain and loss when compared to Al and Ti.

Our interpretation of these results is that there are two fundamental processes influencing the enrichments/depletions between concretions and surrounding sediments: dilution associated with the preferential exclusion of quartz from the concretions and elemental mass transport during concretion formation. Petrographic and major element (SiO₂/ Al₂O₃) data indicate that there is a preferential exclusion of large sand grains from the concretions, likely due to the physical displacive processes of concretion growth. Although these sand grains are mainly quartz, they also include several percent of feldspar, rock fragments, and mica. The result of this would be to make Al effectively a "mobile" element for such calculations. On the other hand, from the geochemical mapping, there is no evidence that Ti is being "diluted" by Fe-rich (hematite-rich) zones of the concretions; and, indeed, if anything, Ti appears very slightly more concentrated in zones where Fe is highest (compare in Fig. 6). This provides evidence that Ti is being redistributed on at least a local level and accordingly is at least suspect as an "immobile" element. Tripathi and Rajamani (2007) also observed evidence for Ti redistribution during pedogenic concretion formation. Zirconium is likely concentrated in the heavy mineral zircon, which is resistant to alteration and fine-grained, but can be heterogeneously distributed within sediments (e.g., along bedding planes). The observation that Zr (and Hf) abundances are fairly uniform (within \pm 7% relative) for bulk sediment (Zr = 219-225 ppm), concretion-free sediment (Zr = 215-219 ppm)and concretions (Zr = 220-240 ppm) may lend some support that this is the most reliable "immobile" element.

Concretions all show a significant negative chondrite-normalized Ce-anomaly (Fig. 7) and, compared to concretion-free sediment, are more enriched in LREE, which possess substantial negative Ceanomalies and slight negative Eu-anomalies (Fig. 8). It is also evident from Fig. 7 that there are no systematic relationships between REE patterns and concretion size.

4.3. Trace element evidence for redox processes

Trace element distributions provide compelling evidence that varying redox conditions influenced concretion formation. All concretions exhibit distinctive negative Ce anomalies with respect to carbonaceous chondrites, average shale, and the surrounding sediment (Figs. 7 and 8), suggesting $Ce^{3+/4+}$ fractionation. This is a distinctive and an unusual feature for most pedogenic concretions that typically exhibit positive Ce-anomalies or no anomalies relative to surrounding soils and sediments (Rankin and Childs, 1976, 1987; Palumbo et al., 2000; Tripathi and Rajamani, 2007; Bowen et al., 2008; Feng, 2010). During weathering, REE are liberated from primary igneous/metamorphic minerals and transported within the soil profile. Under oxidizing conditions, dissolved Ce³⁺ is rapidly oxidized to Ce⁴⁺ and forms highly insoluble Ce-hydroxides and oxides, resulting in the fractionation of Ce from other REE³⁺ (Nesbitt, 1979; Banfield and Eggleton, 1989). In some cases, Ce-enrichment is also related to Mncycling within soil profiles (Rankin and Childs, 1976; Palumbo et al., 2000) and thus is thought to bear some analogy to ocean floor ferromanganese nodules (e.g., Byrne and Sholkovitz, 1996).

Although negative Ce-anomalies are the reverse of what is normally observed in pedogenic concretions, Ce-depletion in the New

Table 3

Gain(+)/loss(-) table for major and trace elements between typical concretion (3C) and surrounding concretion-free sediment (2A). Percent enrichment is calculated using Al_2O_3 as the immobile species for comparison.

Trace element	Percent	Trace element	Percent	Trace element	Percent	Major element	Percent
La	604.5	Tm	241.2	Rb	11.4	SiO ₂	-13.2
Ce	338.1	Yb	214.8	Cs	26.6	TiO ₂	76.4
Pr	473.7	Lu	183.4	Sr	66.2	Al ₂ O ₃	0
Nd	435.5	Ba	72.4	Sc	49.3	Fe ₂ O ₃	453.3
Sm	351.7	Th	94.0	Zr	31.0	MnO	217.1
Eu	279.8	Nb	107.3	Ni	140.7	MgO	-2.0
Gd	309.8	Y	228.9	Cr	37.8	CaO	-15.0
Tb	308.1	Hf	24.8	V	211.4	Na ₂ O	-12.6
Dy	297.5	Ta	64.1	Ga	23.2	K ₂ O	-3.7
Но	284.8	U	193.6	Cu	45.3	P ₂ O ₅	-14.8
Er	270.8	Pb	780.9	Zn	20.8	-	-

Haven concretions is also consistent with redox influence. Accordingly, we interpret these patterns to suggest that fluids carrying REE to the growing concretions were already depleted in Ce relative to other REE due to oxidation and precipitation of Ce-hydroxides near the site of weathering that liberated the REE.

Other trace element features consistent with redox processes include Th/U ratios and V abundances. New Haven concretions exhibit significantly lower Th/U ratios than surrounding sediments, averaging 4.3 (s.d. = 0.6) versus 6.2 (s.d. = 0.5) that result from elevated uranium concentrations in the concretions. This is interpreted to reflect preferential concentration of oxidized U^{6+} in the fluids giving rise to the concretions. We also note that V, another redox sensitive element, is highly enriched compared to other ferromagnesian trace elements in the concretions.

4.4. Implications for New Haven Arkose concretion formation

Caution is warranted in making broad interpretations about the origin and significance of the New Haven Arkose paleosols from our detailed study of a single sample. Nevertheless, a cursory evaluation of the literature demonstrates the remarkable diversity of geometry, mineralogy, and major and trace element chemistry of recent and ancient pedogenic iron-manganese concretions, depending on factors such as soil composition and type, climate, diagenetic history, groundwater chemistry, pH, and redox conditions. Thus, documented pedogenic concretions span a range from dominantly iron-rich, with iron mineralogy consisting of varying proportions of hematite, goethite, and ferrihydrite, to manganese-rich consisting of various Mn-oxide minerals (e.g., birnessite, lithiophorite) and amorphous phases. Concretion sizes, shapes, abundances, and internal structures also vary considerably. Finally, trace element patterns are highly variable with some concretions being depleted in many trace elements and others being enriched. Rare earth patterns vary from being similar to the surrounding sediments to displaying either positive (more common) or negative Ce-anomalies. Accordingly, even though we have only analyzed a single 5 kg sample, it does appear that hematitic concretions within the New Haven Arkose represent an extreme case of trace element enrichments.

The use of paleosols to evaluate paleoclimatic conditions is well established using a variety of proxies (e.g., Kraus, 1999; Stiles et al., 2001; Retallack, 2005). Our results, that focus on hematitic concretions, are of limited relevance to this issue but the high iron contents of the New Haven hematitic concretions (~23% Fe) are consistent with formation under very moist soil conditions and high rainfall. Stiles et al. (2001) evaluated Fe–Mn concretions from modern and paleo-vertisols and suggested that in these environments Fe contents in pedogenic nodules correlated with mean annual precipitation (MAP) with concentrations >20% Fe implying MAP greater than about 130 cm (Stiles et al., 2001; also see Rasbury et al., 2005). In addition, the crude internal concentric banding observed in some of the

New Haven concretions is also consistent with seasonal fluctuations in soil moisture and groundwater redox chemistry (Zhang and Karathanasis, 1997; Stiles et al., 2001; Aide, 2005).

Such concretions commonly are formed in soils composed of mostly clay- or silt-sized particles, exhibiting restricted permeability or impaired drainage (Zhang and Karathanasis, 1997; Stiles, et al., 2001), and in moderate continental to warm subtropical environments (Stiles, et al., 2001). It is hypothesized that the New Haven Arkose was deposited in an environment as described above (Gierlowski-Kordesch and Gibling, 2002).

Several studies of pedogenic concretions observed substantial REE and other trace element enrichment relative to the host sediment (Palumbo et al., 2000; Tripathi and Rajamani, 2007; Feng, 2010). In a study of Mn-rich concretions in Sicilian soils by Palumbo et al. (2000), the presence of manganese phases and Mn redox cycling primarily controlled trace element enrichments (Ba, Sr, Ni, Cu and REE). Exceptions included Pb and V, which were better correlated with iron. In studies of nodules forming in weathered gneisses (Tripathi and Rajamani, 2007) and in terra rosa soils (Feng, 2010), trace elements were interpreted as being derived from the associated weathered rock and transported to the site of concretion precipitation.

The trace element enrichment patterns observed in the New Haven concretions are broadly consistent with derivation from weathering fluids that percolated through the soil to the site of concretion formation and scavenged by the growing concretions. Iron-rich pedogenic concretions typically form in moist subtropical climates with substantial rainfall (Stiles et al., 2001), conditions favoring chemical weathering and development of diffuse weathering profiles (e.g., Nesbitt and Markovics, 1997; Nesbitt, 2003). Under such conditions, mobile trace elements typically are removed from susceptible minerals as they alter and dissolve near the weathering front and are transported down into the soil profile. The fate of these trace elements is then governed by the physicochemical environment. Elements such as alkalis and alkaline earths are rapidly fixed onto secondary clay minerals with high cation exchange capacities. Elements with solubilities that are influenced by pH tend to be transported near the surface where pH is low and then re-deposited at depth, either by precipitation as insoluble oxides/oxyhydroxides or by adsorption onto mineral and particle surfaces, as soil chemistry is buffered and pH increases to near neutral.

The trace elements that are either depleted or least concentrated in the concretions are the alkalis and alkaline earths, P, Zr, Hf, Ta, Cr, Sc, Ga, Cu and Zn (Table 3). Those enriched by about 50% or more (relative to Zr), include, in order of decreasing enrichment, Pb, REE, U, V, Ni, Nb and Th. The limited mobility of Zr and Hf is likely due to their presence in zircon, which is resistant to weathering. Nesbitt and Markovics (1997) observed depletions or limited mobility for alkali and alkaline earth elements, P, Ta, Sc, Ga and Cu (but also V) in the most altered portions of a granodioritic weathering profile. On the other hand, they observed the greatest mobility for REE, Th, U, Cr, Ni, Pb, and As (but also Zn). Apart from the distributions of V and Zn, the pattern of enrichment seen in the New Haven concretions is consistent with such weathering fluids characterized by Nesbitt and Markovics (1997).

As described above, the negative Ce-anomalies observed in the New Haven concretions are also consistent with derivation of trace elements from typical weathering solutions. During weathering of granitic materials, Ce may be oxidized and form insoluble Ce-hydroxides and Ce-phosphates and thus fractionate from the other more soluble REE³⁺, resulting in both positive and negative Ce-anomalies within soil profiles (Nesbitt, 1979; Banfield and Eggleton, 1989; Nesbitt and Markovics, 1997).

4.5. Implications for understanding Martian spherules

The depositional setting, internal characteristics, geometric distribution, and some compositional features of Meridiani spherules differ markedly from the New Haven concretions. The former are interpreted to have grown as a result of groundwater diagenesis of well-sorted eolian sulfate-rich sandstones with an altered 'basaltic' provenance whereas the latter are formed in a pedogenic environment within poorly sorted fluvial arkoses of 'granitic' provenance. It is interesting to note here that the Hartford Basin fill contains basalt flows interlayered with the upper sedimentary formations (Wolela and Gierlowski-Kordesch, 2007). Meridiani spherules lack internal structure at MI resolution (30 µm/pixel) whereas the New Haven concretions incorporate the finer-grained portions (fine sand through clay) of the poorly sorted sandstone and also show crude internal compositional layering. Meridiani spherules possess an over dispersed (uniform) rather than random distribution consistent with competitive concretion growth (McLennan et al., 2005). We did not measure the spatial distribution of the New Haven concretions but visual inspection suggests neither random nor uniform geometries but rather some evidence for clustering, presumably related to pedogenic processes. In both cases, the spherules contain hematite but with the Meridiani examples having at least a factor of two greater hematite abundances. Thus, the New Haven concretions incorporate about 20% hematite/goethite whereas the Meridiani spherules have in excess of 50% hematite.

Other textural and compositional attributes are more broadly comparable and provide some insight into the origin of the Meridiani spherules. The overall abundances of the spherules agree to within about a factor of two. The New Haven concretions represent 6.8% by volume of sediments. In the vicinity of the Opportunity landing area (e.g., Eagle, Fram, and Endurance craters), McLennan et al. (2005) estimated a volumetric proportion of 3.2% (s.d. -2.0%) but ranging up to 4.3% at Fram crater. The size distributions are also similar. The New Haven concretions average 1.53 mm diameter (s.d. = 0.64 mm; coefficient of variation, CV = 42%) with a near-Gaussian size distribution. Calvin et al. (2008) completed the most thorough evaluation of Meridiani spherule sizes. They recorded two populations: a high abundance mode with average diameters of 3.60 mm (s.d. = 1.00 mm; CV = 28%), with a near-Gaussian size distribution, and a minor mode with average diameters of 0.82 mm (s.d. = 0.092 mm; CV = 11%). Shapes are also similar with Meridiani spherule aspect ratios averaging 1.06 (s.d. = 0.04; CV = 4%) and New Haven concretions averaging 1.18 (s.d. = 0.13; CV = 11%). Thus, the New Haven concretions are only slightly more asymmetric and more variable in shape. Most Meridiani spherules are more highly spherical than are the New Haven concretions but observations south of Endurance crater on Meridiani Planum indicate that the Martian spherule shapes commonly are significantly more irregular than those reported by McLennan et al. (2005) closer to the Opportunity landing site (Calvin et al., 2008).

Comparisons of major element abundances, apart from iron, are not particularly insightful given the fundamentally different provenance of the host sediments. Since the Opportunity Rover only routinely analyzes the trace elements Cr, Ni, Zn and Br, the strong enrichments in most trace elements observed in the New Haven concretions similarly cannot be compared meaningfully to the Meridiani spherules. The question of Ni enrichments may be significant in terms of discriminating between the models of Meridiani spherules as its enrichment there has been used to refute a concretion origin (Knauth et al., 2005).

Knauth et al. (2005) listed the major arguments for suggesting that the Meridiani spherules are not sedimentary concretions: (1) high sphericity is uncommon in sedimentary concretions; (2) uniform size distribution is uncommon in sedimentary concretions; and (3) elevated Ni abundances in Meridiani spherules, by about a factor of two over the host sediment, are unlikely in hematite concretions where Ni²⁺ will not substitute for Fe³⁺ in hematite due to the charge imbalance.

Current and past research is generally inconsistent with these arguments, with respect to sedimentary concretion formation mechanisms and trace element partitioning behavior. Remarkably spherical sedimentary concretions as large as meter-scale are well known in the geologic record (e.g., McBride and Milliken, 2006). There are surprisingly few detailed concretion size distribution studies. However, although absolute sizes may vary, having the majority of sedimentary concretions spanning about 3¢ units or less does not appear uncommon (Zhang and Karathanasis, 1997; Palumbo et al., 2000; Bowen et al., 2008; Feng, 2010).

Incorporation of Ni into iron oxides, including goethite (possible precursor to hematite in concretions; e.g. Glotch et al., 2004) and hematite, is not simply controlled by charge differences, although that is important. The literature is replete with examples of natural and synthesized goethite and hematite containing significant levels of nickel (e.g., Singh and Gilkes., 1992; Trolard et al., 1995; Park and Kim, 1999; Singh et al., 2000, 2002; Carvalho-E-Silva et al., 2003; Jeon et al., 2004; Saragovi et al., 2004; Cornu et al., 2005; Landers and Gilkes, 2007). Nickel substitution into the iron oxide structure can be accommodated either by coupled substitutions (e.g., Ti⁴⁺, Mn⁴⁺) or structural defects. Goethite and hematite surfaces are also highly favorable sites for trace element adsorption. This latter process could be relevant to the Meridiani case where proposed precursor minerals might include ferrous sulfates ($Fe^{2+}SO_4 \cdot nH_2O$) and jarosite $((K, Na, H_3O)Fe^{3+}(SO_4)_2(OH)_6)$ (these are minerals that can also incorporate large amounts of Ni) and where diagenetic conditions were likely characterized by highly limited integrated temperature-water/ rock ratio conditions (Tosca and Knoll, 2009).

In addition to these general arguments, the New Haven concretions provide a relevant specific example. The hydrologic regime of muddy sediment within a soil, if anything, is likely less suitable for the formation of highly spherical and uniformly sized concretions than are very well sorted mature to supermature sandstones, such as the Burns formation at Meridiani Planum. Nevertheless, the New Haven concretions have remarkably similar textural attributes compared to the Meridiani spherules. The aspect ratios are within about 10% relative (1.18 versus 1.06) although the New Haven concretions are somewhat more variable. While the New Haven concretions are somewhat more variable in size distribution than is the larger mode of Meridiani spherules (coefficients of variation of 42% versus 28%), greater than 99% of the New Haven concretions are between 0.5 and 4 mm or within about 3ϕ units. In this regard, the New Haven concretions have a similar size range compared to Meridiani spherules (also note that there is a second minor size mode (Calvin et al., 2008) thus increasing the known variability of Meridiani spherule sizes). The suggestion that the highly spherical and uniform size distributions of the Meridiani spherules is inconsistent with their being sedimentary concretions is not in accord with what is known about sedimentary concretions in general and the New Haven concretions in particular.

Comparing absolute Ni abundances in terrestrial hematitic concretions to the Meridiani spherules is hampered by the fact that the sedimentary provenance (e.g., granitic versus basaltic) differs. As such, we focus on the relative degrees of Ni enrichment. As pointed out above, Meridiani spherules are enriched in Ni by about a factor of two over surrounding sediments. The New Haven concretions contain an average of 79 ppm Ni (s.d. = 9) and therefore are similarly enriched by slightly more than a factor of two over the bulk sediments (39.5 ppm Ni). The cause of this enrichment is not entirely clear. Mass balance calculations indicate that at most, about one-half of the enrichment could be due to the dilution effect of the concretions preferentially excluding large quartz grains. Geochemical mapping (Fig. 6) suggests that Ni is uniformly distributed throughout the concretions correlating neither positively nor negatively with Fe content. The degree to which Ni may have been transported into the concretions depends on which element is considered 'immobile' (Table 3); but, in all cases, Ni addition between about 35% and 140% is indicated.

Relevant Ni data for terrestrial concretions are scarce. In many cases, terrestrial Fe-rich concretions also contain a significant amount of Mn-oxides, which are well known to concentrate Ni (Palumbo et al., 2000; Cornu et al., 2005; Tripathi and Rajamani, 2007). Nevertheless, in terrestrial ferromanganese nodules where Mn content is \leq 0.5%, enrichment factors on the order of 50% to well over 100% have been observed (Cornu et al., 2005; Tripathi and Rajamani, 2007; Potter and Chan, 2011).

Thus, based on the textural and chemical results from the New Haven concretions coupled with a review of the literature, we conclude that the spherical nature, limited size distribution, and elevated Ni in the Meridiani spherules do not provide convincing evidence against an origin as sedimentary concretions.

5. Conclusions

In our search to evaluate the New Haven hematite concretion characteristics as they pertain to Mars, the analyses indicate that the New Haven concretions are composed of quartz, goethite, a type or types of unidentified montmorillonite, and ~20% hematite. Although the Meridiani hematite spherules, which originate from a different provenance than the New Haven concretions, are composed of greater amounts of hematite (\geq 50%) and have differing spatial distributions and interior features, both sets of concretions exhibit similarities in shape, size, and volumetric proportions. Geochemically, the high Ni content of the New Haven concretions, where groundwater process is clearly responsible for their formation, indicates that Ni enrichment does not demand an alternative explanation for the formation of Meridiani spherules.

Contributions of this work to knowledge about pedogenic concretion formation on Earth support existing studies, but have some interesting differences from the majority of concretion studies. The factors that agree with previous studies are: (1) concretions are enriched in REE and a variety of other trace elements compared to the surrounding sediment, (2) the REE patterns are characterized by Ce anomalies, and (3) Th/U ratios differ between concretions and surrounding sediments. In contrast to common pedogenic concretions, the iron-rich New Haven concretions do not contain considerable amounts of manganese or Mn-enriched phases and the REE patterns of concretions are characterized by negative Ce-anomalies, rather than the expected positive anomaly. Although the properties of the New Haven concretions differ as described above, the existence of a Ce anomaly, the enrichment of the concretions in V, and the fact that the Th/U ratio of the concretions is lower than the surrounding sediment suggest that redox processes were involved in concretion formation.

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