MINERALOGY, GEOCHEMISTRY AND MÖSSBAUER SPECTROSCOPY OF IRON CONCRETIONS FROM JURASSIC FORMATION OF KUTCH, INDIA: MORE INSIGHTS IN TO THE DEPOSITIONAL HISTORY AND IMPLICATIONS TO MARTIAN "BLUEBERRIES". D. Ray[1], A.D. Shukla[1], and U. Chandra[2]. [1]Physical Research Laboratory, Ahmedabad 380 009, INDIA, [2]University of Rajasthan, Jaipur 302004, INDIA (dwijesh@prl.res.in).

Introduction: The formation history of sedimentary hematite concretions is mostly diagenetic, resulted due to fluid-sediment interactions and they are common and widespread in sedimentary rocks throughout the geologic history. The hematite concretions bearing Jurassic Navajo Sandstone of Southern Utah, USA is one of the well studied Mesozoic hematite concretions studied till date and suggested diagenetic in origin [1]. Precipitations of hematite concretions is thought to occur when Fe(II)-bearing (reduced) fluids get in contact with oxygenated groundwater, where oxidation of Fe at near-neutral pH would produce Fe^{3+} at the mixing interface. Despite their ubiquity, there is limited understanding on growth mechanism (e.g. replacive vs displacive), mineralogy and especially the trace element behavior. The exciting discovery of hematite spherules at Meridiani Planum, Mars (informal name "Martian blueberries") by Mars Exploration Rover (MER) Opportunity has brought surge more in the terrestrial hematite research [2]. The nature of Martian spherules and exact mechanism of the formation process is still debatable. Several hypotheses including the impact origin have been suggested for Martian hematite spherule, but sedimentological evidences so far is found to be the strongest and relevant, however, further studies are necessary to prove the point [3,4].

Until there is sample return mission to Mars, a better understanding on terrestrial hematite formation process will definitely lead an improved insights on diagenetic processes and post depositional changes on ancient concretion bearing terrestrial strata and these can be applied for Mars as well. In this communication, we report petrography, mineralogy, geochemistry and Mössbauer spectroscopic analyses of sedimentary concretions of Mesozoic Jhuran formation, Kutch, India.

Petrography: Preliminary results including the geological setting of Jhuran formation has been described earlier [5]. Concretions bearing sandstones are mostly poorly sorted and composed of angular quartz grains, kaolinised feldspar and a few muscovite and opaque minerals. The matrix proportion is high (>15%) and generally iron-rich. Fine iron grains often occur along the mineral boundaries and mineralogically the sandstone fall under the classification - arkosic wacke. Smaller iron concretions are mostly spherical in shape with rare doublet and triplet types. Interestingly, a few of the concretions show 'comet trails' (Fig. 1a). By contrast, the larger concretions are well exposed and largely affected by the erosion (Fig. 1b).

Fig. 1a Smaller iron concretions with 'comet trail' in Jhuran sandstone

Fig. 1b Large iron concretion as erosional lag deposit in sandstone

Geochemistry: Chemical index of alteration (CIA) of sandstone vary from 66 to 68, which suggest modest weathering. Sandstone and rind concretions fall parallel to the A-CN line of A-CN-K diagram while there is a distinct iron enrichment trend as expected for rind concretion in A-CNK-FM plot (after [6], Fig. 2a,b).

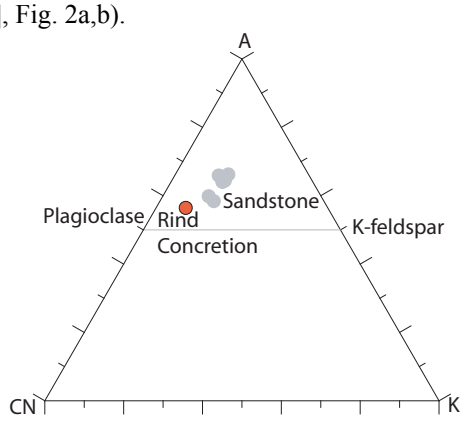

Fig. 2a A-CN-K (Al_2O_3-CaO+Na_2O+K_2O) diagram showing the weathering trend

Chondrite normalized rare-earth element patterns are similar and uniform for sandstone and concretions with characteristic negative Eu anomaly (Fig. 3). Total REE (ΣREE) content of concretion is relatively higher (444 ppm) as compared to the associated sediments (up to 177 ppm). Moreover, core of the smaller sized concretions are REE-rich (444 ppm) as compared to iron-rich rind (230 ppm). By contrast, larger sized concretions are substantially REE-poor (33-47 ppm) and they lack the typical negative Eu anomaly, rather weak negative Ce anomaly is often noticeable.

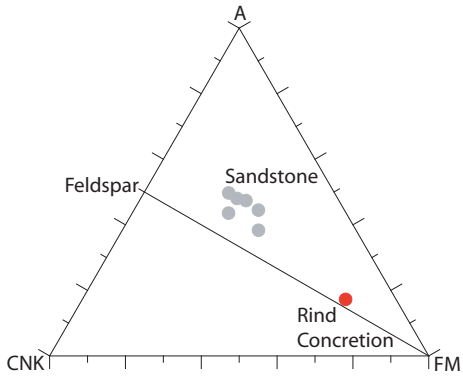

Fig. 2b A-CNK-FM (Al_2O_3+CaO+Na_2O+K_2O-FeO+MgO) diagram showing the weathering trend

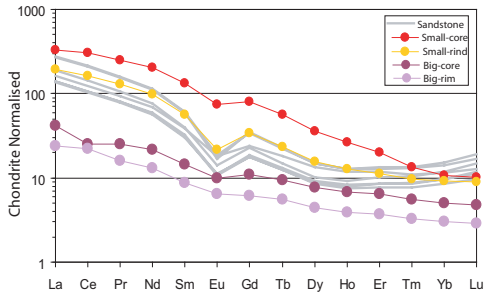

Fig. 3 Chondrite normalized REE of sandstone and concretion core and rind.

Th/U of the concretions vary from 3.3 to 6 while for the sediments it range from 7 to 11. Larger concretions are exceptionally rich in V (up to 152 ppm).

X-ray diffraction and Mössbauer Spectroscopy: XRD and Mössbauer analyses were carried out for identification of mineral phase and to obtain the Fe oxidation state of concretions and the associated sediments. XRD of sediments show distinct and characteristics peaks of Quartz and Kaolinite, respectively.

The Mössbauer analysis on rind of concretion (S1) shows presence of magnetite or γ-Fe_2O_3 (both have spinel structure, Fig. 4). By contrast, iron-rich sediments or core of concretion shows increase in the Fe^{3+} (ferric oxide) composition with the decrease in the magnetic component.

Discussion: The most abundant types of concretions as found in Jhuran sandstone are spheroidal in shape with thin rinds (i.e. rind concretions). In contrast, layering in a concentric fashion is likely more common in larger varieties of concretions rather smaller counterpart. Growth patterns appear to be uniform amidst with lack of inward growth. 'Comet trails' like structure associated with the concretions probably relate with the directional fluid flow.

The Jhuran sandstones are typically poorly sorted combination of quartz and K-feldspar, therefore suggesting fluivial environment.

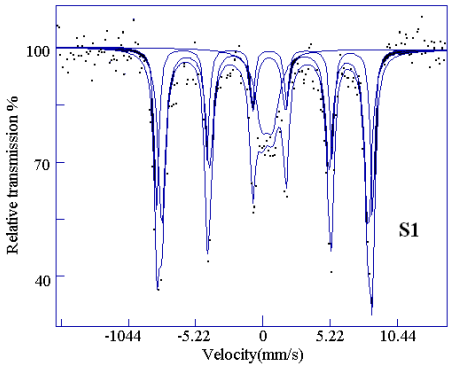

Fig. 4 Room temperature Mössbauer pattern of rind concretions (S1).

However, occasional high angle cross bedding is generally found common in aeolian environment. The paleodepositional environment of Jhuran formation is interpreted as sublittoral to deltaic.

Trace element geochemistry is interesting as they are useful proxies to redox conditions. Concretions are, in general, characterized by low Th/U and V content vis-á-vis higher U content suggesting fluids are oxidized and preferentially incorporated the U^{6+}. Differences in trace element signatures of smaller rind concretions as compared to larger concretions suggest different fluid composition. Negative Eu anomaly vis-à-vis absence of Ce anomaly within rind concretions and host sediments favor redox conditions prevailed during the formation of concretions. Similar trace element geochemistry of sediments and rind concretions probably refer to a single event resulted formation of the rind concretions.

Mössbauer spectroscopy of sandstone and concretions suggest values for the doublet are comparable with reported value of nano phase Fe oxide of Navajo sandstone, Utah [7] and interestingly similar to Burns formation, Meridiani Planum, Mars [8,9].

A synthesis of result suggests uniform fluid composition resulted rind concretions whereas multiple precipitation events are likely for the formation of larger concretions.

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