

SPHERULES IN THE MARTIAN POLYMICT BRECCIAS. II. CHEMICAL SEDIMENTARY PROCESSES ON MARS. M. Humayun¹, S. Sillitoe-Kukas¹, R. Hewins^{2,3}, B. Zanda^{2,4}, D. E. Moser⁵, G. Arcuri⁵, A. J. Irving⁶, and J.-P. Lorand⁷, ¹Florida State University, Tallahassee, FL 32310, USA (humayun@magnet.fsu.edu); ²IMPMC, Sorbonne Université, MNHN-UPMC, 75005 Paris, France; ³Rutgers University, Piscataway, NJ 08854, USA; ⁴IMCCE, Observatoire de Paris - CNRS UMR 8028, 75014 Paris, France; ⁵University of Western Ontario, London, Ontario N6A 5B7, Canada; ⁶University of Washington, Seattle, WA 99123, USA; ⁷CNRS UMR 6112, Université de Nantes, 44322 Nantes Cédex 3, France.

Introduction: The chemical properties (hydration, oxidation, carbonation) of sediments reflect the composition of the atmosphere and hydrosphere from which sediments form, as much as that of the igneous source material from which detritus might be derived. The dominant lithology of martian clastic sediments at Gale crater are clastic rocks (e.g., shales) of basaltic composition that have been only slightly modified by weathering and are crosscut by Ca-sulfate veins [1]. No such rocks have been described from the meteoritic record, which is dominantly igneous [2]. Alteration veins in nakhlites have permitted the first laboratory studies of the martian environment [3].

The discovery of a martian meteoritic breccia [4,5] enabled the exploration for potential martian sediments present as distinct clasts. Vitrophyric spherules formed by impact melting of martian protoliths [6-8] were recognized as containing chemical enhancement of alkalis indicative of the presence of clays in the protolith [9]. In this study, we report detailed chemical studies by LA-ICP-MS of 14 vitrophyric spherules from the paired stones: NWA 7034, NWA 7475, NWA 7533, NWA 8171 and Rabt Sbayta 003, of a single large breccia find, to investigate in more detail the chemical signatures of impact melted martian sediments. A companion abstract described the samples, methodology, origin and internal chemical zoning [10].

Results: Normative compositions are summarized in [10]. Although the spherules are internally zoned [10] bulk compositions were calculated from line scans performed across the spherules. Figures 1-3 show elemental abundances of bulk spherules and an olivine-bearing spherule [6]. The elemental composition of the spherules is similar to that of the bulk breccia with notable exceptions. Fig. 1 shows that the spherules are all enriched in Fe (30 %), Co and Ni relative to the breccia. Extreme enrichments occur in Zn (Fig. 1), Ba (Figs. 2-3) and the alkalis + Tl (Fig. 3). Boron is variably enriched in some spherules (Fig. 1). Depletions in B, P, Cu (Fig. 1) and U (Fig. 2) are possibly related to volatile element depletion during impact melting [10]. Fig. 2 shows positive anomalies in Nb, Ta, Zr, Hf and Ti, which are found to be correlated. Alkali enrichments are not due to feldspar addition (Fig. 3).

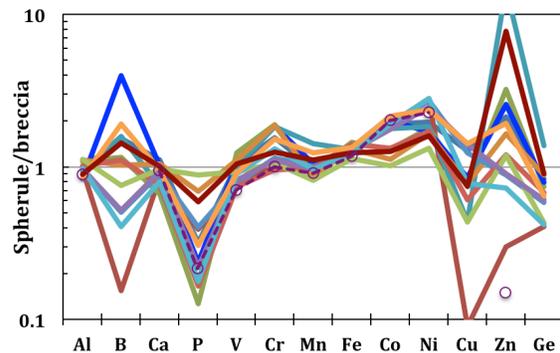


Fig. 1: Transition element and B abundances of spherules normalized to NWA 7533 bulk composition. Purple circles represent the spherule reported by [6].

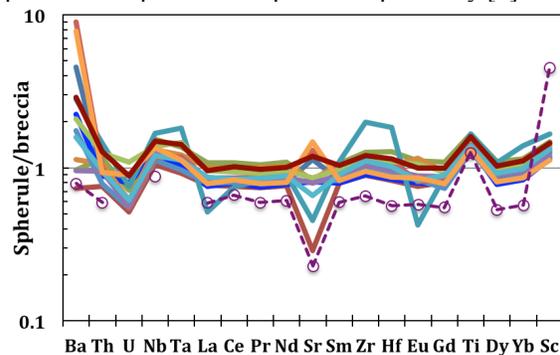


Fig. 2: Refractory element abundances of spherules normalized to NWA 7533 bulk composition.

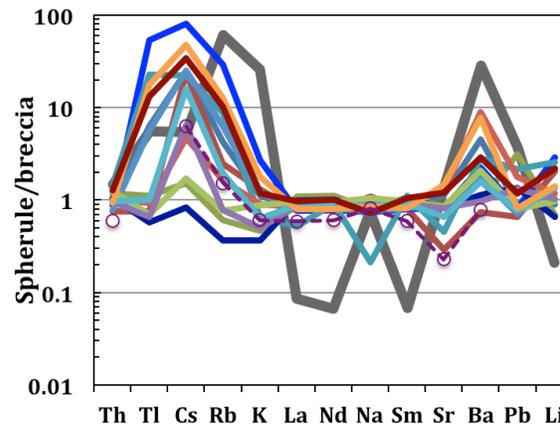


Fig. 3: Selected elemental enrichments of spherules compared with alkali feldspar (dark band) from NWA 7533 [5].

Discussion: The spherules are devitrified impact melts [6-8]. The extreme enrichments of Zn, Rb, Cs, Ba and Tl rule out a primary igneous origin of the spherules.

Evidence for clay minerals in the target rocks. Cation exchange of alkalis and Tl on clay minerals in neutral to alkaline pH waters results in Cs>Rb~Tl>K>Na replacement of protons in the clay lattice [11, 12]. Terrestrial smectites formed by *in situ* alteration of oceanic basalts show similar enrichments of alkalis and Tl [13]. New data on 14 spherules confirm that the protoliths of 11 of the 14 spherules were variably enriched in clays formed in neutral pH waters. The spherule compositions have a chemical index of alteration (CIA) that ranges from 32 to 47, indicating that alkalis have not been leached or rather have been added. Martian clastic rocks from Gale Crater show CIA values <50, a major distinction with terrestrial shales [1]. Since the spherules represent random samples of martian clastic rocks, a CIA<50 is ubiquitous on Mars.

Evidence for detrital heavy mineral enrichment. The main distinction between *in situ* basalt alteration (e.g. terrestrial oceanic crust [13]) and shales lies in the formation and transport of detrital minerals. Such transport processes fractionate dense minerals, e.g. zircons, ilmenites, magnetites, chromites, etc., from silicates resulting in positive anomalies of Ti, Nb, Ta, Zr and Hf. All of the spherules exhibit positive anomalies of Ti, Nb and Ta (Fig. 2). Three spherules with the largest Ti-Nb-Ta anomalies also exhibit positive anomalies in Zr and Hf (Fig. 2) implying zircon enrichment in the detrital minerals. The Ti abundances of the spherules correlate with Fe, in a ratio indicating either titanomagnetite or a mixture of Fe-oxides (magnetite, maghemite, hematite) and ilmenite. This is corroborated by the Fe/Mn ratios of the spherules that are higher than martian igneous rocks and even of the bulk breccia (NWA 7533). However, Fe can be added to sediments both as detrital minerals and as precipitates from solution. In spherules in which heavy mineral enrichment is found, a significant portion if not all of the target rock had to be detrital (e.g., shales). Target rocks that underwent clay formation in the subsurface are not likely to show detrital mineral fractionation.

Evidence for sulfates in the protoliths. In the bulk spherules, there are strong enrichments in Ba more than in Sr (Fig. 1), but not in Ca (Fig. 1). Incorporation of highly insoluble Ba-sulfates (barite) could contribute such a chemical signature. The barite could be detrital barite, or could come from hydrothermal or diagenetic veins that cross-cut the target rocks. The Sheepbed mudstones (Yellowknife Bay, Mars) are criss-crossed by Ca-sulfate bearing veins [14]. A notable feature of these veins is the low relative abundances

of Sr and Ba [14], so the veins are not an adequate component for spherule formation. A model for the Sheepbed veins proposed that a “dirty sulfate” evaporite layer was formed that was re-dissolved to remove Ca-rich fluids that formed the veins [15]. The predicted residues would be strongly enriched in Ba, and somewhat in Sr, due to the low solubility of Ba- and Sr-sulfates. Such sulfate residues would fit well as mixing endmembers for the spherule protoliths.

Constraints from Ni and Co abundances. The presence of high Ni contents (1,021 ppm) in an olivine-bearing spherule led [6] to infer meteoritic contamination of the impact melt. In this study, we noted that the abundances of highly siderophile elements in the spherules are at levels comparable (Ru, Pt) or lower (Re, Os, Ir) than that of the breccia [10]. The high abundances of Ni and Co are harder to appreciate on a breccia-normalized basis since the bulk breccia is strongly enriched in Ni (450 ppm) due to the incorporation of meteoritic impactor debris [5, 7]. The presence of high Ni and Co is likely due to weathering of source rocks similar in composition to the bulk breccia followed by precipitation of Ni and Co as Fe(±Mn) oxyhydroxides into the detrital fraction of sediments deposited in lakes. The enrichment factor measured is proportional to the ratio of the volume of watershed rock leached for Ni to the volume of the deposited sediments. Watersheds that are 4-25 times the lake area are implied. This geochemical estimate is on the lower end of the range of geomorphologically estimated watershed area/lake surface areas for lakes on Mars [16].

Acknowledgements: We are extremely grateful to Mendy Ouzillou (NWA 8171) and Ben Hoefnagels (Rabt Sbayta 003) for their generous loans of polished slabs containing multiple spherules.

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