

FROM MARTIAN REGOLITH BRECCIAS NWA 7533

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Introduction : Martian regolith breccias NWA 7533 and paired samples that contain relicts of the earliest (pre-noachian) martian crust [1][2] are valuable objects for investigating chalcophile siderophile metal cycling inside the early martian crust. Due to repeated impacts and sulfur degassing, early noachian/prenoachian igneous components are nearly devoid of magmatic sulfides. Breccias were re-enriched in S about 1.4 Ga ago by hydrothermal, near neutral S-rich fluids that precipitated accessory pyrite (<1 vol.%) [3].

Materials and methods: Chalcophile-siderophile trace element systematics were investigated on two polished thin sections (7533-5 and 7533-7) from fifty two pyrite crystals mostly located inside late vein systems, lithified matrix and fine-grained impact melt rocks. Thirty elements were analyzed with a Photon machine analyte G2 193 nm laser + Bruker 880 ICPMS using IUSGS standard Mass 1 and in-house PGE-doped sulfides [4].

Results and discussion: Highly siderophile element (HSE) micronuggets were detected in half of the analyzed crystals as concentration spikes in time-resolved LA-ICPMS data (up to 3 nuggets in a single pyrite crystal). These nuggets show various combinations between refractory platinum-group elements (Os-Ir-Ru-Pt-Rh) as well as single Pd peaks. Platinum- and iridium-bearing compounds are predominant over Ru- and Os-bearing compounds, in agreement with the stronger partitioning of the latter two elements in pyrite. Where calculations of concentrations were possible, Pt/Ir and Pt/Os ratios are close to chondritic, while Mo and Re have occasionally been detected. Concentrations of Pt and Mo broadly correlate positively. Such compositions are characteristic of refractory metal nuggets (RMN) found in carbonaceous chondrites

The other chalcophile and siderophile elements analyzed are interpreted as being held in solid solution inside pyrite as they produce more stable, smoother signals in time-resolved LA-ICPMS data. Like previous EMP and SEM analyses [3], LA-ICPMS analyses detect Ni enriched areas (up to 3.0 wt.%) inside the pyrite. Nickel positively correlates with Co and Ni/Co ratios are broadly chondritic (10-20). Hydrothermal fluids delivered the semi-metals As, Se, Te, Bi which now are in solid solution in pyrite or occur as discrete microminerals. A dual origin is also assumed for Mo that occurs both as concentration spikes along with RMN's and a trace element in the pyrite. Selenium concentrations range between 12 and 150 ppm; as expected for hydrothermal sulfides, S/Se is superchondritic (50,000 to 3,300) as is the Se/Ni ratio (0.006). In line with previous EMP data, LA-ICPMS analyses produce a reasonably good positive correlation between Se and Ni which reflects the positive T-dependence of the solubility of both elements in pyrite [3]. Tellurium appears to be strongly enriched with respect to chondritic ratios (Te/Se = 0.3 to >1). Chalcophile metals Ag, As, Au, Hg, Pb, Sb, Tl that usually are strongly concentrated in hydrothermal sulfides occur in low concentration ranges in NWA 7533 pyrite (Cu < 60 ppm; Pb < 30 ppm; Au < 1 ppm; Ag < 1 ppm; As < 6 ppm and Zn < 50 ppm) despite its high-T crystallization. Pyrite appears to be a minor contributor of the whole-rock budget for all these elements. Fe-Ti oxides enclosed in pyrite are repositories for Zn, V, Ga, In and Sn while some mobile elements (As, Sb) were redistributed in Fe-oxyhydroxides by terrestrial alteration.

Pyrite displays mixed signatures, one mostly inherited from repeated meteorite bombardment of the early martian crust and the other from later hydrothermal inputs. Pyrite trapped varied debris of the ancient carbonaceous chondritic impactors [5]. Refractory metals (PGE, Re) were preserved despite the oxidative environment (FMQ+2 log units) that prevailed throughout most of the history of impact breccia [2] while less resistant refractory metals (Mo and Re) were redistributed by late alteration and hydrothermalism. Some RMN's were reprocessed by hydrothermal fluids, as shown by Os-Ir-As-S submicron-sized particles detected by SEM [3] and diffusion haloes of Mo and Te around some RMN's inside pyrite. Nickel and cobalt also track early impactors, although the 1.4 Ga hydrothermal event partly disrupted (disturbed) the correlations inherited from chondrite contribution. Taken as a whole, this event delivered mainly semi metals (Se, Te, As, Bi) along with S. The small input of chalcophile trace elements has no unique explanation. It likely results from i) a strongly degassed, magmatic sulfide-depleted brecciated crust, ii) hydrothermal events involving low salinity, near neutral water-rich fluids that did not provided chloride complexing for extensive transport of these metals and iii) a short duration of the fluid-crust interaction. The negligible substitution of As for Fe likely inhibited the uptake of large cations (i.e., Au, Ag and Pb) in pyrite.

References: [1] Humayun M. et al. 2013. *Nature* 503, 513-516. [2] Hewins R. et al., 2016. *Meteoritics & Planetary Science* (in press) [3] Lorand J.-P. et al. 2015. *Meteoritics & Planetary Sciences* 50, 2099-2120 [4] Lorand J.-P. et al. 2010. *Earth & Planetary Science Letter*, 289, 298-310 [5] Goderis S. et al. 2014, *LPSC XLV*, abstract #2200.