The dynamic history of Mars – adding another puzzle piece from the analysis of Ca-phosphates in martian meteorites

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The existing meteorite record encompasses 208 martian among the ~67,400 classified meteorites in our collections only – some of which may be even paired. In the absence of martian sample return missions so far and in addition to data from martian landers, probes and remote sensing, these rocks, however provide fundamental insights on the formation and evolution of Mars. Martian meteorites are subdivided into (i) nakhlites - olivine-bearing clinopyroxenites, (ii) chassignites - dunites and olivine-chromite cumulates, (iii) Allan Hills (ALH) 84001 - ultramafic orthopyroxenite, (iv) Northwest Africa (NWA) 7034 and paired samples - polymict, regolith breccias, and (v) shergottites - the largest suite of martian rocks. The latter are of magmatic origin and divided into: (a) basaltic, (b) lherzolitic, and (c) olivine-phyric rocks. According to their degree of bulk rock LREE depletion, generated by different degrees of partial melting of the martian mantle, shergottites are subdivided into enriched, intermediate, and depleted rocks. Among the present accessory phases in martian meteorites, apatite group minerals ($Ca_5(PO_4)_3(Cl,F,OH)$) and merrillite ($Ca_{18}Na_2Mg_2(PO_4)_{14}$) are of particular interest, as they occur as abundant, late-stage phases, and, thus are major sinks for incompatible trace elements, such as REEs, U, and Th, making them well-suited for combined chemical- chronological investigations. Martian apatites are prime carrier phases for the halogens F, Cl, Br, I and OH. They are mostly considered to be of magmatic origin, and thus act as a probe for the volatile element and water contents of the mantle sources. Some Ca-phosphates, however, may be affected by assimilation of crustal component(s) on Mars during the latest stages of basaltic crystallization, or interaction with Cl-rich crustal fluids. In this study, a member of the basaltic, enriched suite of shergottites has been selected – the Ksar Ghilane (KG) 002 meteorite, discovered 2010 in Tunisia, hosting an unusually high modal abundance of 3.4 vol.% and up to mm-sized merrillite and apatite grains, exceeding those of other martian meteorites. In a multidisciplinary, high-spatial resolution analytical approach, analysis of Ca-phosphates permits insights into the formation environment and alteration processes of the host rock. The petrological record, together with chronological constraints using the 238U-206Pb systematics reveal that igneous Ca-phosphate in KG 002 formed 80 ± 59 Ma (2σ) ago, the youngest martian phosphate date obtained so far. The REE concentrations, halogen zoning in both phosphate species and variability in x-site occupancy of apatite, together with the chemical record of merrillite indicate crystallization from a highly fractionated, volatile-rich (halogens, OH, and Na), and ferrous source melt and a phosphate crystallization sequence. Microstructural investigation revealed only weak alteration of the grains caused by metamictization and shock metamorphism after crystallization. The halogen (F, Cl, Br, I) and stable chlorine isotope signature, expressed in standard $\delta^{37}Cl$-notation with a positive signature of +0.67 ± 0.14 ‰ (1σ), are different to that of other enriched basaltic shergottites. These findings may be explained by interaction/assimilation of Cl-enriched martian crust to a slightly higher degree when compared to other enriched basaltic shergottites. Hydroxyl-poor merrillite is identified as additional carrier phase for volatiles in martian magmas.