Frontiers in Mars Sample Chronology

Wednesday, 24th Mary 2021

Zoom

14:00	Welcome and intro	
14:10	Chris Herd & James Darling	Martian meteorite chronology: progress and challenges
14:30	Leanne Staddon	Microstructurally constrained baddeleyite chronology: robust age constraints for shocked martian lithologies
14:50	Stephanie Suarez	Pb and Rb-Sr isotope systematics of enriched components in Tissint
15:10	Minako Righter	Still filling the gap of our knowledge: what we know about Shergottites ages and mantle source compositions
15:30	Break	
15:50	James Darling	The rapidly expanding geochronology toolkit for complex planetary materials
16:10	Gabe Arcuri	Episodes of fluid alteration of Mars crust preserved in nanodomains of primordial zircon and baddeleyite
16:30	Alex Sheen	A feasibility assessment of micromill sampling for shergottite Rb–Sr and Sm–Nd geochronology
16:50	Barbara Cohen	Development of in situ geochronology techniques
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17:20	Fred Calef	Looking ahead: martian geochronology
17:30	Discussion	
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18:00	Close	

Microstructurally constrained baddeleyite chronology: robust age constraints for shocked martian lithologies

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Providing absolute age constraints on returned martian materials is crucial to resolve key questions surrounding martian crust-mantle evolution, ancient climate, and potential habitability. Baddeleyite (monoclinic; *m*-ZrO_2) is a widespread accessory phase within martian lithologies [1] and an important target for *in-situ* U-Pb chronology. However, given the continued reworking of planetary crusts by impacts [*e.g.,* 2], constraining the microstructural and isotopic response of baddeleyite to shock metamorphism is critical. While experimental studies indicate robust U-Pb isotope systematics to ~57 GPa [3], partial age resetting has been documented within highly-shocked shergottite Northwest Africa (NWA) 5298 [4,5]. U-Pb isotopic disturbance within NWA 5298 is linked to baddeleyite microstructure [5], formed by reversion from meta-stable, orthorhombic zirconia polymorphs (*o*-ZrO_2) at pressures of ≥ 3.3 GPa, and recrystallisation in areas of shock melting. To provide further constraints within more moderately shocked samples, we present combined microstructural analysis and U-Pb chronology for enriched shergottites Zagami, NWA 7257, NWA 8679 and Tindouf 002.

Electron backscatter diffraction (EBSD) analyses document significant inter- and intra-grain microstructural variability, with widespread transformation to, and subsequent reversion from, *o*-ZrO_2. Magmatic microstructures are rarely preserved, but most baddeleyites possess degraded crystallinity (diffraction at length-scales ≤ 50 nm). Such microstructures are analogous to previously described quasi-amorphous grains [5], formed by reversion from *o*-ZrO_2 at post-shock temperatures inadequate to nucleate significant *m*-ZrO_2 (< ~300 °C). Locally, temperatures were sufficient to allow micron-scale nucleation of *m*-ZrO_2; while rare within moderately-shocked NWA 7257, NWA 8679 and Zagami, these microstructures are observed in increased abundance in Tindouf 002, particularly in areas of enhanced shock melting.

Importantly, we observe no link between baddeleyite microstructure and U-Pb isotopic composition. Instead, all analyses form discordia in Tera-Wasserburg diagrams, indicative of mixing between common Pb reservoir(s) and radiogenic Pb produced by *in-situ* U decay. The absence of resolvable Pb mobility indicates that, within the studied samples, reversion from *o*-ZrO_2 alone does not induce U-Pb isotopic disturbance. Elevated post-shock temperatures (> 500 °C?) are therefore required to induce Pb mobility, with longevity of post-shock heating likely also an important consideration. These data show that, where independent and microstructural constraints indicate low bulk post-shock temperatures, baddeleyite represents a robust chronometer of the magmatic crystallisation of the studied sample. Even under elevated shock metamorphic P-T conditions, shock heterogeneity allows the preservation of baddeleyite with robust U-Pb isotope systematics [4,5]. Our approach therefore yields significant potential for chronology of mass-critical returned martian materials, allowing high-resolution temporal constraints on martian magmatic and impact processes.

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Pb and Rb-Sr isotope systematics of enriched components in Tissint

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Acquiring isotopic data from martian specimens, whether from meteorites or returned samples, is essential in understanding the evolution of Mars. Primary chemical and isotopic signals can be obscured through mobilization of elements during secondary martian processes including impacts and fluid/rock interactions. Direct sample return or meteorite specimens from observed falls offer pristine examples of these martian processes. Tissint, a shergottite that had minimal opportunity to undergo significant modification on Earth's surface, is used to explore primary characteristics related to igneous crystallization as well as element mobility related to ejection.

Depleted shergottite Tissint is geochemically characterized as originating from an incompatible trace element (ITE)-depleted mantle source. Initial Sr, Nd, Hf, and Pb isotope compositions determined from isochron intercepts are some of the most depleted of any shergottite [2, 3, 11, 12], however, solutions from weak acid washes of several whole rock specimens are relatively enriched in radiogenic Sr and Pb isotopic compositions compared to igneous minerals [1,2]. It has been hypothesized that the sources of enrichment are martian soils [3,4], but this is debated [5]. Additional hypotheses include addition of Pb isotopes by fluids [6] and, or impact metamorphism [7].

Multiple specimens of Tissint were analyzed in situ by LA-ICPMS for REE, highly siderophile element (HSE) concentrations, and Pb isotopic compositions. Leachate and residues from 8 specimens representing separate individual fragments were analyzed for Rb-Sr by TIMS. Analyses of Tissint did not reveal the presence of exogeneous materials as previously hypothesized [3,4]. REE and HSE concentrations and Pb isotopic compositions confirm that the enriched components are not hosted in mineral phases or impact glass and associated sulfide. 87Rb/87Sr analyses of leachates indicate that labile components hosting soluble Rb and Sr are not in isotopic equilibrium with the igneous assemblage. The Sr isotopic compositions of the leachate are within the range of 'more enriched' depleted shergottites, perhaps indicating sources from the igneous pile on Mars. The enriched component could represent crack and mineral surface coatings of volatilized materials derived from nearby depleted shergottite rock units during the impact ejection process.

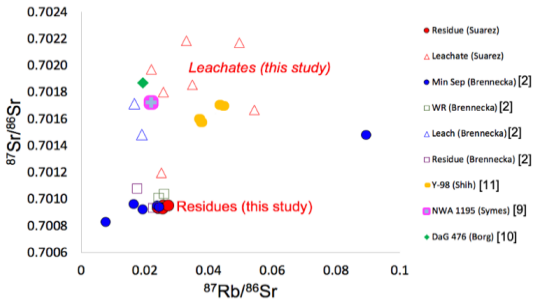

Figure 1. Leachates and Mineral separates of Tissint from this study and [2]. Rb-Sr whole rock from NWA 1195 [9] and DaG 476 [10] Y-98 [11].

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Still filling the gap of our knowledge: what we know about Shergottites ages and mantle source compositions

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Mars has been explored remotely by spacecraft for the last 4 decades. There have been nine successful US Mars landings including the recent Perseverance mission. Despite these efforts to dates, the martian meteorites are still the only samples we can study on the Earth on laboratory settings. Since 2000, the number of martian meteorites has been increasing rapidly from 29 (1999) to 292 (as of March 11, 2021) [1] due to contribution from Saharan dessert finds. The UH has been part of some initial characterization efforts by obtaining initial Nd and Hf isotope compositions in order to geochemically group newly found desert martian meteorites, especially shergottites.

Shergottites are the most abundant martian meteorites that have a range of crystallization ages that span over 2 Ga. With the increase of radiogenic isotopic data of shergottites, the systematics of their mantle source compositions are becoming better constrained. It has been recognized that the source composition of shergottites can be linked by mixing of incompatible trace element depleted and enriched mantle components [2-4]. Here we summarized the existing data of ages and source compositions for shergottites and associated rocks.

Importance of Lu-Hf systematics: While a best fit hyperbola for source Rb/Sr and Sm/Nd compositions of shergottites is defined by enriched and depleted end member components, a best-fit mixing hyperbola for source Lu/Hf and Sm/Nd compositions requires additional shallow upper mantle material (low Lu/Hf, high Sm/Nd, and low Rb/Sr) to account for the compositions of depleted, intermediate and enriched shergottites as well as ALH 84001 [2-4]. Lu-Hf systematics are essential to understand shergottite mantle source compositions due to the sensitivity for the shallow mantle material.

Duration of igneous activities on Mars: The duration of igneous activity is based on surface image analyses [e.g., 5-6] and direct isotope dating of meteorite specimens. Spatial association of most 327 to 2403 Ma depleted shergottites indicates >2 billion years of magmatism from a long-lived and geochemically distinct volcanic center near their ejection site [4]. Given the mantle source composition model for shergottites, bulk rock Sm/Nd and Lu/Hf data can be used to calculate mantle extraction model ages [e.g., 7]. This screening process helped to identify the 2.4 Ga shergottite NWA 7635 for further chronological work.

Several key specimens: There is a still conundrum regarding gaps between the three geochemical groups of shergottites (enriched, intermediate and depleted) and how representative they are in terms of characterizing the mantle of Mars. In the last decade or so, discovery of new martian meteorites have revealed a diversity of sources and magmatic histories. NWA 4480 and NWA 11509 are shergottite specimens that exhibit 'unique' mantle source Lu/Hf and Sm/Nd compositions that are between the three distinct geochemical groups of shergottites [8, 9].

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Episodes of fluid alteration of Mars crust preserved in nanodomains of primordial zircon and baddeleyite

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The application of sub-micrometer analytical techniques on meteorites has proved useful in constraining the timing of the high temperature bombardment effects on early Mars [1] but has not yet been applied to studying the timing and chemistry of lower temperature events such as those involving martian fluid processes. The development of a full suite of methods for extracting maximum information on the records of fluid interaction from these rare samples is timely in regard to future sample returns. As a first step, we present atom probe tomography (APT) [2] data for the primordial suite of igneous zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) from the Martian meteorite Northwest Africa (NWA) 7475 [3] and alteration features thereof. NWA 7475 is a rare sample of martian regolith, and it has been reported that it carries isotopic evidence of alteration by low temperature martian fluids [4-6]. However, the relative chronology and nanochemistry of these fluid events at the martian surface remain to be investigated. Here we combine spatially correlated APT and electron microscopy to describe a range of chemical nanostructures which we interpret to reflect different alteration episodes in the history of the ancient grains, presented here in chronologic order. APT results for a zircon intergrown with K-feldspar show multiple linear features (up to ~80 nm) and clusters (~5-30 nm diameter) defined by trace elements (i.e., Fe, Mg, Ca, Al) at concentrations up to 3 at%, likely introduced by fluids along pathways created during a dynamic metamorphic event early in the zircon's history. The pathways were later annealed, and the contamination 'trapped' in the lattice, most likely during a ~1.5 Ga protracted metamorphic event [6]. A later period of low-temperature aqueous alteration is recorded as secondary zircon at a ~2 μm wide baddeleyite grain margin. The reaction boundary across a ~10 nm gradient is defined by increasing Si content and incompatible trace elements indicative of a type of low temperature Si-rich fluid interaction seen on Earth. We deduce that the timing of this mineral-fluid alteration must have been concomitant with lithification of the breccia at <225 Ga [7-8] based on textural evidence of the baddeleyite core and zircon rim with the adjoining ilmenite and matrix material. This period of late aqueous activity is further supported by elevated concentrations of incompatible elements and Cl (~1 at%) in metamict domains of a second zircon grain indicative of a post-crystallization interaction with a Cl-rich hydrothermal fluid and subsequent low temperature annealing. These results are a first step in demonstrating the value of nanoscale microscopy on current and future samples to complement analyses conducted at larger length scales. This same workflow could be adapted to techniques such as cryo-APT which would enable further measurement of Martian fluid characteristics (e.g., D/H ratios, Cl isotopes) as well as biosignatures.

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A feasibility assessment of micromill sampling for shergottite Rb–Sr and Sm–Nd geochronology

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Micromilling, which combines precision drilling with optical microscopy, enables the extraction of small sample volumes at micron-scale resolutions. The precision control allows sampling to be guided by petrographic and/or textural observations, thus preserving spatial information which would be lost in bulk sampling methods. As the extracted sample powder can proceed to be dissolved for analysis, micromilling also offers an alternative in situations that preclude robust in-situ microbeam or laser analysis.

We assess the feasibility of micromill extraction for Rb–Sr and Sm–Nd geochronology of shergottites. While a minimum drilling diameter of ~30 µm can be achieved by a conical carbide drill bit, the volume required to be extracted from each mineral phase is dependent on 1) the concentration of the analytes in the mineral and 2) the minimum mass of analytes required by the analytical method. Given the typical range of trace element levels in major minerals in shergottites, between 10^6 and 10^8 μm^3 of material is needed to yield 1 ng Sr or Nd for solution isotopic analysis. This relatively high volume poses a challenge as shergottites commonly have sub-millimetre grain sizes, which require 10's to 100's of grains to be drilled to yield one analysis. The necessity to avoid sampling shock veins, shock pockets, and/or terrestrial alteration further requires drilling to spread across areas over ~1–2 cm^2, limiting the number of analyses that can be obtained from a standard thin section-sized sample. We conclude that micromill sampling of major minerals in shergottites for Rb–Sr and Sm–Nd geochronology is not practical given the current minimum required analyte mass for solution isotopic analysis and the general lack of samples coarse enough to support large-volume drilling while minimizing footprint.

Development of in situ geochronology techniques

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Geochronology is an indispensable tool for reconstructing the geologic history of planets. Bombardment chronology bounds models of Solar System dynamics, as well as the timing of volatile, organic, and siderophile element delivery. Absolute ages of magmatic products provide constraints on the dynamics of magma oceans and crustal formation, as well as the longevity and evolution of interior heat engines and distinct mantle/crustal source regions. Absolute dating also relates habitability markers to the timescale of evolution of life on Earth. However, the number of terrains important to date on Mars and across the inner Solar System far exceeds our ability to conduct sample return from all of them. The capability of *in situ* geochronology is highly desired given the limited opportunities for sample return missions.

Geochronology experiments on the Curiosity rover demonstrated the feasibility of *in situ* K-Ar dating on Mars and underlined the utility of acquiring absolute ages along with other geochemical data, such as chemical and mineral composition of rocks [1-4]. However, the results also revealed challenges involved with this implementation, such as difficulty extracting ^{40}Ar from highly-retentive minerals, the incapability of directly measuring the mass of the sample, and the possibility of mineral sorting during sample delivery. To resolve these problems and expand the capability of in situ geochronology, several groups, including ours, have been developing K-Ar dating instruments based on a laser-ablation approach [5-9]. Of these prototypes, the Potassium-Argon Laser Experiment (KArLE) is the most mature; the core technologies of this instrument have already been demonstrated on the Curiosity mission [4, 10-12].

The KArLE experiment simultaneously measures K via laser induced breakdown spectroscopy (LIBS) and Ar via traditional mass spectrometry, and relates K and Ar using the ablation pit volume measured by laser scanning metrology [5]. Using laser ablation enables the technique to be applied to solid, unprepared samples such as chips or pebbles rather than crushed or processed powders, and depth profiling can probe surface effects such as weathering (Maurice et al. 2016). The multiple points investigated by laser ablation on a single sample yields point-by-point sample ages with which to construct whole-rock isochrons, map elemental abundances at microscopic scales, and provide context with which to interpret isotopic age data. The isochron approach also obviates the need to independently assume or determine any initial or trapped contributions to ^{40}Ar in a bulk sample. The same measurements also yield cosmic-ray exposure ages.

The LIBS-MS family of instruments is promising for near-term implementation because its components are flight-proven. Quantification of K by LIBS at the low concentrations expected in planetary samples is the largest source of uncertainty, leading to an estimated uncertainty using this technique of ±8-16% (2σ) in individual measurements. Reduced uncertainty in the inferred age may be realized using multiple-point isochrons, approaching the guidelines set out in the NASA Technology roadmap. We are currently building a brassboard instrument intended to minimize mass, volume, and power resources, satisfy all functional/science requirements, and be qualified to TRL 6 via a system-level demonstration under relevant environmental conditions.

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