In situ U-Pb geochronology of martian baddeleyite by laser ablation MC-ICP-MS. C. D. K. Herd1, A. Simonetti1 and N. D. Peterson2, 1Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, AB, T6G 2E3, Canada (herd@ualberta.ca). 2Department of Earth and Ocean Sciences, 6339 Stores Road, University of British Columbia, Vancouver, BC, V6T 1Z4.

Introduction: Debate about the igneous crystallization ages of the shergottite meteorites has been recently reinvigorated by mineral separate Pb isotopic investigations combined with Sm-Nd and Rb-Sr [1] or Sm-Nd and Lu-Hf [2] on the same separates. Borg et al. [1] interpret Sm-Nd (166 ± 12 Ma) and Rb-Sr (166 ± 6 Ma) ages of Zagami as crystallization ages, and the U-Pb system as disturbed. Bouvier et al. [2] interpret the Pb-Pb age of Zagami (4.05 Ga) as the crystallization age and the Sm-Nd (155 ± 9 Ma) and Lu-Hf (185 ± 36 Ma) ages as the timing of re-equilibration of phosphates with near-surface acidic pore waters.

Baddeleyite (ZrO2) is a common accessory mineral in mafic rocks, forming as a late-stage crystallization product. It has the ability to take up and retain abundant U (up to 3000 ppm), excludes initial common Pb, and undergoes negligible Pb loss, making it ideal for U-Pb geochronology [3]. In the past two decades, baddeleyite has been used extensively for precise U-Pb dating of a variety of mafic igneous rocks using ID-TIMS methods [3]. Recently, advances in laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) technology have enabled U-Pb geochronological studies of accessory minerals (e.g., baddeleyite, zircon, monazite, etc.) in standard petrographic thin sections at high (5-40 µm) spatial resolution, providing results that are comparable to other in situ methods such as SHRIMP [4, 5]. Here we present the results of a preliminary U-Pb geochronological investigation of baddeleyite in shergottites using LA-MC-ICP-MS.

Methods: The following samples were investigated: Zagami dark mottled lithology (DML; UH 218) and a late-stage melt pocket (UH 233), Northwest Africa (NWA) 3171, NWA 1460, NWA 1068, and Dar al Gani (DaG) 476. A JEOL 8900 electron microprobe was used to locate baddeleyite and analyze associated mineral assemblages. Baddeleyite was located by scanning across the sample under high-contrast, low-brightness backscattered electron (BSE) imaging conditions; since the average atomic number of baddeleyite is higher than other phases, it could be easily located in this manner. Identification of baddeleyite was verified by energy-dispersive spectrometry. Associated minerals were analyzed by wavelength-dispersive spectrometry using an accelerating voltage of either 15 or 20 kV and a beam current of 15 nA. Geothermometry and oxybarometry of associated mineral assemblages was carried out using the Ghiorso-Sack [6] and Ca-QUIF [7] models.

U-Pb isotopic data were acquired using a Nu Plasma MC-ICP-MS (Nu Instruments, UK) coupled to a UP213 laser ablation system (New Wave Research, USA). The MC-ICP-MS is equipped with a unique collector configuration that allows for simultaneous acquisition of ion signals ranging from mass 203Tl to 238U, with the 207Pb, 206Pb, and 204Pb ion beams measured on the ion counting channels. The collector configuration allows very low Pb ion signals to be measured at high precision and thereby enables ablation experiments to be conducted using smaller sample volumes compared to those typically consumed for other LA-ICP-MS configurations. The analytical protocol adopted here involves a Tl-doping method for monitoring of instrumental mass bias, which typically yields 2σ relative standard deviations that are ≤1% (206Pb/238U) and ≤3% (206Pb/235U and 207Pb/235U). Further details of the method are described in [4, 5].

Results: Baddeleyite grains were found in all samples with the exception of NWA 1068. The grains range in size from 1 to 30 µm in longest dimension, with most in the 3 – 10 µm range. In general, baddeleyite occurs in association with late-stage phases, such as ulvöspinel, ilmenite, pyrrhotite, merrillite, fayalite, Fe-rich pyroxene, silica-rich glass, mesostasis, and symplectitic intergrowths of fayalitic olivine, silica, and hedenbergitic pyroxene. With the exception of DaG 476, pigeonite associated with baddeleyite is at least Fa66, and in some cases contains no Mg. The symplectites are consistent with the sub-solidus breakdown of Fe-rich metastable pyroxenes [8]. In DaG 476, the (augitic) pyroxene associated with baddeleyite is more Fe-rich than previously reported [e.g., 9], although much more magnesian than in the other samples. In all cases, the composition and texture of the mineral assemblages in association with baddeleyite confirms its occurrence as a late-stage crystallization product. A summary of occurrences, including calculated conditions of crystallization, are shown in Figure 1.

One baddeleyite grain from Zagami DML (Fig. 1a) and one grain from NWA 3171 (Fig. 1b) were ablated using a 8 µm spot size and repetition rate of 4Hz. Given the thin nature of the baddeleyite grains, data acquisition occurred over a short integration period of approximately 3 seconds, yielding rather low signal...
intensities. Regardless, the count rate was above detection, and we obtained minimum $^{206}\text{Pb}/^{238}\text{U}$ ages of $70 \pm 35 \text{ Ma}$ for Zagami and $171 \pm 129 \text{ Ma}$ for NWA 3171. Error is propagated assuming 50% uncertainty associated with external reproducibility of the $^{206}\text{Pb}/^{238}\text{U}$ measured values.

**Discussion and implications:**

**Baddeleyite in martian meteorites.** Baddeleyite stability in mafic melts is dictated by local concentration of Zr. Since Zr is incompatible in the other igneous phases, it becomes stable during the latest stages of crystallization. The bulk Zr contents of Zagami, NWA 3171, NWA 1460 and NWA 1068 are 50 – 70 ppm; DaG 476 contains 10 ppm Zr. Variation in the number and sizes of baddeleyite grains among samples indicates that occurrences are dictated by local melt conditions. For example, 20 baddeleyite grains were found in NWA 3171, but only one in DaG 476.

Oxygen fugacity appears to play an indirect role in the stability of baddeleyite. In all cases, the calculated $f_{\text{O}_2}$ from associated phases is within 2 log units of the QFM buffer (Fig. 1). In the case of DaG 476, the $f_{\text{O}_2}$ is higher, within error, than that of the early-formed assemblages [10]. At lower $f_{\text{O}_2}$ titanomagnetite and ilmenite are more Ti-rich, favoring the uptake of Zr; this is supported by the generally higher Zr contents of lunar vs. terrestrial Fe-Ti oxides [11, 12]. Therefore at higher $f_{\text{O}_2}$, Zr is expected to be more incompatible in the Fe-Ti oxides, resulting in a higher probability of late-stage baddeleyite crystallization. That baddeleyite was not found in NWA 1068 in spite of high bulk Zr and high late-stage $f_{\text{O}_2}$ [13] may be attributable to the large span of oxide compositions and the complex crystallization history of this rock.

**Ages of shergottites.** The $^{206}\text{Pb}/^{238}\text{U}$ ages obtained for baddeleyite in NWA 3171 and Zagami DML are minimum ages because of the possibility of Pb loss since crystallization. The age obtained for NWA 3171 is within uncertainty of the preliminary Sm-Nd age [14]; the age obtained for Zagami DML is about half that obtained by Sm-Nd and Rb-Sr [1]. Discordancy could not be evaluated because the $^{206}\text{Pb}$ ion signal was essentially at background level; however, the lack of detectable $^{207}\text{Pb}$ is indicative of an extremely young age.

The first in situ U-Pb geochronology of baddeleyite in shergottite meteorites reported here precludes a 4.05 Ga crystallization age for the Zagami and NWA 3171 shergottites, and supports the interpretation of Rb-Sr, Sm-Nd and Lu-Hf ages as dating the timing of crystallization. Whereas it is agreed that mineral separate U-Pb ages do not provide adequate chronological constraint [1, 2], baddeleyite promises to be highly useful in martian meteorite geochronology, given its ability to take up and retain U and daughter Pb, and ‘see through’ any post-crystallization processes such as surface alteration or impact shock.

**Acknowledgements:** We thank Ed Scott (University of Hawai‘i) for thin sections UH218 and UH233 and Tony Irving (University of Washington) for the samples of NWA 1460 and DaG 476. Funding was provided by the National Science and Engineering Research Council of Canada, through a Discovery Grant to CDKH and an Undergraduate Student Research Award to NDP.

**References:**


**Figure 1.** BSE images of baddeleyite (bd) occurrences in (a) Zagami DML, (b) NWA 3171, (c) NWA 1460, and (d) DaG 476. Associated phases are titanomagnetite (tmt), fayalitic olivine (fa), maskelynite (mk), Si-rich glass (gl), pyroxene (px), symplectite (sy), ilmenite (ilm), and olivine (ol). Oxygen barometry by either G-S [6] or QUILF [7] methods. The $f_{\text{O}_2}$ given in (a-c) is based on several Fe-Ti oxide pairs in the rock; the $f_{\text{O}_2}$ given in (d) is based on the assemblage shown (ilm+ol+aug+pig).