Baddeleyite Occurrences in Zagami and QUE 94201: 'QUE Q.E.D.' C. D. K. Herd[1] and T. J. McCoy[2], [1]Department of Earth and Atmospheric Sciences, 1-26 Earth Sciences Building, University of Alberta, Edmonton, AB, Canada, T6G 2E3, herd@ualberta.ca. [1,2]Department of Mineral Sciences, Smithsonian National Museum of Natural History, 10th & Constitution NW, Washington, DC 20560-0119, mccoyt@si.edu.

Introduction: Baddeleyite (ZrO_2) is an accessory igneous mineral of increasing interest for the geochronology of martian meteorites [1-2], in particular due its apparent resilience against Pb loss during shock [3-4]. The most promising method for U-Pb chronometry of martian baddeleyite is *in situ*, i.e., by ion probe analysis. The ion probe approach is necessitated by small grain sizes, among other factors [2]. A further advantage of the method, however, is the preservation of textural context – the same grains analyzed by ion probe may be evaluated prior to analysis using scanning electron microscopy (SEM), cathodoluminescence, and electron microprobe (EPMA) [e.g., 1, 2]. Thus, the occurrence of the baddeleyite may be elucidated, including proximity to shock veins and pockets and potential shock effects, enclosure within other mineral grains and relationship to mineral assemblages, and conditions of crystallization.

Establishing the typical occurrence of baddeleyite within martian meteorites is important for finding and characterizing prospective grains for U-Pb chronometry. Occurrences in several martian meteorites were presented by [1]; these authors postulated that oxygen fugacity may play an indirect role by influencing the compositions of Fe-Ti oxides and therefore the relative compatibility of Zr. If correct, then one would expect that baddeleyite occurrences would be less common, or altogether absent, in basalts that crystallized at lower oxygen fugacity. Here we test this hypothesis by examining baddeleyite occurrences in Zagami and QUE 94201, which bracket the range of oxygen fugacity for the shergottites.

Methods and Samples: Baddeleyite searching and analysis of mineral assemblages was carried out on JEOL 8900 and Cameca SX-100 EPMA instruments in the Department of Earth and Atmospheric Sciences at the University of Alberta, and the JEOL 8900 EPMA instrument and FEI Nova NanoSEM 600 field emission SEM in the Department of Mineral Sciences, Smithsonian National Museum of Natural History. Thin sections reflecting the range of Zagami lithologies were examined, including the boundary between normal Zagami and the dark, mottled lithology (DML; USNM 6545-2), DML (UH218) and a late-stage melt pocket (UH233). Thin section QUE 94201,3 was also studied. Once located, baddeleyite grain sizes were measured either using SEM measuring tools or offline using BSE images. Average grain size is defined as the sum of the average length of all grains and the average width of all grains, divided by two.

Zagami is a basaltic shergottite containing progressively evolved lithologies. The majority (~ 80 vol.%), termed normal Zagami, is dominated by subequal amounts of pigeonite and augite (~75 vol.%) and maskelynite (~20 vol.%), with accessory merrillite, titanomagnetite, ilmenite, pyrrhotite, fayalitic olivine and SiO_2 [5]. The fayalitic olivine in normal Zagami is likely the product of subsolidus equilibration [6]. The remaining 20 vol.% of Zagami is an FeO-enriched basaltic lithology with late-stage melt pockets, termed the dark, mottled lithology (DML) due to its appearance in hand specimen [7]. The DML is characterized by pyroxene-rich and maskelynite-poor clumps up to 4 mm across that contain mm-scale pockets of late-stage crystallization products, including Fe-Ti oxides, pyrrhotite, merrillite, apatite, SiO_2, fayalitic olivine, and mesostasis, the latter containing vermicular intergrowths of the same phases plus K-feldspar and fayalitic olivine [7]. The oxygen fugacity of Zagami is among the highest in the martian meteorite suite [6].

QUE 94201 is a basaltic shergottite comprised of coarse-grained pyroxene (44 modal %) and maskelynite (46%) with minor merrillite (4%) and Fe-Ti oxides (ulvöspinel and ilmenite; 2%) [8]. Mesostasis, which makes up nearly 4% of the rock, contains fayalitic olivine, silica, pyrrhotite, apatite, K-rich silica glass, and baddeleyite [8]. The bulk composition of QUE 94201 is enriched in incompatible elements [9]. Unlike in other shergottites, evidence of cumulus phases in QUE 94201 is lacking, and as such its bulk composition represents that of its parental melt [9-10]. QUE 94201 therefore represents a melt – albeit fractionated – from the martian mantle and can be used to infer mantle source characteristics [9, 11-12]. The oxygen fugacity of QUE 94201 is among the lowest in the martian meteorite suite, close to the iron-wüstite buffer [6, 13].

Results: Coexisting ilmenite and titanomagnetite pairs in Zagami DML yield oxygen fugacity and temperature of QFM – 0.8 ± 0.2 and 869 ± 34 °C, respectively (n = 5; 2σ deviation of the mean). These are within uncertainty of results for normal Zagami (QFM – 1.0 ± 0.2 and 841 ± 26 °C; n = 4; 2σ deviation of the mean; results from application of the Ghiorso and Evans oxybarometer [14] to the Fe-Ti oxide compositions of [6]). The Fe-Ti oxide pairs reported by [7] yield QFM – 0.4 and 911°C for normal Zagami and

QFM – 0.7 and 911 °C for DML. The oxygen fugacity of the late-stage melt pocket (UH 233) is QFM – 0.8 and 876 °C, based on one pair of coexisting titanomagnetite and ilmenite. Oxide compositions reported by [7] for late-stage melt pocket oxides yield QFM – 1.0 and T = 885 °C. These results are consistent with DML resulting from fractional crystallization of normal Zagami [7], accompanied by no significant change in redox conditions.

A total of 57 baddeleyite grains have been found in Zagami DML thus far, and searching is not yet complete. Grain lengths range from 0.8 to 18.3 µm, with an average grain size of 4.0 ± 2.8 µm and an average length to width ratio (l:w) of 2.5. The majority of occurrences are either a) enclosed within titanomagnetite, or at its margin or b) within silica-rich mesostasis. Where grains are enclosed within titanomagnetite, they tend to be euhedral and larger (average grain size 5.7 ± 2.9 µm, n = 18) than within mesostasis (average grain size 2.9 ± 2.1 µm, n = 30). The composition of pyroxene directly adjacent to baddeleyite is most often highly FeO-enriched. In general, pyroxene in association with baddeleyite is at least as ferroan as the most ferroan pyroxene reported in DML by [7], and includes pigeonite with compositions $Fs_{61-66}Wo_{8-17}$.

A total of 35 baddeleyite grains were found in the late-stage melt pocket (section UH 233). Most commonly, grains occur within areas of relatively coarse mesostasis composed of fayalitic olivine, silica, and titanomagnetite. Other occurrences are within silica-rich mesostasis, as in DML. Although statistics are poor thus far, grain sizes within coarse mesostasis appear to be larger and more equant (average grain size = 5.2 ± 2.7 µm, n = 9; l:w = 1.8) than those in silica-rich mesostasis (average grain size = 3.6 ± 1.4 µm, n = 5; l:w = 2.0).

To date, a total of 9 baddeleyite grains have been found in QUE 94201. All grains were found within mesostasis, consistent with the observations of [8]. Average grain size is 4.7 µm, and most grains have an acicular habit, with an average l:w = 5.5, ranging in length up to 30 µm. No grains were found enclosed by Fe-Ti oxides. Pyroxene adjacent to mesostasis is FeO-rich, as expected. The composition of pyroxene in mesostasis is hedenbergitic; along with mesostasis silica and fayalitic olivine, this assemblage is consistent with the crystallization of these three phases instead of metastable ferroan pyroxene or pyroxferroite [15], similar to assemblages in Zagami DML [7].

Discussion: Baddeleyite occurrence is governed by the Zr budget of the melt – at some stage during crystallization, sufficient Zr must be present in the melt for baddeleyite to crystallize. The bulk Zr content of normal Zagami is 64 ppm, and 107 ppm for QUE 94201 (average of data found in [16]). Based on the concentration of Zr in pigeonite cores, which are ~1.7 times higher in DML than in normal Zagami [7], we estimate the Zr content of the Zagami DML parental melt to be ~ 110 ppm. Therefore the two melts may have had similar Zr budgets. However, the frequency and habit of baddeleyite in the two shergottites is different, which are attributable to differences in conditions of crystallization.

The occurrence of baddeleyite in mesostasis is common to both Zagami DML and QUE 94201, reflecting the buildup of Zr in late-stage melt. However, Zagami DML contains many more baddeleyite grains, in more than one type of occurrence. The occurrence of euhedral baddeleyite grains enclosed by Fe-Ti oxides in Zagami indicates that baddeleyite crystallization was initiated before the completion of Fe-Ti oxide crystallization. The lack of oxide-enclosed grains in QUE 94201 indicates that Zr concentrations were only sufficiently high for baddeleyite crystallization during the crystallization of mesostasis. This difference may be attributable to differences in Zr compatibility in Fe-Ti oxides. The relative role of the composition of Fe-Ti oxides, and by inference the oxygen fugacity, remains unexplored. Testing this parameter may allow one to get a better handle on the relative importance of bulk Zr concentration versus oxygen fugacity in determining baddeleyite occurrences. The occurrence of baddeleyite in the most reduced martian basalt demonstrates that baddeleyite is a common accessory mineral in martian meteorites: 'QUE Q.E.D.'

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