Remnants of the oldest Martian crust

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Introduction: Mars offers a unique possibility to better constrain the timing of the earliest planet-formation processes because of its history as a stranded planetary embryo [1]. Mars accretionary processes were likely completed within ~5 Myr of Solar System formation, the core of Mars formed contemporaneously with solar system formation, and the Martian mantle differentiated ~30 to ~100 Myr after accretion [1,2]. The recent find of NWA7533 and its pairs, collectively referred to as Black Beauty, have monzonitic clasts with evolved compositions that contain zircon grains that are as old as 4.428 ± 0.050 Ga (2σ) [3]. These clasts are likely products of the differentiation of large melt sheets derived from a Martian protocrust [3]. Thus, the earliest stages of planetary crust formation can be investigated by constraining the timing of formation and chemistry of fragments with different chronological and petrological origins in NWA733. While the solution based analysis of most other radiogenic isotopic systems is difficult to perform on individual minerals, the Pb isotopic system is ideally suited for this purpose and can be performed *in situ* by Secondary Ion Mass Spectrometry (SIMS), which preserves mineralogical-petrological context and limits any surface or terrestrial contamination [4-6].

The Pb isotopic system is comprised of four isotopes ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb, the latter three being daughter products of ^{238}U, ^{235}U, and ^{232}Th, respectively. As such, the Pb isotopic composition of a mineral changes in the presence of U and Th over time and this growth can be quantified with a crystallization age and/or μ (^{238}U/^{204}Pb) and κ (^{232}Th/^{238}U) values. In minerals that contain minimal U and Th together with high concentrations of Pb, such as feldspars or sulfides, there occurs extremely limited to no Pb growth after crystallization, preserving the initial Pb composition at that time. As such, the most primitive Pb in the solar system is preserved in a sulfide mineral (troilite) found in the Canyon Diablo IAB iron meteorite (Canyon Diablo Troilite), which crystallized at 4.57 ± 0.02 Ga and early enough in solar system history to not have incorporated any radiogenic Pb [7,8]. In samples with abundant and diverse feldspar grains, such as NWA7533, Pb isotopic measurements can be made on individual grains *in situ* and provide constraints on the U, Th, and Pb history of each specific grain and potentially delineate multiple events of crust generation. Here, the Pb isotopic composition of individual plagioclase grains (with minor inclusions of pyroxene) in the breccia matrix of NWA7533 were analyzed with SIMS to highlight the diversity and multiple stages of Martian crust preserved in NWA7533.

Results and discussion: Weighted averages of Pb isotopic compositions from the grains with the most primitive Pb lie within uncertainty of Canyon Diablo Troilite [6] but outside of analytical uncertainty of all other initial Pb isotopic compositions in NWA7533 and the rest of the Martian meteorite suite [4,5]. The major element composition of the feldspars measured here has a range of compositions of $An_{29-55}Ab_{44-67}Or_{1-4}$ and the pyroxene inclusions in Clast 2 have a very limited range in composition of $En_{44-45}Wo_{31}Fa_{24-25}$. These compositions are in broad agreement with the compositions measured in previous studies of the primitive basaltic clasts in Black Beauty [9-11]. Additionally, the compositions measured here are in agreement with the most primitive end-member of the trend defined by silica-saturated alkali suite experiments, which have been used to predict the major element compositions of Martian feldspars [12]. Similarly, the compositions for the feldspars and pyroxenes measured here are consistent with experimentally derived compositions of the Martian protocrust from melt experiments of a hypothesized primitive Martian mantle [13]. Thus, the plagioclase and associated pyroxene grains studied here have major element compositions consistent with the major element composition estimates of the most primitive Martian crust and Pb isotopic compositions within uncertainty of the most primitive Pb preserved in the solar system. These compositions could have only been preserved if the plagioclase grains analyzed here formed within uncertainty of CDT and the solar system. Thus, they represent fragmented remnants of what is likely to be the earliest preserved Martian crust.

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