A Unique Differentiation History of Mars Preserved in Martian Meteorite NWA7533. J. J. Bellucci[1], A.A. Nemchin[1], and M.J. Whitehouse[1], [1]Department of Geosciences, Swedish Museum of Natural History, Box 50007 SE-104 05, Stockholm, Sweden. Corresponding author's email: jeremy.bellucci@gmail.com

Introduction: Currently, all of the constraints placed on the chemical and isotopic differentiation of Mars have come from the studies of the shergottite, nakhlite, and chassignite (SNC) meteorites (e.g., [1-7]). These studies have yielded invaluable information about the timing of Martian core formation [1], the timing and formation of a Martian protocrust [2], and the U-Th-Pb history of the Martian mantle [3-7]. However, the chemical composition of these meteorites does not strongly align with the measured composition of the Martian surface determined by the recent orbiters and landers [8-11]. Consequently, it is uncertain to what degree the SNC meteorites can say about large scale processes in the chemical evolution of Mars. The composition of the newly described Martian meteorite NWA7533 is a virtual match to the soils from Gusev crater and may be a more representative example of the Martian crust [12,13]. Here we present the first common Pb isotopic study on a rock from Mars and a new perspective on the U-Th-Pb system in the Martian mantle and crust.

NWA 7533 is a Martian regolith breccia and has recently been described in detail by [12,13]. The fine-grained matrix of NWA 7533 is composed of alkalic basalt and contains evolved igneous clasts with a monzonitic/mugearatic composition, clast-laden impact melt rock, melt spherules, and basaltic clasts [12-14]. The monzonitic clasts are composed of alkali feldspar, plagioclase, chlorapatite, ilmenite, and trace zircon [13]. The monzonite clasts were formed by either differentiation of large impact melt sheets or re-melting of primary Martian crust at depth/in the presence of volatiles [13,14]. To further corroborate the intrusive history of the monzonite clasts, the alkali feldspars and pyroxenes have exsolved textures, which can only be present if the crystals cooled slowly [13]. Zircons preserved in the monzonitic clasts have U-Pb concordant ages of 4.4 Ga and discordant ages of 1.7 Ga [13]. Additionally, these clasts have chlorapatite with U-Pb ages of 1.7 Ga, which indicates a strong thermal event at this time. While the exact timing for the formation of the Martian protocrust is unknown, based on ^{142}Nd-^{143}Nd systematics in SNC meteorites, it must have been within the first 100 Myr of Martian history [2]. Hence, the monzonitic clasts in NWA 7533 probably represent products of Martian crust emplaced at ~4.5 Ga, re-melted at 4.4 Ga, and re-equilibrated with the regolith at 1.7 Ga. Therefore, the Pb isotopic compositions of K-feldspar and plagioclase should yield a great deal of information about the differentiation history of Mars. Specifically, the U-Th-Pb isotopic signatures of the early Martian mantle, the primary Martian crust, and the Martian regolith from 4.4 Ga-1.7 Ga should be preserved.

Analytical Methods: The Pb isotopic compositions of plagioclase and alkali-feldspar grains were determined using a CAMECA IMS1280 instrument at the Swedish Museum of Natural History, Stockholm (NordSIM facility) using the experimental protocol from [15,16]. An area of 25x25 μm was rastered for 70 s prior to Pb isotopic analysis to minimize surface contamination. A 150 μm aperture was used resulting in a 12 nA O_2^- primary beam and 15μm circular spot on the surface of the sample. The mass resolution of the mass spectrometer during Pb isotopic analyses was 4860 (M/ΔM). Analyses were conducted in multi-collector mode using an NMR field sensor to control stability of magnetic field. Lead isotopic ratios were measured in low noise ion-counting electron multipliers for 160 cycles with a count time of 0.10 s, resulting in a total collection time of 1600 s. Mass bias correction and gain calibrations between detectors were performed by the bracketing the unknowns with analyses of basaltic reference glass BCR2-g (11 μg/g Pb), using values from [17], the exponential law of fractionation, and a linear gain calibration. External reproducibility in ^{208}Pb/^{206}Pb and ^{206}Pb/^{204}Pb of BCR 2-g was 0.2% and 0.6%, respectively (95% confidence on the weighted mean). Subsequent to Pb isotopic analyses, the ^{238}U/^{208}Pb was measured on each analytical spot. U/Pb ratios were measured by peak jumping between masses ^{208}Pb and ^{238}U. Ions were collected in the center electron multiplier. U/Pb ratios were monitored in and corrected to BCR 2-g to ensure that pristine common Pb was measured.

Results and discussion: The Pb isotopic compositions of plagioclases and alkali-feldspars in leucocratic clasts of NWA7533 display a linear trend with a roughly bi-modal distribution (Fig. 1). Some of the plagioclases have extremely un-radiogenic Pb isotopic compositions in ^{206}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb and plot within error of the 4.4 Ga or 4.5 Ga Geochron (Fig. 1). All of the alkali feldspars and some plagioclases have a significantly more radiogenic composition, but still plot to the left of the modern day Geochron (Fig. 1). All of the measured compositions here lie above the field defined by the leached residues of whole rock and mineral separates from the SNC meteorites (green field, Fig. 1 [3-7]). This enrichment in ^{207}Pb/^{204}Pb is indicative of an early differentiation event and longterm residence in a higher μ environment than the SNC meteorites. Thus, NWA 7533 records a unique differentiation history of Mars. The large majority of $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ compositions lie on a linear trend with the SNC meteorites in indicating a consistent Martian κ (Fig.1).

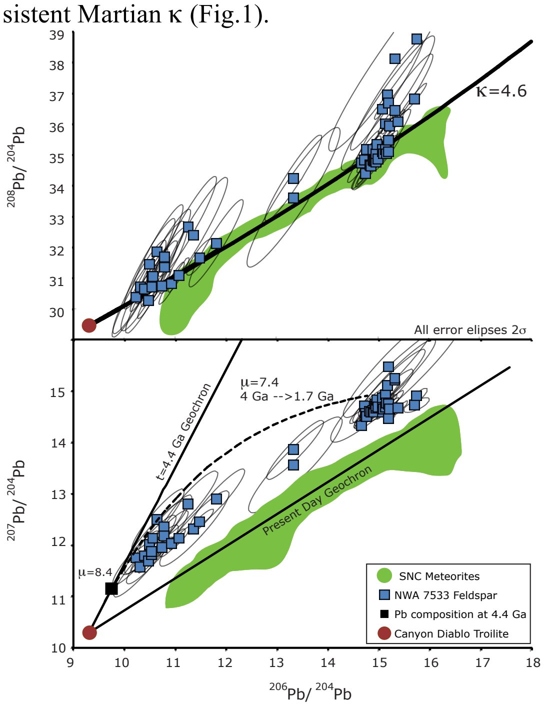

Figure 1. Pb isotopic compsitions of Martian meteorites

Linear trends in Pb isotopic data can be a result of mixing between two components or can result from the in growth of radiogenic Pb from the *in situ* decay of U and Th. To rule out the latter hypothesis, U/Pb ratios were measured in each analytical spot directly following Pb isotopic analysis. The U/Pb ratios measured in plagioclase and K-feldspar are similar (<0.05), do not correlate with Pb isotopic ratios, and would not result in the spread in isotopic data shown in Fig. 1, even after 4.4 Ga of U and Th decay. As such, the data is interpreted as being the result of heterogeneous resetting/mixing between feldspars and the whole rock at 1.7 Ga (the discordant age of zircon and U-Pb age of apatites in the same monzonitic clasts). Due to the heterogeneous nature of the re-equilibration, the thermal event at 1.7 Ga was likely very short lived. This thermal pulse, evidently, did not have time to completely re-equilibrate all of the feldspars and preserved the mostly bimodal distribution seen here.

Since the data are interpreted to reflect partial resetting during a thermal event at 1.7 Ga, a common Pb model can be constructed given the independent time constraints presented in [13]. The initial Pb composition at 4.57 Ga used for this model is the Canyon Diablo Troilite (Fig. 1 [18]). The common Pb composition of the plagioclase plots within error of the 4.4 Ga & 4.5 Ga Geochron and the exact timing for the formation of the Martian protocrust has yet to be determined. As such, determining the exact μ value for the early Martian mantle/protocrust is difficult to constrain within our current measurements. Therefore, we have simplified this model and tried to determine the mean μ between 4.57 Ga and 4.4 Ga needed to achieve the un-radiogenic plagioclase Pb isotopic compositions. This μ value has been determined to be ~8.4. If the protocrust was extracted from a mantle similar to the SNC meteorites (μ of 2-4 [3-7]) at ~4.5 Ga, the μ of the Martian protocrust would need be extremely high (~12-15) to achieve the Pb isotopic compositions observed in the plagioclase at 4.4 Ga. These results imply one of two things: 1) the Martian mantle is significantly more heterogeneous in μ values than previously thought or 2) the Martian protocrust was significantly enriched in U.

The dotted Pb evolution curve in Figure 1 is a representation of whole rock equilibration with alkali-feldspar at 1.7 Ga. As NWA7533 is a regolith breccia, this curve could be interpreted to be the μ of the regolith of Mars. The values obtained by our simple model yield a μ of ~7.4. This value is significantly higher than the estimate of the bulk silicate Martian μ value of ~3 [6]. Lastly, regardless of the model results for the Martian μ, the κ-value remains constant at ~4.6, in agreement with previous studies.

In conclusion, common Pb measurements of plagioclase and K-feldspar in leucocratic clasts in NWA 7533 preserve a unique differentiation history of Mars. This differentiation history includes residence in higher μ reservoirs than previously sampled by the SNC meteorites. The crustal μ value of ~7.4 provides the first radiogenic isotopic constraints for the surface of Mars. Lastly, since the bulk composition of this meteorite is more similar in composition to what is observed on the Martian surface, NWA7533 may paint a more representative and radiogenic picture of the chemical composition and differentiation of Mars than the SNC meteorites.

References: [1] Lee, D.C. and Halliday, A.N. (1997) *Nature*, 388, 854-857. [2] Debaille, V. et al. (2007) *Nature*, 450, 525-528. [3] Bouvier et al. (2008) *EPSL*, 266, 105-124. [4] Borg et al. (2005) *GCA*, 69, 5819-5830. [5] Bouvier et al. (2005) *EPSL*, 240, 221-233 [6] Gaffney et al. (2007) *GCA*, 71, 5016-5031. [7] Bouvier et al. (2009) *EPSL*, 280, 285-295. [8] McSween et al. (2009) *Science*, 324, 736. [9] Gellert et al. (2006) *JGRP*, 11, E02S05. [10] Ming et al. (2008) *JGRP*, 113, E12S39. [11] Boynton et al. (2007) *JGRP*, 112, E12S99. [12] Agee et al. (2013) *Science*, 339, 780. [13] Humayun et al. (2013) *Nature*, 503, 513-517. [14] Stolper et al. (2013) *Science*, 341, 6153. [15] Rose-Koga et al. (2012) *Chem Geol.*, 334, 266-279. [16] Whitehouse et al., (2005) *Chem Geol*., 222, 112-131. [17] Woodhead and Hergt (2000) *Geostand. Geoanal. Res.*, 24, 33-38. [18] Chen and Wasserburg (1983) *GCA,* 47, 1725–1737.