

OXYGEN ISOTOPE COMPOSITIONS AND TI AND REE CONCENTRATIONS OF ZIRCON FROM MARTIAN METEORITE NWA 7533. A. A. Nemchin¹, M. Humayun², M. Whitehouse¹, R. H. Hewins^{3,4}, J.-P. Lorand⁵, A. Kennedy⁶, M. Grange⁶, B. Zanda³, C. Fieni³, S. Pont³ and D. Deldecq⁷, ¹Laboratory for Isotope Geology, Swedish Museum of Natural History, SE-104 05 Stockholm, Sweden, ²Department of Earth, Ocean & Atmospheric Science and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, USA, ³Laboratoire de Minéralogie et Cosmochimie du Muséum, CNRS and Muséum National d'Histoire Naturelle, 75005 Paris, France, ⁴Department of Earth & Planetary Sciences, Rutgers University, Piscataway, NJ 08854, USA, ⁵Laboratoire de Planétologie et Géodynamique de Nantes, CNRS UMR 6112, Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cédex 3, France, ⁶Department of Applied Geology, Curtin University, Perth, WA 6845, Australia, ⁷Ecole Normale Supérieure, UMR 8538, 75231 Paris CEDEX 5, France.

Introduction: During the last decade investigations of zircon in terrestrial rocks, especially of a unique set of Hadean zircon populations, made this mineral not only the most widely utilised geochronometer, but also enabled use of its chemistry, oxygen and hafnium isotope systems to determine conditions of its formation and evolution of the rocks where zircon crystallised. Discovery of c.a. 4.4 Ga zircon grains in monzonite-norite clasts of brecciated Martian meteorites NWA 7533/7034/7475 makes it possible to apply this set of tools to gain additional information about the evolution of Mars. Here, we report measurements of oxygen isotopes and of Ti and REE contents of five zircon grains from a single section of NWA 7533 previously measured for U-Pb which demonstrated that the zircons formed at 4428 ± 25 Ma and were variably reset at 1712 ± 85 Ma [1].

Analytical technique: The SIMS REE analyses were performed on a SHRIMP II instrument at Curtin University, Western Australia. The O_2^- primary beam was directed through a 50 μm Kohler aperture, producing a spot approximately 10 μm in length. The instrument source slit and collector slit were set at 80 μm and 100 μm respectively, which gave a mass resolution ($M/\Delta M$) of >5000 at the 1% peak height. The zircon reference material for REE was BR231, a Sri Lankan gem that has been analysed for REE in two LA-ICP-MS labs, showing good homogeneity of trace elements.

SHRIMP analyses of Ti contents followed that of REE contents in the same session and under the same analytical conditions. Analytical spots used for REE analyses and in some cases previous U-Pb analyses have been also used to obtain Ti data. The Ti content of Martian grains was estimated using Ti concentration in zircon standard 91500 (from the same session).

Oxygen isotope ratios ($^{18}O/^{16}O$ and $^{17}O/^{16}O$) were determined in situ using a Cameca IMS1280 ion microprobe at the Swedish Museum of Natural History. A ca. 1 nA Cs^+ primary beam with impact energy of 20 kV was used in critically focused (Gaussian) mode to sputter secondary oxygen ions from selected regions of interest. Data were acquired over 160 seconds (40 cy-

cles) using static multi-collection in two Faraday cups ($^{16}O^-$ and $^{18}O^-$) operating at low mass resolution ($M/\Delta M = 2460$) and the axial ion counting electron multiplier ($^{17}O^-$) operating at a mass resolution sufficient to resolve $^{17}O^-$ from $^{16}O^1H^-$ ($M/\Delta M = 7500$). Corrections for instrumental mass bias and differences in detector efficiency were made using repeat analyses of the Geostandards 91500 reference zircon.

Results: As expected, the oxygen isotope compositions of Martian zircon grains fall above the terrestrial fractionation line (Fig.1). However, the analyses also appear to follow a trend that deviates from the mass dependent Martian fractionation line and roughly coincides with the mixing line identified by Ziegler et al. [2] on the basis of oxygen isotope analysis of separated plagioclase and pyroxene fractions in NWA 7034. This mixing line was interpreted as addition of oxygen from a different reservoir during a low temperature fluid alteration of the sample near the surface [2]. However, close examination of the multiple analyses obtained for individual zircon grains suggests that internally they follow mass dependent fractionation lines, but there is a difference in $\Delta^{17}O$ between different zircon grains. This apparent decoupling of $\Delta^{17}O$ and $\delta^{18}O$ in the analysed zircon grains is difficult to explain by a simple two-component mixing and is most likely a result of two different processes perhaps separated in time. The Martian hydrosphere/atmosphere appears to have higher $\Delta^{17}O$ than the lithosphere represented by silicate minerals in SNC meteorites and ALH 84001 [3, 4, 5]. The range in $\Delta^{17}O$ observed in NWA 7533 zircons ($+2\%$) is larger than that yet reported from Martian carbonates or water extracted from nakhlites, $\Delta^{17}O < +0.8\%$ [3, 4, 5], indicating the preservation of a large difference in $\Delta^{17}O$ between lithospheric and hydrospheric or atmospheric reservoirs of oxygen on ancient (>1.7 Ga) Mars. Very low rates of oxygen isotope exchange during weathering, hydrothermal alteration, etc., would preserve such differences over billion year timescales represented by ALH 84001 carbonates, NWA 7533 zircons and nakhlite alteration phases.

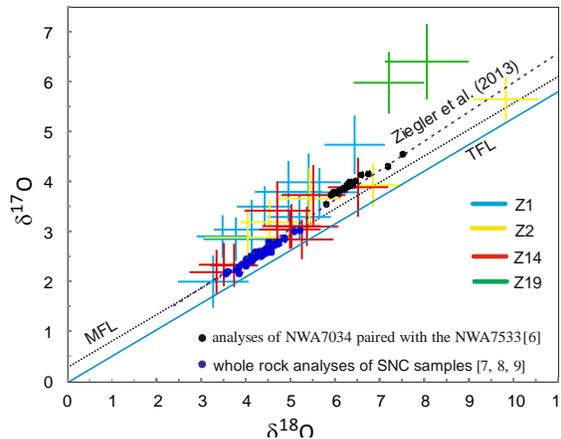


Figure 1: $\delta^{17}\text{O}$ vs. $\delta^{18}\text{O}$ data obtained for zircon grains from NWA 7533 (TFL-terrestrial fractionation line; MFL-martian fractionation line)

Ti concentrations were determined in the three largest zircons, as it is difficult to place the analytical spot in smaller (~ 10 - 15 micrometres) grains without risking a partial overlap with the surrounding matrix. Multiple analyses of individual grains show a slight scatter beyond analytical error. In addition there is a significant difference in Ti-concentration recorded in different grains. One grain has the lowest Ti content varying between 8 and 14 ppm, while two others show Ti concentrations as high as 66 ppm.

Although large-sized (several hundreds of micrometres) Ti-magnetite + ilmenite clasts (as well as rutile microclasts) are disseminated in the fine-grained matrix of NWA 7533 and are also present in the monzonitic clasts, some of which contain zircon, the heterogeneous nature of this breccia makes it difficult to determine whether any of these Ti-rich phases and the analyzed zircons are cogenetic. However, assuming that Ti activity during zircon crystallization is equal to one, the observed variation of Ti concentrations in analysed zircon translates into the temperature range between 726 ± 18 and $956 \pm 22^\circ\text{C}$ (2 sigma). This range is difficult to reconcile with Ti equilibrium being reached during zircon crystallization. Nevertheless, an apparent correlation between U and Ti content, where all analytical spots with U content less than 100 ppm give temperatures below 800°C , while spots having U concentration higher than 100 ppm give temperatures in excess of 870°C , suggests the possibility of Ti exchange between zircon and surrounding minerals after the zircon formation and proportional to the accumulated degree of radiation damage. Alternatively, similar variability has been noted in Hadean zircon grains from Jack Hills in Western Australia and attributed to accumulation of Ti in the fractures [10]. While it is difficult to find areas completely devoid of fractures to analyse in NWA

7533 zircon, analysis of two such areas in one grain gives the lowest temperature estimates of 726 ± 18 and $748 \pm 18^\circ\text{C}$, and these represent the minimum temperature for zircon crystallisation. These lower temperature estimates are close to the $\sim 800^\circ\text{C}$ estimate for the crystallisation temperature of monzonites based on two-pyroxene thermometry [11].

Unlike Ti, REE concentrations in NWA 7533 in all five zircon grains showed restricted intragrain variability, although the overall range between different grains is slightly more than an order of magnitude. The lower heavy REE concentrations for a single analysed zircon are consistent with its host being noritic rather than monzonitic. The chondrite normalised REE pattern displays clear positive Ce and negative Eu anomaly making overall patterns identical to those recorded in many terrestrial zircons. $\text{Log}(f\text{O}_2)$ calculated from the Ce anomaly depends on the crystallisation temperature of the zircon grains. Consequently, the observed range of Ti temperatures determined in Martian zircons precludes precise calculation of $\text{log}(f\text{O}_2)$. Nevertheless, calculating $\text{log}(f\text{O}_2)$ using different combinations of temperatures within the observed range suggests that all investigated zircons have formed at a $\text{log}(f\text{O}_2)$ between the FMQ and MH buffers.

Conclusions: REE and Ti concentrations determined in Martian zircons indicate crystallization under oxidizing conditions at relatively low (700 - 800°C) temperature (probably from a water- and/or volatile-rich magma). However, it is not possible to determine whether these conditions characterise a local environment formed in the parent magma just prior to zircon crystallization as a result of extensive differentiation or can be used to infer existence of oxidized, fluid rich reservoirs in the Martian crust and/or mantle. The complexity of oxygen isotope signatures of Martian zircons suggests the existence and long-term isolation of different oxygen reservoirs with very different isotope compositions ($\Delta^{17}\text{O} > 2\text{‰}$) during both zircon formation and subsequent near surface alteration.

References: [1] Humayun M. et al. (2013) *Nature*, 503, 513-516. [2] Ziegler K. et al. (2013) *Lunar Planet Sci.* XLXV abstract #2639. [3] Karlsson H. R. et al. (1992) *Science* 255, 1409. [4] Farquhar J. et al. (1998) *Science* 280, 1580. [5] Shaheen R. et al. (2010) *PNAS*, 107, 20213-20218. [6] Agee C. B. et al. (2013) *Science* 339, 780-785. [7] Franchi I.A et al. (1999) *Meteoritics & Planetary Science* 34,657-661. [8] Clayton R.N. and Mayeda T.K. (1996) *Geochim. Cosmochim. Acta*, 60, 1999-2017 [9] Rumble D. and Irving A.J. (2009) *Lunar Planet Sci.* XL abstract #2293. [10] Harrison T.M. & Schmitt, A.K. (2007) *EPSL*, 261, 9-19. [11] Hewins R.H. et al. (2013) *Meteorit. Planet. Sci.* 47 Abstract #5252.