

**Introduction:** Zircon's unique chemical characteristics, notably its enrichment in U, HREE and Hf, create an opportunity to constrain the origin and age of its source rocks. The remarkable physical resistance of zircon also ensures that these characteristics are preserved and accessible for study even when it is separated from its host, for example in sedimentary rocks on the Earth or impact and regolith breccias as well as soils on the Moon and Mars.

This presentation aims to compare the isotopic and trace element signatures preserved in zircon grains from the Moon, Mars and Earth. Such a comparison can help to reconcile existing diverse interpretations of individual zircon suites, which remain highly controversial.

Zircon grains with ages exceeding 3.9 Ga have been known to exist in some metasedimentary rocks in Western Australia since the early 1980's [1] and have been extensively studied during the last decade to gain information about the early stages of Earth's evolution [2-4]. These studies, although still a subject of substantial debate, have resulted in some profound changes in our understanding of Earth's history.

The first lunar zircon grains were also analysed in the early 1980's [e.g. 5] and since then more have been found in a significant number of lunar highland breccia samples, where they are commonly associated with a variety of rock clasts ranging in composition from troctolites and anorthosites to quartz-monzodiorites and granites.

Discovery of Martian zircon grains in the meteorite sample NWA 7533 interpreted as regolith breccia was reported last year. Zircon present in this sample is found both as separate mineral fragments and included in monzonite clasts.

**U-Pb ages:** The oldest terrestrial zircon grain was found in the detrital population from a conglomerate sample collected at Jack Hills (Western Australia) and reported to be  $4404 \pm 8$  Ma [2]. However, this age is based on a single analysis within a single zircon grain and a more reliable age estimate of the oldest terrestrial zircon, obtained using several grains from the same detrital population is 4370 Ma. Remarkably 4370 Ma also marks the start of one of the major peaks in the zircon age distribution pattern of lunar zircons, although four grains from the Moon appear to be older with ages between 4.40 and 4.42 Ga. A similar age of  $4428 \pm 25$  Ma was determined for the oldest Martian zircon [6]. The overall age distribution patterns of lunar and terrestrial zircons show broad similarities, comprising several major peaks, that, while not coinciding precisely, indicate extensive magmatic activity on both Moon and Earth. While

the Martian zircon pool is more restricted, the variability of their ages [6, 7] suggests a possibility of similar activity on Mars. Finally an important characteristic of terrestrial zircon grains is the variability of ages recorded within individual crystals, which suggests multiple periods of ancient reworking during metamorphism and/or partial melting, resulting in preservation of inherited cores with multiple complex overgrowths and recrystallization domains. Similar features are absent in lunar zircon, where the possible presence of inherited grains has not been demonstrated convincingly so far; limited examples where different parts of individual grains show different ages are interpreted as a reflection of impact related modification of these grains [8]. In turn unambiguous evidence for impacts has not (yet) been observed in the ancient terrestrial populations. On Mars partial Pb loss towards 1.4-1.7 Ga [6, 7] is recorded in some zircon grains, while others define upper intercept ages close to 1.4 Ga, tentatively interpreted as the age of a major impact that consolidated the host breccia sample. However, more work is needed to determine if these ages are true representation of an impact or can reflect new magmatic (or metamorphic) growth or even some low temperature Pb loss from zircon fragments residing for a long time in the Martian regolith.

Regardless of remaining questions, it is becoming increasingly clear that by about 4.4 Ga Earth, Moon and Mars had formed geochemically distinct enriched reservoirs capable of generating melts, which can crystallise zircon after some degree of fractionation. On the Moon this reservoir is identified as KREEP, a residuum of magma ocean fractionation, which is perhaps uniquely linked to the specific crystallisation sequence resulting in the formation of mafic cumulates followed by flotation of anorthositic crust and separation of Ti-rich phases. On Mars, the early crust sampled by NWA 7533 clast-laden melt rock particles and crystalline matrix of the sample, is compositionally similar to alkali basalt [6]. It was successfully modelled by low (<4%) degree partial melting of a garnet bearing Martian mantle and did not require a specific K, REE, P-enriched reservoir in the early Martian mantle [6]. While the source of the Jack Hills zircon is unknown, discovery of Martian grains of similar age (or slightly older) and also with very similar chemical and isotopic characteristics, indicates that zircons on Earth could have been formed as a result of remelting of similar, evolved basaltic crust rather than continental crust comparable to that existing on the Earth today.

**Ti-temperatures:** Temperature estimates for Martian zircon are at the higher end or slightly above

the range recorded in the Jack Hills grains. However, they indicate that both planets have conditions (i.e. water) that could have produced low temperature melts. The observed difference can readily be explained by the slight difference in the host rocks on Mars and Earth. Martian zircon is related to monzonite, which explains the somewhat elevated temperature of their crystallisation. While the source of Jack Hills zircon remains elusive, slightly lower temperatures, ranging between about 600 and 700°C, indicate the possibility of more granite-like differentiates as their host rocks. In contrast, all lunar zircon grains indicate formation temperatures in excess of 900°C, with the majority showing Ti-temperatures between 1000 and 1200°C.

**REE patterns:** The overall REE patterns of the three groups of zircon grains generally reflect the ability of zircon to incorporate different trivalent ionic radius REE into its lattice and are therefore mostly similar and characterised by enrichment in heavy REE and significant depletion in light REE. However, a significant difference between terrestrial and Martian zircon on the one hand and lunar grains on the other is shown by Ce behaviour, which can exist either as Ce(III) or Ce(IV), the latter partitioning very favourably into zircon. The Ce anomaly in the Jack Hills zircons has been interpreted as evidence of an oxidised environment during their formation [9]. Similarly, REE patterns of Martian grains indicate oxidising conditions during their crystallisation. However, the majority of lunar zircon do not show a Ce-anomaly, which is taken as a confirmation of reducing conditions that exist on the Moon. Nevertheless, several zircon grains from lunar breccia samples exhibit a clear positive Ce-anomaly, suggesting that the concentration of Ce in zircon is a factor of very localised change in oxidation conditions, rather than feature that can be used to infer global oxidation state of major planetary reservoirs. Consequently, it is not possible to determine whether the source of the monzonitic melt crystallising zircon on Mars was oxidized or instead, oxidising conditions were a result of melt formation and fractionation. Chlorine-rich volatile degassing, water dissociation and hydrogen escape are processes capable of strongly affecting the oxygen fugacity during magmatic differentiation [10-13]. Similarly, the presence of Ce-anomaly in terrestrial zircon should not be taken as *a priori* evidence of oxidizing conditions existing on the Earth during the early history of the planet

**O isotope compositions:** The observed variability of oxygen isotope compositions indicates that Mars was not homogenised with respect to oxygen, resulting in variable  $\Delta^{17}\text{O}$  in different zircon grains. In addition within grain variation of  $\delta^{18}\text{O}$  exceeds range that can be formed as a result of magmatic fractionation, with some estimates as heavy as 7-8% and one even up to 10%. A similar spread in  $\delta^{18}\text{O}$  in the Jack Hills zircon suite has been

interpreted as a primary feature indicative of sediment recycling and presence of surface water on the Hadean Earth. However, study of oxygen isotope compositions in Martian zircon shows that variations of  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  are not correlated and while one can be an indication of assimilation of surface materials by the magma during the zircon formation, the other has to be related to the reaction of metamict zircon with a low temperature fluid near the surface, significantly long after the zircon crystallisation. This also suggests that perhaps some of heavy oxygen compositions in the Jack Hills grains could be a result of very late alteration of these zircons during an intense lateritic weathering of the Australian continent. This possibility is also supported by U-Pb systems of investigated Martian and terrestrial grains. Both show clear evidence of secondary disturbance of their U-Pb system resulting in formation of discordia arrays on Concordia diagrams. On Mars the discordia has a lower intercept at 1.7-1.6 Ga, while Jack Hills zircon grains are affected by a recent Pb loss. Sample NWA7533 is interpreted as an impact breccia, therefore it is likely that the secondary disturbance of the U-Pb system is induced by impact or impacts at about 1.7-1.6 b.y. In contrast, in terrestrial zircon it is related to the regolith development in Australia. Consequently it is also possible that the surface weathering is at least partly responsible for the observed Pb loss on Mars and the planet could have developed regolith and weathering processes, similar to those currently occurring in Australia, prior or close to 1.7-1.6 Ga.

Contrary to the variability of oxygen isotope compositions observed in Martian and terrestrial zircon, lunar grains show an isotope composition of oxygen that is very restricted and mantle-like, consistent with the high temperature, low fluid concentration melts and an absence of post-crystallisation surface processes involving water, chemical weathering and sedimentary transportation.

**References:** [1] Froude, D. O. *et al.* (1983) *Nature* 304, 616-618, [2] Wilde, S.A. *et al.* (2001) *Nature* 409, 175-178, [3] Harrison, T.M. *et al.* (2005) *Science* 310, 1947-1950, [4] Peck, W.H. *et al.* (2001) *Geochim Cosmochim Acta* 65, 4215-4229, [5] Compston W. *et al.* (1984) *J. Geophys. Res.*, 89, B525-B534, [6] Humayun, M. *et al.* (2013) *Nature*, 503, 513-516, [7] Yin, Q.Z. *et al.* (2014) 45<sup>th</sup> LPSC., Abstract #1320, [8] Nemchin, A.A. *et al.* (2009) *Nature Geoscience*, 2, 133-136, [9] Trail, D. *et al.* (2011) *Nature*, 480, 79-82, [10] Sato M., and Wright T.L., (1966) *Science* 153, 1103-1105, [11] Candela P.P. (1986) *Geochim Cosmochim Acta*, 50, 1205-1211, [12] Mathez E.A. (1984) *Nature* 310, 371-375, [13] Bell A.S. and Simon A. (2011) *Geology* 39, 499-502.