

**ISOTOPIC COMPOSITION OF OXYGEN IN LUNAR ZIRCONS.** A.A. Nemchin<sup>1</sup>, M.J. Whitehouse<sup>2</sup>, R.T. Pidgeon<sup>3</sup>, and C. Meyer<sup>4</sup> <sup>1</sup>Western Australian School of Mines, Curtin University of Technology, Bentley Western Australia, 6102, Australia. <sup>2</sup>Laboratory for Isotope Geology, Swedish Museum of Natural History, S-104-05 Stockholm, Sweden. <sup>3</sup>Department of Applied Geology, Curtin University of Technology, Bentley, Western Australia, 6102, Australia. <sup>4</sup>NASA Johnson Space Center, Houston, Texas, USA.

**Introduction:** The recent discovery of heavy oxygen in zircons from the Jack Hills conglomerates Wilde et al. [1] and Mojzsis et al. [2] was interpreted as an indication of presence of liquid water on the surface of Early Earth. The distribution of ages of Jack Hills zircons and lunar zircons appears to be very similar and therefore analysis of oxygen in the lunar grains may provide a reference frame for further study of the early history of the Earth as well as give additional information regarding processes that operated on the Moon.

In the present study we have analysed the oxygen isotopic composition of zircon grains from three lunar samples using the Swedish Museum of Natural History CAMECA 1270 ion microprobe. The samples were selected as likely tests for variations in lunar oxygen isotopic composition.

**Samples:** Zircon from the soil sample 14163 is a large (~0.5mm) fragment, which is homogenous with respect to the age and concentration of trace elements. It was selected for the oxygen analyses in order to provide a test of analytical technique and also as a measure of the isotopic homogeneity of the grain.

Sample 14321 is a polymict breccia containing a complex variety of igneous and clastic components. Fourteen zircon grains have been found in the sawdust collected during the initial cutting of the sample. These zircons show a wide range of ages between 4.44 and 3.90 Ga and U and Th concentrations from 1600 to 18 ppm and from 300 to 3 ppm respectively. This variation is inferred to reflect significant difference in the zircon origin not only in terms of age but also with respect to the potential source rocks.

Sample 73235 is a cataclastic breccia, which contains a bytownite clast with an unusual zircon in the section 73235-82. This zircon consists of multiple fragments enclosed by bytownite and was termed pomegranate by Smith et al. [3], referring to its shape in transmitted light. Meyer et al. [4] suggested that the fragments are parts of a single primary magmatic zircon grain with the age of 4.31 Ga, and are surrounded by a much younger (4.18Ga) zircon that apparently lost all features indicative of crystalline nature. Pidgeon et al. (this volume) interpreted this younger zircon as a result of shock and/or temperature pulse associated with meteoritic impact. The sample therefore was selected for the oxygen analysis in order to test possible effect of this impact on the oxygen fractionation.

**Analytical technique:** Oxygen isotopes have been measured in the multicollector mode with O<sup>17</sup> placed on the electron multiplier and O<sup>16</sup> and O<sup>18</sup> on the faraday cups. A total number of 54 spots within three separate standard chips from three different mounts were analysed indispersed with analyses of lunar zircons during a continuous two-day session. Both  $\delta\text{O}^{18}$  and  $\delta\text{O}^{17}$  show some degree of fluctuation (Fig.1), which does not appear to depend on the analysed standard chip and therefore is unlikely to be a result of switching from one mount to another. This gives confidence that there is no systematic variation of oxygen composition resulting from the standard analysed in the mounts separate from the lunar zircons. Nevertheless, the observed fluctuation is slightly outside the counting statistics errors obtained for individual analyses. This resulted in the weighted average calculated with MSWD higher than one and external 2-sigma error of individual analyses of about 0.4‰ for both  $\delta\text{O}^{18}$  and  $\delta\text{O}^{17}$ . These errors have been included into the final errors estimated for the lunar samples

**Hf concentration:** Hervig et. al [5] and Eiler et al. [6] found a general correlation between the mean atomic mass of minerals and the instrumental mass fractionation during the oxygen analysis. This translates into a possible dependence of observed oxygen compositions on the Hf concentration in zircons (e.g. Peck et al. [7]). These authors analysed several zircons with the known oxygen composition and estimated that the 1% change in Hf concentration may result in about 1‰ change of  $\delta\text{O}^{18}$ . Although relationships are very poorly defined they appear to correlate with the theoretical constraints of Eiler et al. [6].

Hf concentrations in analysed zircons are very uniform at about 1% with the exception of three grains from sample 14321, two with a HfO<sub>2</sub> concentration of 0.85 and one with 1.6%. The HfO<sub>2</sub> concentration in the standard is 0.66%, which translates to a possible correction of observed data for most of analysed lunar zircons close to 0.3-0.4‰.

**Oxygen results:** All analyses combined determine a weighted average  $\Delta\text{O}^{17}$  of  $-0.02 \pm 0.1\%$  (2 $\sigma$  of the mean) and fall on the terrestrial fractionation line (Fig.2). Eighteen analytical spots within the sample 14163 show variation of  $\delta\text{O}^{18}$  between 6.2 and 7.2‰,

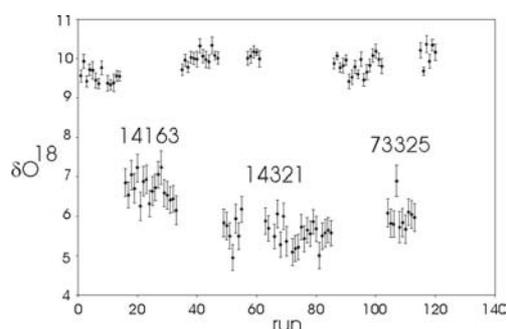


Fig.1. Sequence of analysed  $O^{18}/O^{16}$  ratios for the standard zircon 91500 and lunar samples recalculated to  $\delta O^{18}$ .

with the weighted average of  $6.69 \pm 0.16\%$  (MSWD=0.8). This zircon appears to be homogenous with respect to the oxygen isotope composition within the analytical errors.

The fourteen separate grains from the sample 14321 display similar homogeneity within the analytical errors. The  $\delta O^{18}$  values range between 5.0 and 6.2‰ with an average of  $5.58 \pm 0.13\%$  (MSWD=0.9). Six analyses of old primary zircon in the grain from the sample 73235 vary from 5.7 and 6.1‰. The secondary zircon in this sample forms very thin rims that are very difficult to sample even with the small ion probe spot. Three out of four analyses of the rims in fact represent a mixture of primary and secondary zircon as was revealed by the study of the sample under the transmitted light after the oxygen analyses and show  $\delta O^{18}$  values indistinguishable from the heavier analyses of primary zircon. A single spot, placed entirely within the secondary zircon (82-4) has  $\delta O^{18}$  value of  $6.9 \pm 0.4\%$ .

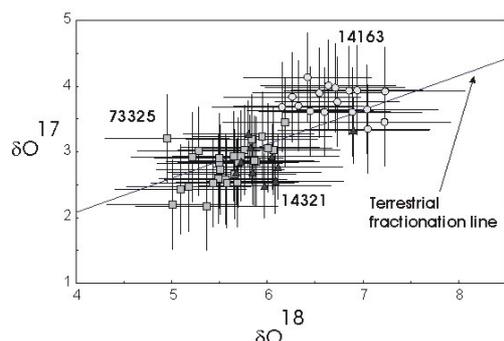


Fig.2.  $\delta O^{17}$  vs.  $\delta O^{18}$  plot for the analysed lunar zircon samples.

**Discussion:** The range of  $\delta O^{18}$  observed in the fourteen zircon grains from the sample 14321 is about 1‰ and very similar to the range shown by MORB (e.g. Eiler [8]), although it is slightly larger than the spread of oxygen compositions reported for the lunar rocks by

Wiechert et al. [9]. The small variation of oxygen isotope composition in these zircons suggests a very small degree of isotopic fractionation despite the inferred differences in zircon origin and in their age. It is, however, in agreement with the late crystallisation of zircon from the melt already enriched in heavier oxygen isotope by a significant fractionation of major minerals such as olivine, pyroxene and plagioclase combined with the fractionation of light isotope by zircon relative to the coexisting melt.

It is difficult however to apply similar explanation to the oxygen compositions observed in the zircon grain from the sample 14163. This oxygen composition is significantly heavier than any other material found on the Moon so far and suggests an even heavier composition for the melt from which this zircon was formed. It is still possible to explain this composition by an extreme fractionation of rock forming minerals or extremely small degrees of melting of the source to form such an unusually high  $\delta O^{18}$  melt. However, both significant fractionation of basaltic melt and small degrees of melting of a source rock will probably result in substantial enrichment of the melt in incompatible elements including U. This must be reflected in the relatively high concentration of U in the zircon. This zircon however, shows one of the lowest concentrations of U (17 ppm) in the population analysed during this study.

One of the rim analyses in the sample 73235 shows equally high  $\delta O^{18}$ , which probably can be explained by the inferred heat pulse associated with an impact. This pulse could probably drive the lighter isotope of oxygen out of the zircon or facilitate oxygen exchange between the zircon and surrounding plagioclase. The other three rim analyses however are indistinguishable within the errors from the main group, although as mentioned earlier they represents mixtures of rim material and the primary zircon.

**References:** [1] Wilde S.A., et al. (2001) *Nature* 409, 175-178. [2] Mojzsis S.J., et al. (2001) *Nature* 409, 178-181. [3] Smith J.M. et al. (1986). *LPS XVII*, 805-806. [4] Meyer C. et al. *LPS XVI*, 557-558. [5] Hervig R.L., et. al (1992) *Int. J. Mass Spectrom.* 120, 45-63. [6] Eiler J.M., et al. (1997) *Chem. Geol.* 138, 221-244. [7] Peck W.H., et al. (2001) *Geochim. Cosmochim. Acta.* 65, 4215-4229. [8] Eiler J.M., (2001) *Reviews in Min & Geochem.* 43, 319-363 [9] Wiechert U. et al., (2001) *Science* 294, 345-348.