**HF-W CHRONOMETRY OF THE MOON – NEW RESULTS FROM FERROAN ANORTHOSITES AND LOW-TI MARE BASALT 15555**. M. Touboul[1], T. Kleine[1], B. Bourdon[1], H. Palme[2] and R. Wieler[1]. [1]Institute for Isotope Geology and Mineral Resources, ETH Zürich, 8092 Zürich, Switzerland (touboul@erdw.ethz.ch), Institut für Mineralogie und Geologie, Universität zu Köln, 50674 Köln, Germany.

**Introduction:** Hf-W chronometry is a powerful tool for dating the formation and differentiation of planetary objects but its application to the Moon has been hampered by the presence of cosmogenic $^{182}$W in lunar samples [1-4]. It had been thought that there are $^{182}$W/$^{184}$W variations among lunar samples that reflect $^{182}$Hf-decay within the Moon , implying formation and differentiation of the Moon in the first ~60 Ma of the solar sytsem [1-4]. However, we have shown recently that metals from KREEP-rich samples, low- and high-Ti mare basalts have indistinguishable W isotope compositions [5]. These metals do not contain any Ta, such that their $^{182}$W/$^{184}$W is unaffected by cosmogenic $^{182}$W production. The homogeneous $^{182}$W/$^{184}$W ratios of the metals indicate the lunar magma ocean crystallized to more than ~60% later than ~60 Ma after CAI formation [5].

However, two issues remain to fully understand the Hf-W chronology of the Moon. First, the W isotope composition of the lunar crust is not known precisely and the available data for ferroan anorthosites [1] yield inconclusive results. Second, our recent results suggest that elevated $^{182}$W/$^{184}$W ratios in lunar whole-rocks should generally reflect cosmogenic $^{182}$W production. However, elevated $^{182}$W/$^{184}$W ratios in some lunar ferroan anorthosites having young exposure ages (<2 Ma) [1] as well as in mineral separates from low-Ti mare basalt 15555 [3] cannot readily be explained by the presence of cosmogenic $^{182}$W. Instead, the elevated $^{182}$W/$^{184}$W in these samples [1,3] would appear to reflect $^{182}$Hf-decay within the lunar mantle, in conflict with homogeneous $^{182}$W/$^{184}$W ratios of KREEP and the mare basalt sources [5]. To address these issues, we obtained new W isotope data for plagioclase separates from two ferroan anorthosites (60025 and 62255) having young exposure ages (~2 Ma) and for a non-magnetic fraction of low-Ti mare basalt 15555.

**Methods:** The anorthosites were gently crushed in an agate mortar and sieved to obtain a 40-500 µm fraction. High-purity plagioclase separates were obtained using heavy liquids and hand-picking. They were finely powdered and any remaining metal grains were removed with a hand-magnet. The non-magnetic fraction of low-Ti mare basalt 15555 consists of material that remained after the metal extraction performed by Kleine et al. [4]. The samples were dissolved in Savillex beakers using HF-$HNO_3$ at 120°C for 72 h. After drying, the samples are re-dissolved several times in $HNO_3$-$H_2O_2$, and finally in 6 M HCl-0.06 M HF. At this stage, complete dissolution is achieved and an ~5% aliquot was spiked with a mixed $^{180}$Hf-$^{183}$W-$^{180}$Ta tracer for isotope dilution measurements.

The low W contents of anorthosites (~2 ppb W) require processing of large amounts of sample (~4-5 g). We developed new techniques to quantitavely extract W from 4-5 g of plagioclase. The large amounts of Ca were first removed by cation exchange chromatography before W was extracted using previously established anion exchange techniques [6]. The latter is repeated once to ensure complete Ti removal. The W blank of this procedure was 50±20 pg (2σ) and is negligible. All measurements were performed using a Nu Plasma MC-ICPMS at ETH Zurich. Tungsten isotope ratios of the samples were determined relative to two bracketing measurements of the W standard. Each run was performed with ~1.5 V on $^{182}$W and 40 ratios were measured. The external reproducibility of the $^{182}$W/$^{184}$W measurement is ±0.3 $\varepsilon^{182}$W (2σ).

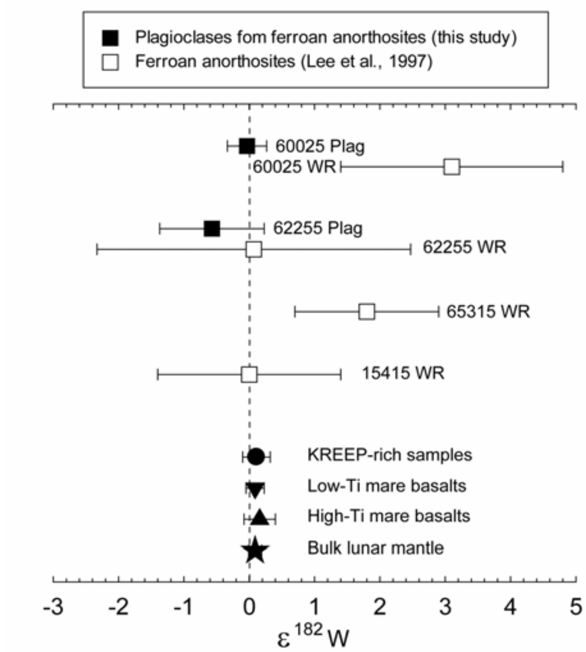


Fig. 1: W isotope composition of plagioclase separates from ferroan anorthosites 60025 and 62255. Previously published W isotope data for ferroan anorthosites [1] and metals from KREEP-rich samples [4,5] and low- and high-Ti mare basalts [5] are shown for comparison. $\varepsilon^{182}$W is the deviation of the $^{182}$W/$^{184}$W ratio of a sample relative to the terrestrial standard in parts per 10,000.

**Results:** Plagioclase separates from both ferroan anorthosites have low W contents (~2 ppb) and identical W isotope compositions that are indistinguishable from the terrestrial standard (Fig. 1).. Compared to previously published results for ferroan anorthosites [1], our new W isotope data are more precise by a factor of ~5. Most importantly, in contrast to an earlier reported positive $\varepsilon^{182}W$ of 3.1±1.7 for a 60025 whole rock [1], we find no $^{182}W$ anomaly for its plagioclase.

The non-magnetic fraction of the low-Ti mare basalt has $\varepsilon^{182}W$=0.9±0.3, ~58.5 ppb W and ~271 ppb Ta [10], corresponding to Ta/W~4.6 (Fig. 2). The $\varepsilon^{182}W$ seems to be somewhat lower than the average $\varepsilon^{182}W$ previously reported for 15555 [3] and the Ta/W ratio is slightly higher than those reported for a 15555 whole-rock and an ilmenite separate.

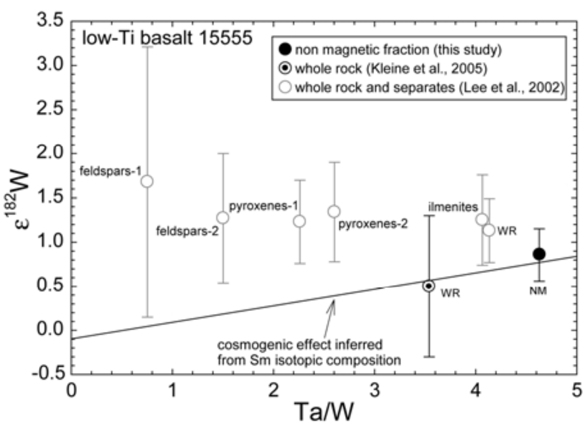


Fig. 2: W isotope composition of mineral separates and whole rocks from low-Ti mare basalt 15555. Cosmogenic effects are calculated as a function of Ta/W using correction equations [2] and the Sm isotopic composition of 15555 [9].

**Discussion:** *Ferroan anorthosites.* Our new W isotope data for ferroan anorthosites show that the lunar crust and mantle have indistinguishable $^{182}W/^{184}W$ ratios (Fig. 1). This indicates that the lunar crust formed when $^{182}Hf$ became effectively extinct, consistent with $^{147}Sm$–$^{143}Nd$ ages of ~4.45 Ga for ferroan anorthosites [8]. Plagioclase crystallization starts after ~70% crystallization of the lunar magma ocean [9], such that the similarity in W isotope composition of the lunar crust and mantle indicates that ~70% crystallization of the magma ocean was reached later than ~60 Ma after CAI formation. This is consistent with the Hf-W constraints obtained from KREEP and the mare basalt sources that require that the lunar magma ocean crystallized to more than ~60% later than ~60 Ma after CAI formation [5].

The reasons for the discrepancy between our W isotope data for 60025 plagioclases and those reported for 60025 by Lee et al. [1] are unclear. It seems unlikely that the higher $^{182}W/^{184}W$ reported earlier reflects the presence of cosmogenic $^{182}W$ because the exposure age of this sample is only ~2 Ma; the cosmogenic $^{182}W$ producion by neutron capture of $^{181}Ta$ in this case is less than ~0.1 ε units. The elevated $\varepsilon^{182}W$ reported earlier for 60025 may therefore be an analytical artefact or may be due to the presence of a yet unidentified cosmogenic component in the mafic component of this sample. Note that this component is not present in our sample because pure plagioclase separates were obtained.

*Low-Ti mare basalt 15555.* Lee et al. [3] argued that the average $\varepsilon^{182}W$=1.3±0.4 of low-Ti mare basalt 15555 reflects $^{182}Hf$ decay and that this sample contains no significant cosmogenic $^{182}W$ because it exhibits no correlation between the $^{182}W/^{184}W$ of mineral separates having variable Ta/W. Using the $^{149}Sm/^{150}Sm$ ratio of sample 15555 [8] and correction equations [2], the expected $^{182}W$ variations due to neutron capture of $^{181}Ta$ can be calculated as a function of their Ta/W ratios. In Fig. 2 we assume that the $\varepsilon^{182}W$ of 15555 unaffected by cosmic-ray effects is identical to that of all other lunar rocks ($\varepsilon^{182}W$ ~0). Our new data for a non-magnetic fraction of 15555, as well as previously reported data for a 15555 whole-rock [4], are remarkably consistent with the predicted cosmogenic effects in this sample (Fig. 2). In contrast, the data for mineral separates of 15555 reported by Lee et al. [3] do not fall on this trend but plot systematically above the line for the predicted cosmogenic $^{182}W$ production. The reasons for this are unclear but our new data for sample 15555 indicate that there is no evidence for an elevated $^{182}W/^{184}W$ in this sample. After correction for cosmogenic $^{182}W$ using Ta/W ratios and the Sm isotope composition of 15555, the non-magnetic fraction and the whole rock have $\varepsilon^{182}W$ values of 0.1±0.4 and -0.1±0.8, respectively. We therefore conclude that, after proper correction for cosmogenic effects, sample 15555 has $\varepsilon^{182}W$~0, indistinguishable from the $\varepsilon^{182}W$ values of metals from other low-Ti mare basalts [5].

**Conclusions:** New W isotope data for ferroan anorthosites reveal that, contrary to a previous report [1], these samples have W isotope compositions identical to that of the lunar mantle. This indicates that crystallization of plagioclase in the lunar magma ocean occurred later than ~60 Ma after CAI formation, consistent with both $^{147}Sm$–$^{143}Nd$ ages for ferroan anorthosites and Hf-W time constraints obtained from KREEP and the mare basalt sources [5]. We also show that, after proper correction for cosmogenic $^{182}W$, low-Ti mare basalt 15555 has a $^{182}W/^{184}W$ identical to those of metals from other low-Ti mare basalts.

**References:** [1] Lee D.C. et al., (1997) *Science 278*, 1098-1203. [2] Leya I. et al. (2000) *EPSL 175*, 1-12. [3] Lee D.C. et al. (2002) *EPSL 198*, 267-274 [4] Kleine T. et al. (2005) *Science 310*, 1671-1674. [5] Touboul M. et al. (2007) *Nature 450*, 1206-1209. [6] Kleine T. et al. (2004) *GCA 68*, 2935-2946 [7] Nyquist L.E. et al. (1995) *GCA 59*, 2817-2837. [8] Norman M. D. et al. (2003) *MAPS 38*, 645-661. [9] Longhi J. (2003) *JGR 108 (E8)*, #5083. [10] Münker et al. (2003) *Science 301*, 84-87.