TUNGSTEN STABLE ISOTOPE VARIATIONS IN METEORITES AND TERRESTRIAL SAMPLES BY DOUBLE SPIKE MC-ICPMS. N. Krabbe, T.S. Kruijer, and T. Kleine, Institut für Planetologie, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (nadine.krabbe@wwu.de).

Introduction: Mass-dependent isotope variations among terrestrial rocks and meteorites have emerged as a new tool for investigating high temperature processes. Some of the observed stable isotope variations, such as those in Mo, Cr, and Si, may be attributed to isotope fractionation during planetary core formation [e.g., 1-6], although this remains debated [e.g., 7]. The strongly different bonding environments of metal and silicate phases—which are in part controlled by varying oxidation states of these elements—provide a potent driving force of stable isotope fractionation [e.g., 8]. Hence, stable isotope variations can in principal be used to infer the (temperature) conditions during core formation in the Earth, other terrestrial planets and asteroids [e.g., 1-6]. However, establishing the full extent and significance of stable isotope variations during core formation still warrants further investigation.

Tungsten, a refractory and moderately siderophile element, is strongly redox sensitive, and hence, despite its high mass, significant mass-dependent W isotope fractionations can potentially be expected during metal silicate separation in a planetary body. Hence, W stable isotope signatures may directly constrain the temperature conditions of core formation in Earth. In turn, this might also provide information on the degree to which precursor planetary bodies equilibrated with the mantle during Earth's main accretion phase, information that is essential for accurately dating terrestrial core formation using the Hf-W system [e.g. 9].

Several studies reported W stable isotope data for terrestrial samples and meteorites, obtained using both the conventional standard-sample bracketing [10, 11] as well as using the double spike technique [12]. Of particular note are large W isotope variations with a total range of ~0.4 ‰ amu^{-1} reported by a previous study [10], but these data are in apparent conflict with smaller variations among terrestrial samples observed in two other studies [11, 12]. Hence, the full extent of W stable isotope variations remains unclear.

To better understand the extent and origin of W stable isotope variability during high temperature processes, we initiated a W stable isotope study of terrestrial and extraterrestrial materials using a double spike, with the ultimate aim of assessing the conditions of planetary core formation in Earth and other planetary bodies. Here we present new W stable isotope data for a suite of meteorites and terrestrial rock standards.

Samples and analytical methods: After mixing two single spikes enriched in ^{180}W and ^{183}W (acquired from Oak Rich National Laboratory) in optimal proportions [13], the ^{180}W-^{183}W double spike was calibrated against a certified isotopic W standard (NIST SRM 3163). A total of seven terrestrial rock standards (AGV-2, BCR-2, BHVO-2, GSP-2, RGM-2, SBC-1, and NIST129C), nine iron meteorite samples, and three chondrite samples (Allende, Gujba, and Gao) were investigated in this work. All samples were spiked prior to digestion. Iron meteorite samples (~0.1g-0.4g) were digested in reverse aqua regia, and silicate samples (~0.08-0.5g) in concentrated HF-HNO_3 (2:1). Analytical techniques for W separation and purification are based on previously developed procedures [14]. Tungsten isotope ratios were measured on a ThermoScientific Neptune *Plus* MC-ICPMS at the University of Münster. The chemical separation efficiently removes most Hf, which can potentially induce severe interferences on ^{180}W. Nevertheless, remaining Hf interferences were corrected by monitoring interference-free ^{178}Hf, and doping tests were performed to assess the accuracy of this correction. Also, to correct for bias in measured W isotope ratios between measurement sessions [e.g. 6], each sample measurement was bracketed by measurements of a double spike–standard (NIST 3163 W) mixture. Data deconvolution was performed with the Double Spike Toolbox [13] in MATLAB and a script that iteratively corrects for Hf interferences. The W stable isotope data are expressed in $\delta^{184/183}W$ as the permil deviation from the NIST SRM 3163 W isotope standard.

Results: The terrestrial rock standards reveal a narrow range in $\delta^{184}W/^{183}W$ between ~-0.01 and ~0.05 ‰ amu^{-1} (Fig. 1). Only the NIST 129C high-S steel exhibits a heavier $\delta^{184}W/^{183}W$ of ~0.19, a signature that may have been induced during industrial production of the steel. The iron meteorite and chondrite samples exhibit a narrow range in $\delta^{184}W/^{183}W$ between ~-0.025 and ~0.001 ‰ amu^{-1}, mostly indistinguishable from the terrestrial rock standards.

Discussion: Tungsten stable isotope variations may not only occur during metal-silicate separation [1-6], but potentially also during during magmatic differentiation in the mantle. A signature of core formation potentially results in distinct W stable isotope signatures between silicate rocks and chondrites, while magmatic differentation may result in W stable isotope variations among rocks derived from different magmatic reservoirs. The terrestrial rock standards analysed here show a small range in $\delta^{184/183}$W (~0.05 ‰ amu^{-1}), suggesting that, overall, the extent of W stable isotope fractionation during magmatic processes is small. In particular, we do not reproduce the large fractionation of δ^{184}W/^{183}W~0.36 reported for AGV-2 in an earlier study [10]. Although the results also hint at very small $\delta^{184/183}$W variations between the terrestrial rock standards, which seem to vary as a function of bulk SiO_2 content, these variations are barely resolvable and more work is needed to validate this observation. Ultimately the likely narrow range in $\delta^{184/183}$W among silicate rocks implied by the rock standard analyses may ease an estimation of the W stable isotope composition of the bulk silicate Earth.

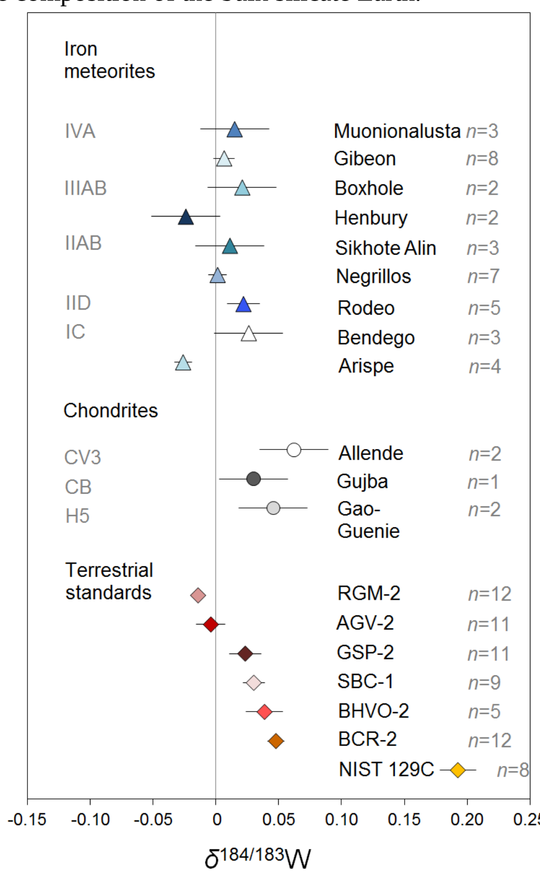

Fig. 1: Tungsten stable isotope signatures of terrestrial standards and meteorites. Error bars represent external uncertainties (2s.d. of the terrestrial rock standards or 95% conf. for samples with $n \geq 4$).

The iron meteorites analysed here exhibit a narrow range in δ^{184}W/^{183}W (Fig. 1). Although some data points (e.g. Arispe, Henbury) may hint at small variations, more work is needed to assess if these variations are significant. The chondrites exhibit a similar narrow range in $\delta^{184/183}$W, but their mean value seems slightly offset (though not resolved) relative to the iron meteorites. More analyses of chondrites are needed to assess whether this is significant. We note that, for a siderophile element like W, core formation on iron meteorite parent bodies should not induce a significant isotope fractionation between chondrites and iron meteorites, as most of the W budget is hosted in the metal [4].

Our data are inconsistent with the large range in δ^{184}W/^{183}W of ~ –0.3 to ~0.1 ‰ amu^{-1} reported previously for chondrites and iron meteorites [10]. The discrepancy with this earlier study likely reflects that the double spike is a more sensitive and reliable tracer for W stable isotope variations than conventional standard-sample bracketing.

Overall, the chondrites, iron meteorites, and terrestrial rock standards exhibit a very narrow range in δ^{184}W/^{183}W without significant variations (Fig. 1). If core formation in Earth induced a significant mass-dependent W isotope fractionation, then this should have led to distinct $\delta^{184/183}$W between chondrites and terrestrial mantle rocks, but this it not observed. Hence, our data obtained so far suggest that the W stable isotope variations during high temperature processes are relatively small, and in particular, we have not found evidence for a W stable isotope signature of core formation. This either implies that W stable isotope variations in nature are much smaller than expected, or perhaps more likely, that core formation in the terrestrial mantle occurred at sufficiently high temperatures to not induce a measurable W isotope fractionation. However, more W stable isotope data for chrondrites, iron meteorites, and terrestrial samples as well as experimental work are needed to validate this idea.

Conclusions: Tungsten stable isotope data for chondrites, iron meteorites, and terrestrial rock standards reveal a narrow range in δ^{184}W/^{183}W, suggesting that mass-dependent W isotope variations induced during high temperature processes are small. Further work is needed to assess if W stable isotope fractionation occurs during core formation and whether such signatures can be resolved in samples derived from the silicate porition of differentiated objects.

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