TUNGSTEN ISOTOPES PROVIDE EVIDENCE THAT CORE FORMATION IN SOME ASTEROIDS PREDATES THE ACCRETION OF CHONDRITE PARENT BODIES. T. Kleine<sup>1,2</sup>, K. Mezger<sup>1</sup>, H. Palme<sup>3</sup> and E. Scherer<sup>1</sup>, <sup>1</sup>Zentrallabor für Geochronologie, Universität Münster, Corrensstr. 24, 48149 Münster, Germany (kleine@erdw.ethz.ch), <sup>2</sup>Institut für Isotopengeologie und Mineralische Rohstoffe, Departement für Erdwissenschaften, ETH Zürich, Sonneggstr. 5, 8092 Zürich, Switzerland, <sup>3</sup>Institut für Mineralogie und Geochemie, Universität zu Köln, Zülpicherstr. 49b, 50674 Köln, Germany

**Introduction:** Chondrites are generally assumed to be the most primitive rocks of the solar system and to represent the precursor material from which asteroids accreted and then differentiated. Chondrites contain CAIs and chondrules, the former representing the oldest yet dated material formed in the solar system [1]. Age differences between CAIs and chondrules based on the U-Pb and <sup>26</sup>Al-<sup>26</sup>Mg chronometers show that chondrule formation persisted for at least ~2.5 Myr [1-3], indicating that accretion of chondrite parent asteroids lasted for at least ~2.5 Myr. These results contrast with estimates from planetary accretion models that propose that the first planetary objects formed within 1 Myr after condensation of the first solid matter [4]. <sup>182</sup>Hf-<sup>182</sup>W ages for iron meteorites show that differentiation (i.e., core formation) of their parent bodies occurred within ~5 Myr of each other [5]. For the first time, we link this differentiation event to the ages of CAIs, chondrules, and chondrite parent asteroids, by applying the <sup>182</sup>Hf-<sup>182</sup>W chronometer to CAIs, primitive chondrites, and iron meteorites.

Results: A Hf-W isochron based on the Allende CAIs A37 and A44a [6], four separates from CAI All-MS-1, and the mean of carbonaceous chondrites yields an initial  $^{182}$ Hf/ $^{180}$ Hf of  $(1.07\pm0.10)\times10^{-4}$  and an initial  $\varepsilon_{\rm W}$  of  $-3.47\pm0.20$  ( $\varepsilon_{\rm W}$  is the deviation from the terrestrial standard value in parts per 10,000). Metal and silicate separates from the CH chondrite Acfer 182 define an isochron with an initial <sup>182</sup>Hf/<sup>180</sup>Hf of  $(0.93\pm0.15)\times10^{-4}$  and an initial  $\varepsilon_{\rm W}$  of  $-3.29\pm0.21$ , indicating a Hf-W age of 1.5±2.5 Myr relative to CAIs. Metals HH237, Bencubbin, and Gujba have a weighted average  $\varepsilon_{\rm W}$  of -2.97±0.16 and postdate the last Hf-W fractionation in CAIs by 4.9±2.5 Myr. This relatively late formation is consistent with late volatilisation and re-condensation of material during highenergy planetary impacts[7].

All iron meteorites have  $\varepsilon_{\rm W}$  between -3.9 and -2.7, consistent with previous studies [5]. Group IIIAB, IVB, and IC irons have the least radiogenic  $^{182}{\rm W}/^{184}{\rm W}$  ratios, yielding a weighted average  $\varepsilon_{\rm W}$  of  $-3.79\pm0.06$ . This is lower than the initial  $^{182}{\rm W}/^{184}{\rm W}$  of the CAI isochron, indicating that the last equilibration of the Hf-W system in CAIs apparently postdates the onset of core formation in asteroids by  $2.5\pm1.7$  Myr. The IIAB iron meteorites have a weighted mean  $\varepsilon_{\rm W}$  of -

 $3.38\pm0.10$ , reflecting core segregation in the IIAB parent body at  $0.7\pm1.8$  Myr relative to CAIs. The IAB irons are more radiogenic (weighted mean  $\varepsilon_{\rm W}=-2.78\pm0.14$ ) than the other irons and  $7.4\pm2.7$  Myr younger than CAIs. This relatively young W model age reflects a late metal-silicate equilibration, possibly as a result of impact-related mixing processes on the IAB parent asteroid [8].

**Discussion:** Hf-W systematics of CAIs. Several observations indicate that the Hf-W age for CAIs dates processes occurring before parent body accretion and that it is not related to alteration or metamorphism on the CV parent asteroid. First, temperatures of the thermal metamorphism on the CV parent asteroid [9] were below ~500 °C, which would not have reset the Hf-W system [10]. Second, the well preserved U-Pb and <sup>26</sup>Al-<sup>26</sup>Mg age differences between CAIs and chondrules [1, 3] indicate that aqueous alteration did not reset these isotope systems. It is thus unlikely that the relatively immobile elements Hf and W were affected by aqueous alteration. This is endorsed by the low MSWD of 0.79 for the CAI isochron indicating a closed system behaviour of Hf and W in the examined CAIs. Third, the absolute Hf-W age for CAIs of 4568.0±1.7 Ma (as calculated relative to the H chondrite Ste. Marguerite) predates the ages of most chondrules (i.e., ~4567–4564 Ma) and thus cannot reflect parent body processes.

Cosmogenic effects on W isotope ratios. Spurious <sup>182</sup>W excesses can be caused by neutron-capture of <sup>181</sup>Ta, which is subsequently converted to <sup>182</sup>W. This effect is significant for samples having Ta/W>0.22, resulting in high 182W/184W in some lunar samples [11], however, CAIs and chondrites have lower Ta/W of ~0.15 and were not affected. Burnout of W isotopes by exposure to cosmic rays may change the W isotope composition of iron meteorites having exposure ages of several 100 Myr [12]. This effect would be more pronounced for <sup>182</sup>W/<sup>183</sup>W normalized to <sup>186</sup>W/<sup>183</sup>W than for <sup>182</sup>W/<sup>184</sup>W normalized to <sup>186</sup>W/<sup>184</sup>W, because different W isotopes would be affected to a different extent. A decrease of <sup>182</sup>W/<sup>184</sup>W by <sup>182</sup>W-burnout should also be accompanied by an upward, though less significant, shift of <sup>183</sup>W/<sup>184</sup>W [12]. However, we did not observe these effects and the average  $\varepsilon^{183}W$  of all iron meteorites examined here is  $0.00\pm0.04$  (2 $\sigma$ ).

Moreover, the exposure ages of Hoba, Arispe, and Tlacotepec differ substantially (340, 945, and 955 Ma, respectively [13]), but their W isotope compositions agree within the analytical uncertainty (less than ±0.25  $\varepsilon$ ). Based on the  $^{182}$ W/ $^{184}$ W difference between Arispe  $(\varepsilon_{\rm W} = -3.78\pm0.14)$  and Hoba  $(\varepsilon_{\rm W} = -3.74\pm0.23)$  of - $0.04\pm0.27$  (2 $\sigma$ ), we estimate that a ~600 Ma exposure to cosmic rays (i.e., the difference in exposure ages between Arispe and Hoba) can lower the <sup>182</sup>W/<sup>184</sup>W ratio by at most  $\sim 0.3 \varepsilon$  units, consistent with previous estimates [12]. The IIAB irons tend to have the lowest exposure ages (e.g., ~30 Myr for North Chile, ~45 Myr for Negrillos [11]) and the highest  $\varepsilon_{W}$  values among magmatic irons, suggesting that the slightly lower  $\varepsilon_{W}$ of groups IC, IIIAB, IVA, and IVB may be caused by  $^{182}$ W-burnout. Moreover, the lowest  $\varepsilon_{W}$  for irons reported here is higher than previously reported values for the IIAB iron Lombard [5] and the IVB iron Tlacotepec [5, 14]. The reason for these discrepancies is unclear but the different  $\varepsilon_{\mathrm{W}}$  values for Tlacotepec (- $4.5\pm0.4$  [5],  $-4.4\pm0.4$  [14],  $-3.66\pm0.18$  [this study]) may be interpreted to indicate that the W isotope composition in some parts of this iron meteorite has been altered by interactions with cosmic rays. Taken together, it is currently unclear if the <sup>182</sup>W/<sup>184</sup>W ratios of iron meteorites having old exposure ages have been slightly lowered by cosmogenic effects.

*Possible implications of the low*  $ε_W$  *of some iron meteorites.* Provided that the  $ε_W$  values of the IIIAB, IVA, IVB, and IC irons have not been affected by cosmogenic effects, our data indicate that the last equilibration of the Hf-W system in CAIs postdates core formation in the oldest asteroids by 2.5±1.7 Myr. This indicates that the solar system may be slightly older than suggested by the 4567.2±0.6 Ma U-Pb age for CAIs, consistent with earlier estimates from  $^{53}$ Mn- $^{53}$ Cr and  $^{129}$ I- $^{129}$ Xe systematics [15-17]. The initial  $^{26}$ AI/ $^{27}$ Al of the solar system is thought to be  $\sim 5\times 10^{-5}$  (as constrained by CAIs), but the 2.5±1.7 Myr gap between the oldest irons and CAIs might indicate that the solar system initial  $^{26}$ AI/ $^{27}$ Al was higher than  $\sim 1\times 10^{-4}$ .

Early core formation in the parent asteroids of magmatic irons. Currently, the most reliable age constraints for the formation of iron meteorites are provided by the IIAB irons because their low exposure ages preclude cosmic ray induced effects on the W isotope composition. Combining the formation intervals for CAI-irons and CAI-chondrules shows that the IIAB irons ( $\Delta t = 0.7 \pm 1.8$  Myr) formed before or at the same time as chondrules in the primitive chondrites Semarkona ( $\Delta t = 2.0 \pm 0.2$  Myr [18]) and Yamato81020 ( $\Delta t = 2.6 \pm 0.2$  Myr [2]). This observation is corrobo-

rated by W isotope data for the IIAB North Chile indicating formation no later than 1.7 Myr after CAIs and thus significantly earlier than chondrules in the aforementioned chondrites. Even if the <sup>182</sup>W/<sup>184</sup>W ratios of IIIAB, IVA, IVB, and IC irons have been lowered by <sup>182</sup>W burnout, this effect must have been small (see above). We therefore conclude that these irons formed before most chondrules.

Conclusions: Our new age constraints lead to a revised model for asteroid formation and the origin of chondrites. The relatively late formation of chondrules indicates that the parent asteroids of chondrule-bearing chondrites (i.e., all groups except CI) must represent second-generation planetesimals that may be the reaccreted debris produced during collisional disruption of first-generation planetesimals [19]. Chondrules may have formed by thermal processing of material derived from these early asteroids, implying that chondrules are not primary nebula objects. Iron meteorites appear to be the only vestiges of first-generation planetesimals, suggesting that the complementary silicate rocks have been completely destroyed during collisional break-up, but silicate inclusions in IVA irons may be remnants of these early silicates. The most plausible heat source for melting and differentiation of firstgeneration planetesimals is decay of <sup>26</sup>Al, which was abundant at the time of core formation in the oldest asteroids (26Al/27Al ~5×10-5, as constrained by CAIs [1,3]). In contrast, the preservation of the primitive appearance of chondrites reflects the late formation of their parent asteroids after <sup>26</sup>Al had decayed to levels insufficient to cause planet-wide melting.

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