Earth and Planetary Science Letters 270 (2008) 106–118

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Hf–W thermochronometry: Closure temperature and constraints on the accretion and cooling history of the H chondrite parent body

Thorsten Kleine [a,*], Mathieu Touboul [a], James A. Van Orman [b], Bernard Bourdon [a], Colin Maden [a], Klaus Mezger [c], Alex N. Halliday [d]

[a] Institute for Isotope Geochemistry and Mineral Resources, Department of Earth Sciences, ETH Zurich, Clausiusstrasse 25, 8092 Zurich, Switzerland
[b] Department of Geological Sciences, Case Western Reserve University, 10900 Euclid Ave, Cleveland, Ohio 44106-7216, United States
[c] Institut für Mineralogie, Universität Münster, Corrensstrasse 24, 48149 Münster, Germany
[d] Department of Earth Sciences, University of Oxford, Parks Road, OX1 3PR, United Kingdom

ARTICLE INFO

Article history:
Received 19 December 2007
Received in revised form 3 March 2008
Accepted 4 March 2008
Available online 15 March 2008

Editor: R.W. Carlson

Keywords:
W isotopes
closure temperature
H chondrites
thermochronometry
chondrules

ABSTRACT

We obtained Hf–W metal-silicate isochrons for several H chondrites of petrologic types 4, 5, and 6 to constrain the accretion and high-temperature thermal history of the H chondrite parent body. The silicate fractions have ^{180}Hf/^{184}W ratios up to ~51 and ^{182}W/^{184}W ratios up to ~33 ε units higher than the whole-rock. These high ^{180}Hf/^{184}W and radiogenic W isotope ratios result in highly precise Hf–W ages. The Hf–W ages of the H chondrites become younger with increasing metamorphic grade and range from $\Delta t_{CAI}=1.7\pm0.7$ Ma for the H4 chondrite Ste. Marguerite to $\Delta t_{CAI}=9.6\pm1.0$ Ma for the H6 chondrites Kernouvé and Estacado. Closure temperatures for the Hf–W system in H chondrites were estimated from numerical simulations of W diffusion in high-Ca pyroxene, the major host of radiogenic ^{182}W in H chondrites, and range from 800±50 °C for H4 chondrites to 875±75 °C for H6 chondrites. Owing to these high closure temperatures, the Hf–W system closed early and dates processes associated with the earliest evolution of the H chondrite parent body. Consequently, the high-temperature interval of ~8 Ma as defined by the Hf–W ages is much shorter than intervals obtained from Rb–Sr and Pb–Pb dating. For H4 chondrites, heating on the parent body probably was insufficient to cause W diffusion in high-Ca pyroxene, such that the Hf–W age of $\Delta t_{CAI}=1.7\pm0.7$ Ma for Ste. Marguerite was not reset and most likely dates chondrule formation. This is consistent with Al–Mg ages of ~2 Ma for L and LL chondrules and indicates that chondrules from all ordinary chondrites formed contemporaneously. The Hf–W ages for H5 and H6 chondrites of $\Delta t_{CAI}=5.9\pm0.9$ Ma and $\Delta t_{CAI}=9.6\pm1.0$ Ma correspond closely to the time of the thermal peak within the H chondrite parent body. Combined with previously published chronological data the Hf–W ages reveal an inverse correlation of cooling rate and metamorphic grade: shortly after their thermal peak H6 chondrites cooled at ~10 °C/Ma, H5 chondrites at ~30 °C/Ma and H4 chondrites at ~55 °C/Ma. These Hf–W age constraints are most consistent with an onion-shell structure of the H chondrite parent body that was heated internally by energy released from ^{26}Al decay. Parent body accretion started after chondrule formation at 1.7±0.7 Ma and probably ended before 5.9±0.9 Ma, when parts of the H chondrite parent body already had cooled from their thermal peak. The well-preserved cooling curves for the H chondrites studied here indicate that these samples derive from a part of the H chondrite parent body that remained largely unaffected by impact disruption and reassembly but such processes might have been important in other areas. The H chondrite parent body has a ^{180}Hf/^{184}W ratio of 0.63±0.20, distinctly lower than the ^{180}Hf/^{184}W = 1.21±0.06 of carbonaceous chondrite parent bodies. This difference reflects Hf–W fractionation within the first ~2 Ma of the solar system, presumably related to processes in the solar nebula.

1. Introduction

Hafnium–tungsten chronometry has been applied widely to determine the timescales of differentiation of asteroids and terrestrial planets (Harper and Jacobsen, 1996; Schoenberg et al., 2002; Yin et al., 2002; Halliday, 2004; Kleine et al., 2004b; Jacobsen, 2005; Nimmo and Agnor, 2006; Nimmo and Kleine, 2007) but its potential for dating chondrites and constraining the thermal evolution of their parent bodies has yet to be explored. To utilize Hf–W chronometry of meteorites meaningfully it is necessary to know the closure temperature (T_c) for diffusive exchange of parent and daughter elements among the different minerals in a rock (Dodson, 1973; Ganguly and

---

* Corresponding author.
E-mail address: kleine@erdw.ethz.ch (T. Kleine).

doi:10.1016/j.epsl.2008.03.013

Tirone, 2001). Knowledge of T_c is essential for evaluating whether an age dates the time of mineral growth or some time along the cooling path. Such information is critical for the interpretation of Hf–W ages in comparison to results from other chronometers and within the framework of models for the thermal evolution of asteroids.

Closure temperatures can be calculated from diffusion rates of the element of interest in the appropriate minerals. Such data are not available for W but here we determine closure temperatures from numerical simulations of W diffusion in silicates using the model of Van Orman et al. (2001, 2006). These results are compared to values of T_c estimated by age comparison. Ideal samples for this (i) should be well dated with different chronometers (i.e., have a well-defined cooling history), (ii) should exhibit protracted cooling, such that differences in closure temperatures result in well-resolved age differences, and (iii) should contain components having substantially different Hf/W ratios, such that precise Hf–W isochrons can be determined. These criteria are met by ordinary chondrites. First, the thermal evolution and structure of their parent bodies has already been studied with several chronometers (Wasserburg et al., 1969; Podosek and Brannon, 1991; Göpel et al., 1994; Trieloff et al., 2003; Amelin et al., 2005; Bouvier et al., 2007). Second, ordinary chondrites exhibit a wide range of metamorphic conditions from type 3 (unequilibrated) to type 6 (highly equilibrated), reflecting widely different cooling histories (Dodd, 1969). Third, ordinary chondrites contain abundant metal, which makes them ideal for Hf–W chronometry. Metals are virtually Hf-free but are enriched in W, resulting in ^{180}Hf/^{184}W ~ 0 in metals and elevated ^{180}Hf/^{184}W ratios in the corresponding silicates. For instance, Kleine et al. (2002) reported ^{180}Hf/^{184}W ~ 14 coupled with radiogenic ^{182}W/^{184}W for a silicate fraction from the H4 chondrite Ste. Marguerite. Such high ^{180}Hf/^{184}W and radiogenic ^{182}W/^{184}W ratios make it possible to obtain high-precision Hf–W ages.

We present Hf–W isochrons for several equilibrated H chondrites. Most of the samples investigated here were previously dated with other chronometers, including the ^{207}Pb–^{206}Pb system (Göpel et al., 1994; Amelin et al., 2005; Bouvier et al., 2007). The diffusivity of Pb in the relevant minerals is relatively well constrained (Cherniak et al., 1991; Cherniak, 1998), facilitating estimates of closure temperatures by age comparison. These estimates are compared to results from numerical simulations of W diffusion in a metal-silicate assemblage, which, in conjunction with the Hf–W ages, are used to assess the significance of the Hf–W ages and to constrain the thermal evolution of the H chondrite parent asteroid.

2. Analytical methods

Pieces of meteorite were cleaned with abrasive paper and with 0.05 M HNO_3, de-ionized H_2O and ethanol in an ultrasonic bath to remove any contamination introduced during cutting from larger samples. Each fragment was crushed in an agate mortar and separated into <40 μm and 40–150 μm fractions using nylon sieves. During crushing metal grains were removed using a hand-magnet and separated into two fractions using a 40 μm nylon sieve.

Where sufficient material was available, the coarser fraction was further separated into several fractions, depending on the size of the metal grains. Silicate dust attached to or intergrown with the metal grains was removed by repeated crushing of the magnetic fraction under ethanol. Although all visible metal grains were removed, the 40–150 μm fractions were still slightly magnetic, most likely reflecting the presence of tiny metal inclusions in the silicate and oxide grains. The 40–150 μm fractions were further separated using a hand-magnet to obtain several "non-magnetic" fractions. These were labeled NM-n, *n* = 1, 2, 3…, NM-1 always denoting the least magnetic fraction for each chondrite. The NM-1 fractions are non- magnetic (i.e., with the hand-magnet used here) and might be entirely metal-free, the NM-2 fractions are slightly more magnetic, and the NM-3 fractions again are slightly more magnetic than the NM-2 fractions.

All NM fractions were inspected under the binocular microscope. They consist mainly of olivine and pyroxene but most fractions also contain some ilmenite, feldspar and phosphates. All NM fractions were cleaned with ethanol in an ultrasonic bath and powdered in an agate mortar. Remaining metal grains were removed from these powders using a hand-magnet.

The metal separates were dissolved in 15 mL Savillex® vials at ~120 °C on a hotplate using 6 M HCl–0.06 M HF. In some cases, a few drops of concentrated HNO_3 were added. The NM fractions were dissolved in 60 mL Savillex® vials at ~180 °C on a hotplate using HF–HNO_3–$HClO_4$ (5:4:1). After digestion, the samples were dried and re-dissolved in HNO_3–H_2O_2 to remove organic compounds. Then the samples were completely dissolved in 6 M HCl–0.06 M HF and a ~10% aliquot was spiked with a mixed ^{180}Hf–^{183}W tracer that was calibrated against pure Hf and W metals (Kleine et al., 2004a).

The methods for the separation of Hf and W from the sample matrix were slightly modified from those outlined in Kleine et al. (2004a). The metal separates were dried, re-dissolved in 1 M HF–0.1 M HNO_3 and loaded onto pre-cleaned anion exchange columns (2 mL BioRad® AG1X8, 200–400 mesh). The matrix was washed from the column using ~5 resin volumes 1 M HF–0.1 M HNO_3 and W together with other high field strength elements and Mo was eluted in 6 M HNO_3–0.2 M HF (Münker et al., 2001; Weyer et al., 2002; Kleine et al., 2004a). After drying down, the W cut was re-dissolved in 1 M HF–0.1 M HNO_3 and loaded onto a pre-cleaned anion exchange column (1 mL BioRad® AG1X8, 200–400 mesh).

Again, the matrix was washed from the column using ~5 resin volumes 1 M HF–0.1 M HNO_3 but high field strength elements (Hf, Zr, Nb, Ti) were first removed in 6 M HCl–0.01 M HF before W was eluted in 6 M HCl–1 M HF. In this acid mixture, Mo is strongly adsorbed on the anion resin (Kleine et al., 2004a).

The first part of the ion exchange procedure employed for the NM fractions is similar to the first step in the Hf chemistry of Salters and Hart (Salters and Hart, 1991). After aliquoting, the NM fractions were dried and re-dissolved in 4 M HF. The solution was centrifuged and decanted and the residue washed several times with 4 M HF. The solution was ultrasonicated several times to ensure optimal release of W from the fluoride residue and was loaded onto pre-cleaned anion exchange columns (3.5 mL BioRad® AG1X8, 100–200 mesh). The matrix was washed from the column using ~6 resin volumes of 4 M HF and W together with Zr, Hf, Ti, Nb, Mo was eluted using 6 M HNO_3–0.2 M HF. After drying, this cut was re-dissolved in 1 M HCl–0.5 M HF and loaded onto pre-cleaned anion exchange columns (3 mL BioRad® AG1X8, 100–200 mesh), where W was purified following the procedure of Kleine et al. (2004a). Titanium was washed from the column using HAc–HNO_3–H_2O_2, Zr, Hf, and Nb were rinsed off in 6 M HCl–0.01 M HF and W was eluted in 6 M HCl–1 M HF.

Total procedural blanks ranged from ~50 to ~350 pg for the W isotope composition measurements and ~12 to 50 pg W and ~10 pg Hf for the isotope dilution measurements. The variable W blanks are caused by the use of different batches of acetic acid.

All isotope measurements were performed using a *Nu Plasma* MC-ICP-MS at ETH Zürich, equipped with a Cetac Aridus desolvating nebuliser. Prior to measurement, the samples were re-dissolved and dried several times in HNO_3–H_2O_2 to remove organic compounds and, in the case of metal-rich samples, volatile Os oxides and then taken up in a 0.56 M HNO_3–0.24 M HF mixture. Tungsten isotope compositions of metals and whole-rocks were typically measured with a signal intensity of ~2 V on ^{182}W, which was obtained for a ~20 ppb W solution. For these samples, 60 ratios (3 blocks of 20 ratios) were measured resulting in within-run statistics of the order of 0.2 ε units (2σ). Owing to the low W contents in the NM fractions, their W isotope compositions were measured in 1 or 2 blocks of 20 ratios each with signal intensities of ~0.5 to 1 V on ^{182}W. The within-run statistics of these measurements were typically between 0.5 and 1 ε unit. Instrumental mass bias was corrected relative to ^{186}W/^{183}W = 1.9859