

**CLOSURE TEMPERATURE OF THE  $^{182}\text{Hf}$ - $^{182}\text{W}$  SYSTEM IN CHONDRITES: A MODEL.** James A. Van Orman<sup>1</sup>, Thorsten Kleine<sup>2</sup>, Bernard Bourdon<sup>2</sup>, <sup>1</sup>Dept. of Geological Sciences, Case Western Reserve University ([james.vanorman@case.edu](mailto:james.vanorman@case.edu)), <sup>2</sup>Institute for Isotope Geochemistry and Mineral Resources, Department of Earth Sciences, ETH Zürich

**Introduction:** Hafnium-tungsten chronometry has significant potential for dating chondrites and constraining the thermal histories of their parent bodies, and may preserve information on the pre-accretional histories of chondrites that have experienced limited thermal processing. To utilize Hf-W chronometry of meteorites meaningfully it is necessary to determine the conditions under which the system becomes closed to diffusive transfer of daughter nuclides among the minerals in the rock. This knowledge is essential for evaluating whether a Hf-W age dates the time of mineral growth, or some time along the cooling (or heating) path. Such information is critical for interpreting Hf-W ages in comparison to results for other chronometers, and within the framework of models for the thermal evolution of asteroids.

The cooling age for a specific geochronologic system is defined to be the time since diffusive exchange ceased, and the closure temperature is the temperature along the cooling path that corresponds with the observed age. Dodson<sup>1</sup> and Ganguly and Tirone<sup>2</sup> presented rigorous mathematical analyses of the closure of geochronologic systems, but to obtain analytical solutions were forced to make simplifying assumptions that are not necessarily met for the Hf-W system in chondrites. For example, these models assume (i) an infinite sink for radiogenic daughters; (ii) a radioactive decay time that is long compared to the cooling time; and (iii) that heating at the peak temperature was sufficient to homogenize the mineral(s) of interest, erasing all memory of the prograde metamorphic path. Condition (i) is never rigorously satisfied for an isochron system, which depends on daughters being distributed between multiple finite reservoirs, but it may be an adequate assumption for meteorites in which the metal fraction (the major sink for W) is sufficiently large. Conditions (ii) and (iii) are satisfied only if the cooling time is  $\ll 9$  Myr and the peak temperature is sufficiently high.

Because the analytical solutions for closure temperature may not be applicable, we instead developed a numerical model for radiogenic production and diffusive exchange of daughter nuclides among multiple phases. The model does not depend on the assumptions outlined above, and allows us to simulate complicated temperature histories, with both heating and cooling segments.

**Numerical Model:** The spatial distribution of  $^{182}\text{W}$  is calculated as a function of time in a rock consisting of multiple minerals.  $^{182}\text{Hf}$  and  $^{182}\text{W}$  are initially distributed among the minerals according to their

equilibrium partition coefficients. As  $^{182}\text{W}$  is produced by  $^{182}\text{Hf}$  decay, a disequilibrium distribution develops and  $^{182}\text{W}$  is transferred among the minerals by diffusion. The minerals in the rock are assumed to remain in partitioning equilibrium with each other at their surfaces throughout the simulation. Because not all minerals that host Hf and W are likely to be in physical contact, this assumption is likely justified only if  $^{182}\text{W}$  is transferred efficiently through a fast grain boundary network, which appears plausible according to recent experimental measurements<sup>3</sup>. If this assumption is not justified, then the diffusive exchange of W will be less efficient and the closure temperature higher. Thus, the closure temperatures we calculate can be taken as lower limits for the selected parameter values.

The age is calculated after all  $^{182}\text{Hf}$  has decayed, using the integrated W isotopic composition in each phase. For simulations with monotonic cooling, the closure temperature is calculated as the temperature along the cooling path that corresponds to the calculated age. Further details on the numerical model and its solution are given in Ref. [4].

**Application to Ordinary Chondrites:** To determine the conditions for closure of the Hf-W system, it is necessary to know W diffusion coefficients in the appropriate minerals, and their temperature dependence. Such data are not yet available from experimental measurements except for metallic iron, which is unlikely to limit W transfer due to its rapid diffusivity. The major host for Hf in ordinary chondrites is probably high-Ca pyroxene, and we estimate the diffusion parameters for W in this mineral according to the model presented in Ref. [5]. Tungsten is assumed to have a charge of +4, an ionic radius of 0.066 nm [6] and is assumed to reside on the 6-fold coordinated M1 site, which has an ideal radius of 0.072 nm and metal-oxygen bond length of 0.22 nm. Assuming that the Van Orman et al. [5] model applies to cations that occupy the M1 site - which appears reasonable since the model predicts diffusion coefficients for  $\text{Fe}^{2+}$  on the M1 site that are in good agreement with experimental data [7] - gives an activation energy estimate of 453 kJ/mol and a pre-exponential factor of  $9.53 \times 10^{-5} \text{ m}^2/\text{s}$ .

We simulated a simple system consisting of high-Ca pyroxene and metal. We found that the metal fraction did not have a significant influence on the closure temperature unless it was much lower than typical of ordinary chondrites (on the order of 1% metal or less). We also investigated whether W isotope heterogeneity resulting from  $^{182}\text{Hf}$  decay prior to the accretion of the parent body could be erased at peak metamorphic tem-

peratures. The system was allowed to develop isotopic heterogeneity under cold, non-diffusive conditions for 1 Myr, then heated instantly to 950 °C and cooled slowly at ~30 °C/Myr. For a high-Ca pyroxene grain size on the order of a few microns the system homogenized rapidly at the peak temperature, completely erasing the pre-accretional history. However, for a grain size on the order of one hundred microns, or for a lower peak temperature on the order of 700 °C the initial W isotopic heterogeneity is not erased and the age is influenced by the cold pre-accretional history. Thus we can provisionally conclude that Hf-W ages sample the cooling path for ordinary chondrites that have been heated above ~900 °C (e.g. H5 and H6), but may record pre-accretional ages for less metamorphosed ordinary chondrites (e.g. H4).

Calculated Hf-W closure temperatures for a high-Ca pyroxene/metal system with peak temperature of 1000 °C (sufficient to erase pre-existing isotopic heterogeneity) and a range of linear cooling rates and grain sizes are shown in Fig. 1.

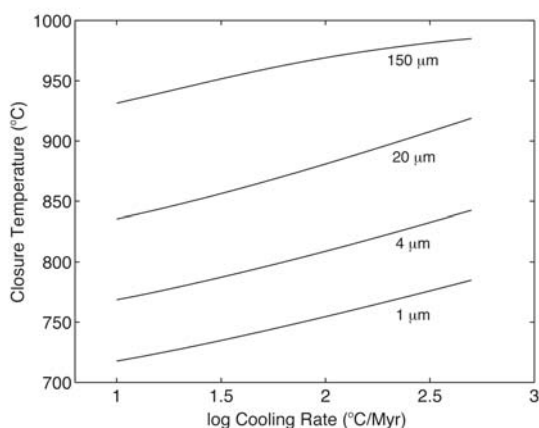


Fig. 1. Calculated closure temperatures for the Hf-W system.

**Hf-W ages for ordinary chondrites:** These closure temperature estimates can be used in conjunction with Hf-W ages for chondrites to constrain the thermal evolution of their parent bodies. For this task we obtained Hf-W ages for a suite of H chondrites [8] that cover the entire range of metamorphic conditions reached inside the H chondrite parent body. The Hf-W ages for the H chondrites Ste. Marguerite, Kernouvé and Estacado are the oldest reported for these meteorites so far; for Richardton the Hf-W and Pb-Pb chondrule ages [9] are indistinguishable. This is consistent with the high closure temperature of the Hf-W system estimated here.

Owing to its high closure temperatures, the Hf-W system dates processes associated with the earliest evolution of the H chondrite parent body. Consequently, the high temperature interval of ~8 Ma as de-

finer by the Hf-W ages [8] 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 allow W loss from high-Ca pyroxene, such that the Hf-W age of Ste. Marguerite was not reset and most likely dates chondrule formation. The Hf-W age of  $1.7 \pm 0.7$  Ma is identical to Al-Mg ages for chondrules from L and LL chondrites [10,11]. Because Hf-W closure temperature and peak metamorphic temperature of H5 and H6 chondrites are similar, the Hf-W ages for these chondrites 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 are most consistent with an onion-shell structure of a relatively large H chondrite parent body (radius ~100 km) that was heated internally by energy released by  $^{26}\text{Al}$  decay (Fig. 2).

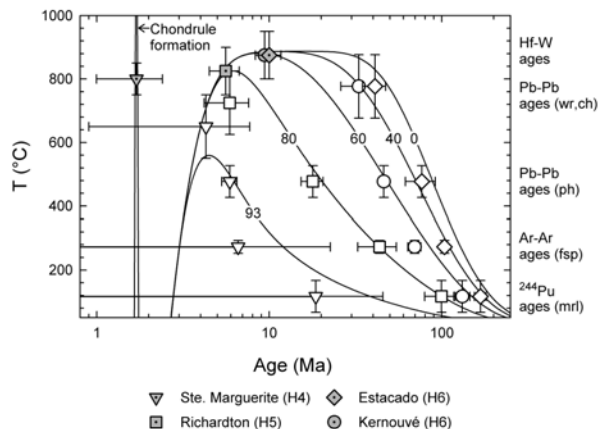


Fig. 2: Cooling curves for H chondrites. Dashed lines indicate calculated temperature profiles for different depths (indicated by numbers on curves) in a spherical body with 100 km radius. Details regarding the thermal modelling and references for the ages are given in ref. [8].

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