

IRON ISOTOPE FRACTIONATION BETWEEN METAL AND TROILOITE: A NEW COOLING SPEEDOMETER FOR IRON METEORITES. M. J. Krawczynski¹, J. A. Van Orman¹, N. Dauphas², E. E. Alp³, and M. Hu³, ¹Case Western Reserve University, Cleveland, OH (mjk181@case.edu), ²Origins Laboratory, The University of Chicago, Department of the Geophysical Sciences and Enrico Fermi Institute, ³Advanced Photon Source, Argonne National Laboratory.

Introduction: Iron meteorites are remnants of differentiation processes in planetesimals. Determination of their subsolidus cooling rates is one of the only available methods for estimating parent body sizes, with bigger bodies having more thermal insulation around a differentiating core, and thus slower cooling rates.

Cooling rates of iron meteorites are often estimated by modeling the subsolidus evolution of exsolved kamacite and taenite [1]. However, this approach is difficult to apply to meteorites with exsolution patterns that are either as coarse as the sample size (hexahedrites), or with no clear exsolution textures due to high Ni contents (ataxes) [2]. Some classes of meteorites also show variability in their estimated cooling rates (*i.e.*, the IVA group), and independent estimates would be valuable for understanding these variations.

Here we present a new method for estimating the cooling rate of iron meteorites based on metal-troilite partitioning of Fe isotopes. The equilibrium partitioning of Fe isotopes is strongly dependent on temperature, with larger fractionation at lower temperatures. Slowly cooled iron-troilite pairs will preserve larger Fe isotope fractionations than rapidly cooled pairs because they are able to equilibrate to lower temperatures. Troilite is a ubiquitous phase in all Fe-meteorite groups [2, 3], and Fe self-diffusion data have been determined experimentally for metal and sulfides [4, 5]. We present here new data on the equilibrium fractionation of Fe isotopes between metal and troilite, and a numerical model for determining closure temperatures.

Experimental methods:

Synthesis of ⁵⁷Fe enriched minerals: Taenite, troilite, schreibersite, and cohenite were synthesized using nearly pure ⁵⁷Fe, the Mössbauer-active isotope of iron. Troilite samples were synthesized in evacuated and sealed silica glass tubes using ⁵⁷Fe:S starting materials in 1:1 molar ratios. The starting materials were packed in graphite capsules (used as an oxygen-getter) and were run at 930 °C for 1 week.

Taenite was synthesized from a mixture of ⁵⁷Fe and Ni metal in a 1:1 molar proportion, heated to 1100 °C in an evacuated silica glass double capsule for 14 days. All synthesis experiments produced polycrystalline aggregates with large mono-mineralic portions. Phase identification and verification was done by powder

XRD at Case Western Reserve University, and purity and composition were confirmed with the electron microprobe at the University of Chicago.

NRIXS determination of isotope β-factors: Synchrotron source nuclear resonant inelastic x-ray scattering (NRIXS) spectra were obtained on the ⁵⁷Fe enriched samples at Sector 3 of the Advanced Photon Source at Argonne National Lab. Force constants for all phases were determined using the general moment approach of [6] as implemented in the SciPhon code.

Using the force constant data, the β factors for ⁵⁶Fe/⁵⁴Fe can be determined by the equation:

$$10^3 \ln \beta (\text{Fe}^{56}/\text{Fe}^{54}) = 2904[\langle F \rangle / T^2] \quad (1)$$

where $\langle F \rangle$ is the force constant and T is temperature (K). The temperature dependence of the β-factor for each phase is shown in Fig. 1. The β-factors can then be related to the more common Δ notation at a single temperature by the equation:

$$\Delta \text{Fe}_{i,j} = 10^3 \ln \beta_i - 10^3 \ln \beta_j \quad (2)$$

where subscripts *i* and *j* denote the two phases of interest.

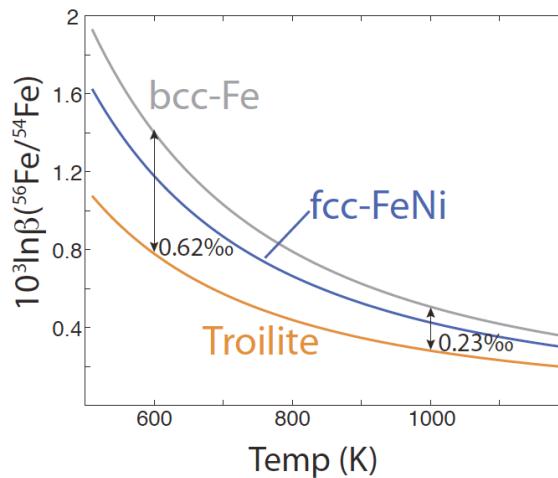


Figure 1: β-factors for kamacite (bcc-metal) [6], taenite (fcc-FeNi) [this study], and troilite [this study]. Shown for reference are the equilibrium ΔFe^{56} between bcc-metal and troilite at 600 and 1000 K.

The force constant of troilite is 97 N/m, which is close to the low pressure extrapolation of existing high pressure data on FeS [7]. The force constant for taenite (fcc-FeNi) is determined to be 147 N/m. The only previous measurements on fcc-Fe were made on nano-precipitates in copper, which contained no Ni [8]. The results of [8] are dependent on particle size below ~ 30 nm, but are in reasonable agreement with our results at large particle size. The force constant for bcc-Fe has previously been estimated using the general moment approach by [6] at 175 N/m.

Numerical methods: The intercrystalline closure temperature for stable isotope diffusion between two minerals is a function of cooling rate, modal abundance, grain size, and diffusivity. Eiler et al. [9] presented a numerical finite difference model to determine the closure temperature for stable isotope exchange among minerals, based on the assumption of a grain boundary transport network that provides for efficient communication between the grains.

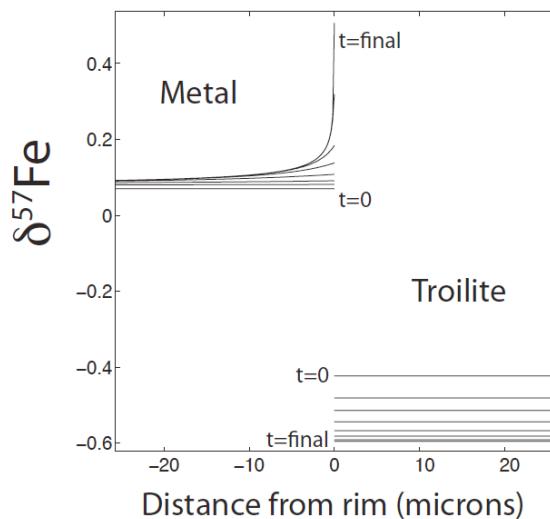


Figure 2: Profiles of Fe isotope ratios at various time steps in a model with linear cooling from 600 to 300°C. Initially ($t=0$) the temperature is high enough that the grains maintain an equilibrium distribution of isotopes (flat profiles). During cooling, isotope diffusion profiles develop in response to the gradient developed at the surface by the change in equilibrium isotopic fractionation with temperature, and cease to evolve when the temperature is too cold for significant diffusion in kamacite. Note that troilite profiles remain homogeneous throughout the simulation, due to the much faster diffusion of Fe in troilite.

In this model, the diffusive exchange is controlled by volume diffusion in the minerals, not by transport through the grain boundary network, which is assumed to be very fast. We used a similar model, based on the MATLAB code developed by [10], to determine the distribution of Fe isotopes within kamacite and troilite

as a function of time during linear cooling (Fig 2). The closure temperature corresponds to the apparent temperature recorded by the bulk Fe isotope compositions of the two grains after cooling has progressed to the point that diffusive exchange stops. Figure 3 shows how the closure temperature varies with the cooling rate and grain size. This provides the basis for a cooling speedometer for iron meteorites containing kamacite and troilite, given data on the bulk Fe isotope compositions of these two phases. The bulk Fe isotope compositions provide an apparent temperature/closure temperature (using Eqs. 1 and 2), which can be used to infer the cooling rate at the appropriate grain size.

Iron isotope measurements on natural materials of known grain size will provide us with the closure temperature and grain size inputs into the above model. With this relationship we will be able to put new bounds on the cooling rates of iron meteorites.

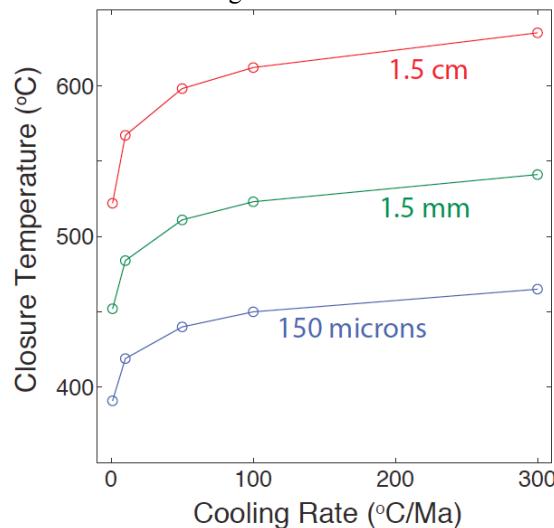


Figure 3: Closure temperature vs. cooling rate for various grain sizes of kamacite equilibrating with troilite of arbitrary grain size (because Fe self-diffusion is so fast compared to the metal). The larger the grain size the higher apparent temperature is recorded in the bulk Fe-isotope partitioning between metal and troilite.

- References:** [1] Yang J. and Goldstein J. I. (2006) *GCA*, 70, 3197-3215. [2] Buchwald V. F. (1975) *Handbook of Iron Meteorites*, UCLA, 1418 pp. [3] Mittlefehldt D. W. et al. *RIMG*, 36, 4.1-4.195. [4] Lubbehusen M. and Mehrer H. (1990) *Acta metal. mater.*, 38, 283-292. [5] Condit R. H. et al. (1974) *Oxidation of Metals*, 8, 409-455. [6] Dauphas N. et al. (2012) *GCA*, 94, 254–275. [7] Kobayashi H. et al. (2004) *Phys. Rev. Lett.* 93, 195503. [8] Tsunoda Y. et al. (2002) *Phys. Rev. B*, 66, 214304. [9] Eiler et al. (1992) *Contrib. Min. Petrol.* 112, 543-557. [10] Van Orman et al. (2006) *Geochim. Cosmochim. Acta* 70, 4797-4812.