



# Iron and nickel isotope fractionation by diffusion, with applications to iron meteorites



Heather C. Watson<sup>a,\*</sup>, Frank Richter<sup>b</sup>, Ankun Liu<sup>b</sup>, Gary R. Huss<sup>c</sup>

<sup>a</sup> Union College, Schenectady, NY, United States

<sup>b</sup> University of Chicago, United States

<sup>c</sup> University of Hawai'i at Mānoa, United States

## ARTICLE INFO

### Article history:

Received 11 February 2016

Received in revised form 16 June 2016

Accepted 18 June 2016

Available online 27 July 2016

Editor: B. Marty

### Keywords:

experimental geochemistry

Fe isotope fractionation

meteorites

diffusion

## ABSTRACT

Mass-dependent, kinetic fractionation of isotopes through processes such as diffusion can result in measurable isotopic signatures. When these signatures are retained in geologic materials, they can be used to help interpret their thermal histories. The mass dependence of the diffusion coefficient of isotopes 1 and 2 can be written as  $(D_1/D_2) = (m_2/m_1)^\beta$ , where  $D_1$  and  $D_2$  are the diffusion coefficients of  $m_1$  and  $m_2$  respectively, and  $\beta$  is an empirical coefficient that relates the two ratios. Experiments have been performed to measure  $\beta$  in the Fe–Ni alloy system. Diffusion couple experiments between pure Fe and Ni metals were run in a piston cylinder at 1300–1400 °C and 1 GPa. Concentration and isotopic profiles were measured by electron microprobe and ion microprobe respectively. We find that a single  $\beta$  coefficient of  $\beta = 0.32 \pm 0.04$  can describe the isotopic effect in all experiments. This result is comparable to the isotope effect determined in many other similar alloy systems. The new  $\beta$  coefficient is used in a model of the isotopic profiles to be expected during the Widmanstätten pattern formation in iron meteorites. The results are consistent with previous estimates of the cooling rate of the iron meteorite Toluca. The application of isotopic constraints based on these results in addition to conventional cooling rate models could provide a more robust picture of the thermal history of these early planetary bodies.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Following the work by Bigeleisen and Mayer (1947) and Urey (1947), equilibrium isotope fractionations became a major tool for geochemistry in large part because the fractionations depend on temperature and thus can provide thermal-history information. Equilibrium isotope fractionations decrease with increasing temperature and thus become less important at the high temperatures of partially molten systems. The isotope fractionations at high temperature are dominated by kinetic process such as unidirectional chemical reactions, and mass transport between phases (e.g. evaporation) or within a phase (e.g., chemical and/or thermal diffusion). Recent experiments motivated by topics in geochemistry and cosmochemistry have documented and quantified kinetic isotope fractionations by chemical and thermal diffusion in silicate melts (see for example Richter et al., 2009a), by diffusion in silicate minerals (Richter et al., 2014), and by vacuum evaporation of silicate liquids (see for example Richter et al., 2007). Starting in the mid-twentieth century the isotope fractionation by diffusion in al-

loys was extensively studied to gain insight into the nature of the diffusion mechanism operating in metals (see Fig. 8 of Richter et al., 2009b and references listed in the caption). However, a major omission from the point of view of cosmochemistry involves high-precision determinations of the isotopic fractionation during interdiffusion in iron–nickel alloys. Iron–nickel alloys are the dominant metal phases in meteorites, so understanding isotopic fractionation within these alloys is of great interest for understanding the origin and evolution of these meteoritic materials. The work presented below involves laboratory diffusion-couple experiments that are used to demonstrate and quantify the kinetic isotope fractionation during iron–nickel interdiffusion.

The relationship of the strength of the isotope effect on diffusion to the masses of the two isotopes can be expressed as:

$$E = \left[ \frac{D_1}{D_2} - 1 \right] / \left[ \left( \frac{m_2}{m_1} \right)^{1/2} - 1 \right] = f \Delta K \quad (1)$$

Where  $E$  is the “isotope mass effect”,  $D_1$  and  $D_2$  are the diffusivities of the light and heavy isotope respectively,  $m_1$  and  $m_2$  are the light and heavy isotope masses,  $f$  is the correlation factor, which is less than 1 if diffusion happens by a correlated mechanism such as vacancies and equal to 1 for non-correlated diffusion, and  $\Delta K$  is the fraction of translational kinetic energy possessed by

\* Corresponding author.

E-mail address: watsonh@union.edu (H.C. Watson).

the diffusing atom in the diffusion direction at the saddle point (e.g. Peterson, 1975 and references therein). In most metals and silicates, where the difference in the isotope masses is relatively small,  $f\Delta K \approx 2\beta$ , where  $\beta$  parameterizes the mass dependence of diffusion as  $D_1/D_2 = (m_2/m_1)^\beta$ . A  $\beta$  value of 0.5 applies in the special case of the mobility of isotopes of a rarefied gas, but for all other materials,  $\beta$  is an empirical quantity that has to be measured by laboratory experiments, or potentially calculated by computer simulations (Van Orman and Krawczynski, 2015). Several recent studies have been conducted to experimentally measure  $\beta$  in geologic materials. Most of these studies have focused on silicate melts (Richter et al., 1999, 2003, 2008, 2009b; Watkins et al., 2009, 2011, 2014), but there have also been some new recent measurements of  $\beta$  in metals. Roskosz et al. (2006) reported  $\beta$  for iron isotopes diffusing in Pt, and Mueller et al. (2014) reported  $\beta$  for carbon isotopes diffusing in iron. In all cases, the experimental results show that there can be significant isotope fractionation due to diffusion in a variety of geologic materials over a wide range of temperatures. An interesting point is that isotopic fractionation by diffusion in minerals and in metals is characterized by significantly larger  $\beta$  than in silicate melts, showing that there is the potential for diffusion in metals to produce very large isotope fractionations. Surprisingly, until now, there were no experimental kinetic isotope fractionation data available for the Fe–Ni system, despite its importance in both metallurgy as the main constituents of steels, and in geochemistry as the main constituents of iron meteorites.

The processes of diffusion and phase separation in Fe–Ni alloys are used to estimate the cooling rates of iron meteorites, which in turn give insight into the sizes of their parent bodies and the nature of the heat source that contributed to the melting of these parent bodies (e.g. Chabot and Haack, 2006). The growth of the characteristic Widmanstätten pattern in iron meteorites is a diffusion-controlled process. The pattern is created during cooling when the lower temperature, kamacite ( $\alpha$ ) phase of FeNi grows into the higher temperature, taenite ( $\gamma$ ) phase. When diffusion is not fast enough to maintain equilibrium as cooling proceeds, a well-defined Ni concentration profile develops in the taenite phase. A cooling rate can be determined by modeling a simulated profile with known diffusion coefficients, and matching it to the profile measured in the natural sample. The basic idea of this method was first established by Wood (1964) and was expanded upon by Goldstein and Ogilvie (1965) and others over the past several decades (e.g. Moren and Goldstein, 1979; Narayan and Goldstein, 1985; Saikumar and Goldstein, 1988; Hopfe and Goldstein, 2001; Yang and Goldstein, 2006). This technique is known as the “metallographic method” and has become the main method used to determine cooling rates of iron meteorites. In addition to the well-known concentration profiles of Ni, it has recently been established that there are significant Ni isotopic variations between the two phases in iron meteorites as well (e.g. Cook et al., 2007). However, Fe isotopes are not significantly fractionated in the iron meteorites measured by several studies (e.g. Poitrasson et al., 2005; Horn et al., 2006; Cook et al., 2007). The observed Ni isotope fractionation may be caused by equilibrium fractionation at the interface during grain growth, diffusive fractionation due to differences in the diffusivities of the isotopes, or some combination of these two. The total observed fractionation of Fe due to these same processes is expected to be approximately an order of magnitude smaller because of the relative high concentration of Fe throughout both phases of the iron meteorite, resulting in the diffusing Fe atoms being diluted by a much higher abundance of non-diffusing Fe atoms in the matrix. Although no experimental data were available, Dauphas (2007) modeled Fe and Ni isotopic fractionation by diffusion during Widmanstätten formation, and showed that a  $\beta$  value of 0.25 (comparable to that of other metals such as Fe–V) could potentially create discernable isotopic fractionations in iron

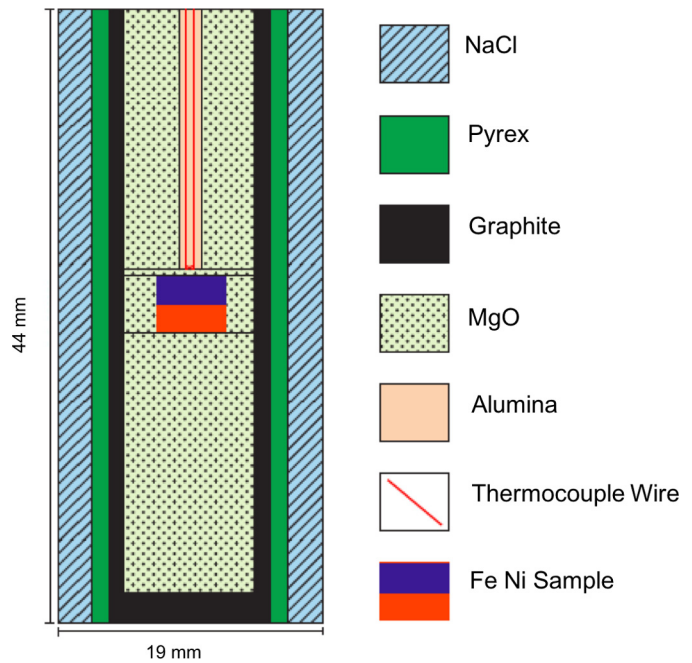


Fig. 1. Schematic of piston cylinder assembly for running diffusion experiments, after Watson and Watson (2003).

meteorites. Here, we present results from experiments aimed at measuring the degree of isotope fractionation occurring in Fe–Ni alloys due to interdiffusion of Fe and Ni. The empirically derived  $\beta$  values are then used in modeling of the Widmanstätten texture in iron meteorites to gain further insight into their thermal histories.

## 2. Experimental and analytical methods

### 2.1. Sample synthesis and diffusion experiments

The interdiffusion experiments were conducted in a standard 19 mm diameter piston cylinder assembly (Fig. 1) at Lawrence Livermore National Laboratory (LLNL) and Rensselaer Polytechnic Institute (RPI). The Fe–Ni diffusion couples were prepared from either high purity Fe (99.995%, Alfa Aesar, Puratronic) and Ni (99.999%, Alfa Aesar, Puratronic) metal rods of 5 mm diameter in size or pre-synthesized metal alloy rods with compositions of  $\text{Fe}_{99}\text{Ni}_1$  and  $\text{Fe}_1\text{Ni}_{99}$ . The pre-synthesized alloys were prepared as described in Watson and Watson (2003), and Watson et al. (2008). In both cases, the rods were cut into  $\sim 2$  mm thick wafers with a low speed diamond saw. The wafers were then manually polished on one circular side with  $\text{Al}_2\text{O}_3$  powder to a grain size of 0.3  $\mu\text{m}$ . After being thoroughly cleaned in ethanol in an ultrasonic bath, the Fe–Ni rods were stacked with polished faces juxtaposed to form a classical diffusion couple, which was then placed into the MgO filler pieces of the piston cylinder assembly. The sample assembly was placed in an end-loaded piston cylinder, pressurized to 1 GPa at room temperature, and heated to the target temperatures between 1200 to 1400 °C. Experiments were held at these conditions for time periods ranging from 24 h to 240 h (Table 1), then quenched by shutting off the power and cooled within about 20 to 30 s. Temperature was monitored and controlled with a type D thermocouple (W-3%Re/W-25%Re) over the course of each experiment, and the uncertainty in temperature measurement was less than  $\pm 5$  °C. The experimental conditions were consistent with face centered cubic (FCC) structure for both iron and nickel. Following quench, the diffusion couples were recovered, mounted in epoxy, sectioned perpendicular to the diffusion interface, polished, and

Download English Version:

<https://daneshyari.com/en/article/6427261>

Download Persian Version:

<https://daneshyari.com/article/6427261>

[Daneshyari.com](https://daneshyari.com)