Abstract—Iron meteorites show resolvable Fe and Ni isotopic fractionation between taenite and kamacite. For Toluca (IAB), the isotopic fractionations between the two phases are around +0.1‰/amu for Fe and −0.4‰/amu for Ni. These variations may be due to i) equilibrium fractionation, ii) differences in the diffusivities of the different isotopes, or iii) a combination of both processes. A computer algorithm was developed in order to follow the growth of kamacite out of taenite during the formation of the Widmanstätten pattern as well as calculate the fractionation of Fe and Ni isotopes for a set of cooling rates ranging from 25 to 500 °C/Myr. Using a relative difference in diffusion coefficients of adjacent isotopes of 4‰/amu for Fe and Ni (β = 0.25), the observations made in Toluca can be reproduced for a cooling rate of 50 °C/Myr. This value agrees with earlier cooling rate estimates based on Ni concentration profiles. This supports the idea that the fractionation measured for Fe and Ni in iron meteorites is driven by differences in diffusivities of isotopes. It also supports the validity of the value of 0.25 adopted for β for diffusion of Fe and Ni in Fe-Ni alloy in the temperature range of 400–700 °C.

INTRODUCTION

Diffusion is a key process in earth sciences because it can provide constraints on geological time scales (e.g., what the closure temperature of a mineral to a specific radiochronometer is, how fast a rock cooled after solidification from a melt). In geological systems, diffusion is most often revealed by concentration gradients, which reflect differences in chemical potentials and nonequilibrium conditions. Diffusion may also leave its imprint on stable isotope ratios. Indeed, isotopes, which have identical chemical properties but different masses, diffuse at different speeds in matter (light isotopes diffuse faster than heavy ones) (e.g., Chapman and Cowling 1952; Mullen 1961; Coleman et al. 1968; Heumann and Imm 1968; Graham 1969; Walter and Peterson 1969; Fishman et al. 1970; Oviedo de González and Walsöe de Reca 1971; Irmer and Feller-Kniepmeier 1972; Iijima et al. 1988; Richter et al. 1999, 2003; Rodushkin et al. 2004; Lundstrom et al. 2005; Beck et al. 2006; Roskosz et al. 2006; Teng et al. 2006).

Phase growth in a diffusion-limited regime is a ubiquitous process in earth sciences. It can occur during rapid cooling and crystallization from a melt, during concretion growth in aqueous systems, and during subsolidus reactions. Surprisingly, little work has been done on modeling isotopic fractionation associated with this phenomenon (Jambon 1980). Frank (1950) and Berner (1968) showed that during growth of planar and spherical concretions in a semi-infinite medium, the system reaches a self-similar asymptotic regime whereby the interface moves as the square root of time and the rate of growth depends on the degree of supersaturation at infinity relative to the surface. Dauphas and Rouxel (2006) extended this work to isotopes and showed that when the degree of supersaturation at infinity is high, the phase grows rapidly, and isotopic fractionation due to diffusion is maximal, but any equilibrium fractionation at the interface is expressed in the surrounding medium. On the contrary, when the degree of supersaturation is low, the phase grows slowly, there is no fractionation due to diffusion, but any equilibrium fractionation at the interface is expressed in the growing phase.

Melting of undifferentiated precursors and subsequent segregation of metal from silicate is responsible for the formation of iron meteorites. Some of these meteorites have peculiar textures known as the Widmanstätten pattern. At high temperature, the stable Fe-Ni phase is taenite (γ, face-centered cubic). When meteorite parent bodies cool through the temperature range of 500–800 °C, they enter the two phase
field of kamacite (α, body-centered cubic) + taenite. In most instances, the growth of kamacite out of taenite is diffusion-limited, which results in Fe-Ni concentration gradients in the two phases that can be used to retrieve cooling rates of iron meteorite parent bodies (Wood 1964; Goldstein and Ogilvie 1965). Knowing the cooling rate of iron meteorites is crucial because it can help restrain the nature of the heat source responsible for differentiation of planetesimals (decay of short-lived nuclides $^{26}$Al and $^{60}$Fe, collisions between planetesimals, electromagnetic induction) as well as the size of asteroids present in the inner part of the early solar system (2–100 km) (Chabot and Haack 2006). Following the seminal studies of Wood (1964) and Goldstein and Ogilvie (1965), a great deal of work has been done on modeling the formation of the Widmanstätten pattern. This involved i) developing fast and stable computer algorithms for simulating phase growth in a finite system (Wood 1964; Goldstein and Ogilvie 1965; Goldstein and Short 1967; Willis and Wasson 1978; Rasmussen 1982; Saikumar and Goldstein 1988), ii) measuring Fe-Ni interdiffusion coefficients in taenite and kamacite as a function of temperature and composition of the alloy (Hirano et al. 1961; Borg and Lai 1963; Goldstein et al. 1964; Dean and Goldstein 1986; Cermak et al. 1989; Meibom et al. 1994; Yang and Goldstein 2004), iii) refining the Fe-Ni phase diagram in the temperature range 300–900 °C, including the influence of phosphorus on the positions of the phase boundaries (Goldstein and Ogilvie 1965; Doan and Goldstein 1970; Willis and Wasson 1978; Moren and Goldstein 1979; Romig and Goldstein 1981; Meibom et al. 1994; Yang et al. 1996; Yang and Goldstein 2006), and iv) identifying the conditions for nucleation of kamacite, which controls the degree of undercooling that affected the meteorite (Narayan and Goldstein 1985; Rasmussen et al. 1995; Yang and Goldstein 2005, 2006).

Recently, several groups have reported Fe and Ni isotope variations in adjacent taenite and kamacite in some iron meteorites (Fig. 1) (Poitrasson et al. 2005; Horn et al. 2006a; Cook et al. 2006, Forthcoming). It is not clear at present what the mechanism responsible for this fractionation is. It could be due to i) equilibrium fractionation at the interface between the two phases, ii) differences in the diffusion coefficients of the different isotopes, or iii) a combination of both processes. Whatever the mechanism is, it should depend on and therefore record cooling rates. Indeed, if equilibrium fractionation is involved, diffusion will control how the signal propagates on each side of the interface and that will depend on how fast the meteorite cooled. Similarly, if differences in diffusion coefficients are involved, the resulting isotopic profile will depend on the cooling rate. Thus, isotopic ratios provide us with a means of testing the models of formation of the Widmanstätten pattern. In order to understand the implications of the isotopic variations that have been documented so far in taenite and kamacite and guide future analyses, one must be able to simulate such fractionation. At the annual Meteoritical Society meeting in 2006, Bourdon et al. reported preliminary results of modeling of isotopic fractionation due to differences of diffusivities of isotopes. They used an approximate solution initially derived by Pawel (1973/1974) in the context of isothermal metal oxidation for diffusion in a finite system with a moving boundary. Although this is useful as a first-order approach, one cannot make the economy of a numerical model, taking into account the complexity of phase relationships and interdiffusion coefficients as a function of temperature and composition, in order to compare measurements made on natural samples and theoretical predictions. This is the topic of the present paper, which builds on preliminary results reported at the same meeting (Dauphas 2006).
OBSERVATIONS

The primary motivation for undertaking this work was the discovery by several groups of Ni and Fe isotopic fractionation between adjacent taenite and kamacite (Fig. 1). In the following, we shall use the \( F_{\text{Fe}} \) and \( F_{\text{Ni}} \) notations, which are deviations in parts permil per atomic mass unit relative to the composition of a reference material (IRMM-014 for Fe, SRM-986 for Ni, or bulk meteorites when specified):

\[
F_A = \left[ \left( \frac{A_i}{A_j} \right)_{\text{sample}} / \left( \frac{A_i}{A_j} \right)_{\text{reference}} - 1 \right] \times 10^3 / (i - j) \tag{1}
\]

where \( i \) and \( j \) are two stable isotopes of element A. As discussed by Dauphas and Rouxel (2006), the virtues of this notation are that it does not depend on the pair of isotopes that are used (as long as isotopic variations are mass-dependent) and it allows direct comparison between the isotopic compositions of different elements (here Fe and Ni). Commonly used pairs of isotopes for calculation of \( F_{\text{Fe}} \) and \( F_{\text{Ni}} \) are \( ^{56}\text{Fe} / ^{54}\text{Fe} \) and \( ^{61}\text{Ni} / ^{58}\text{Ni} \), respectively.

The database of bulk Fe isotope measurements published to date contains 36 analyses representing six iron meteorite groups. The average of these data is 0.031‰/amu relative to IRMM-014 (Zhu et al. 2001; Kehm et al. 2003; Poitrasson et al. 2005; Schoenberg and von Blanckenburg 2006; Cook et al., Forthcoming). There is no clear evidence for Fe isotope heterogeneity at a bulk scale in iron meteorites (Dauphas and Rouxel 2006). Note that Cook et al. (Forthcoming) have not substantiated the results of Mullane et al. (2005), who found variable Fe isotopic compositions in IIIAB iron meteorites.

The database of bulk stable isotope measurements of Ni in iron meteorites is limited and the results available seem to suggest that there are small yet resolvable Ni isotopic variations in iron meteorites (Moynier et al. 2005; Cook et al. 2006, Forthcoming). Overall, iron meteorites have heavy Ni isotopic compositions relative to SRM-986 of around +0.2‰/amu (Moynier et al. 2005; Cook et al. 2006, Forthcoming; Bourdon et al. 2006).

Poitrasson et al. (2005) first reported Fe isotope measurements using multicolonlector–inductively coupled plasma mass spectrometry (MC-ICPMS) of associated taenite and kamacite in Toluca and Cranbourne, both IAB meteorites. Sampling was done by microdrilling; the results represent bulk measurements of individual phases. In both meteorites, taenite was enriched in the heavy isotopes of Fe by −0.05–0.1‰/amu relative to kamacite. Horn et al. (2006a) analyzed taenite and kamacite using laser-ablation (LA) MC-ICPMS. They also found that taenite was enriched in the heavy isotopes of Fe relative to kamacite by ~+0.15‰/amu. Cook et al. (Forthcoming) measured the Fe isotopic composition of Toluca using computer-assisted sample microdrilling; they could not resolve any fractionation between taenite and kamacite outside of error bars. The difference in the magnitude of the fractionation in Toluca (or lack thereof) can possibly be attributed to differences in sampling. As shown in this study, in a single meteorite sample, the Fe isotopic composition should depend on the location of sampling and on the distance of nucleation between kamacite crystals. A more practical complication arises from the fact that none of the crystals were oriented in any of the three studies. It is possible that during sampling of one phase, the drill or the laser spot penetrated into the other phase, resulting in mixing of the isotope signal. More work is required but it is clear from the studies available that the fractionation between taenite and kamacite sampled at a scale of 35–100 m in Toluca is small, presumably lower than 0.1‰/amu. Košler et al. (2005) reported large Fe isotopic fractionation between taenite and kamacite of up to 1‰/amu by LA-ICPMS but these results may be plagued by analytical problems (Horn et al. 2006b; however, see Košler et al. 2006) and will not be discussed any further.

Bourdon et al. (2006) reported Ni isotope measurements of iron meteorites. Kamacite is enriched in the heavy isotopes of Ni relative to taenite by ~+0.5‰/amu. This is similar to the value documented by Cook et al. (2006, Forthcoming) for Toluca of ~0.4‰/amu. The latter authors analyzed Ni isotopes in the same aliquots that were microdrilled for Fe, allowing direct comparison of the behavior of the two elements.

The observations made of Fe and Ni isotope fractionation between taenite and kamacite lend support to the idea that differences in diffusivities played a role in explaining the isotopic fractionation. Indeed, during formation of the Widmanstätten pattern, growth of kamacite is mainly limited by Ni diffusion in taenite. Because light isotopes diffuse faster than heavy ones, one would expect the center of taenite to have light Ni and heavy Fe isotopic compositions relative to adjacent kamacite. The second observation that supports the idea that the isotopic fractionation is predominantly kinetic is the fact that the fractionation of Fe is smaller than that of Ni (<0.1‰/amu for Fe versus >0.4‰/amu for Ni). At 500 °C in Toluca, the equilibrium Ni concentration in kamacite is 7.6 wt% and that in taenite is 26.6 wt%. In contrast, the concentrations of Fe in kamacite and taenite are 92.4 wt% and 7.6 wt%, respectively. Because of dilution effects, one would expect lower kinetic isotope fractionation for Fe compared to Ni, as observed. However, at 500 °C, one cannot completely rule out the possibility that equilibrium fractionation contributed to the overall isotopic fractionation that is measured (e.g., Polyakov and Mineev 2000; Poitrasson et al. 2005; Williams et al. 2006; Schuessler et al. 2007).

Here a numerical model is developed to address more quantitatively the question of what caused Fe and Ni isotopic fractionation in iron meteorites as well as to evaluate the potential of this system as a proxy for estimating cooling rates in iron meteorites. Because Toluca has been extensively studied for both Ni concentration profiles (Wood 1964; Saikumar and Goldstein 1988; Meibom et al. 1995; Hopfe and Goldstein 2001; Yang and Goldstein 2003) and Fe-Ni
isotope systematics (Poitrasson et al. 2005; Horn et al. 2006a; Cook et al. 2006, Forthcoming), it provides a good case example for the present study.

**INPUT PARAMETERS**

A number of parameters go into the computer model used to simulate growth of kamacite out of taenite and to calculate isotopic fractionation associated with this process. The present paper follows Hopfe and Goldstein (2001) for the phase diagram and the diffusion coefficients. Yang and Goldstein (2003, 2005, 2006) developed a model with improved treatment of nucleation and updated interdiffusion coefficients. This may become important as the quality of isotopic measurements improves in terms of precision and spatial resolution. The polynomials given by Hopfe and Goldstein (2001; their Table 1) are used for the phase boundaries. The Ni and P concentrations in Toluca are 8.14 wt% and 0.16 wt%, respectively (Buchwald 1975). Wasson and Kallemeyn (2002) revised the Ni concentration of Toluca to 8.02 wt%, but the earlier value of Buchwald (1975) was adopted to facilitate comparison with the results of Hopfe and Goldstein (2001). The influence of phosphorus on the phase diagram is taken into account by using the pivot method described by Moren and Goldstein (1979). As long as P is undersaturated (T > 520 °C in Toluca), the phase boundaries lie between the phase boundaries for P-saturated and P-free systems. After saturation, the phase boundaries follow P-saturated curves. During cooling, Toluca (8.14 wt% Ni, 0.16 wt% P) crosses the stability field of kamacite at 727.43 °C. In model simulations, nucleation is not allowed to occur until the temperature reaches 700 °C. The interdiffusion coefficients (b) were calculated for Toluca at the interface between the two phases (the values depend on the Ni concentration and the degree of saturation in P). $D^\gamma$ is always lower than $D^\alpha$ by many orders of magnitude.

The interdiffusion coefficients in taenite and kamacite depend on the degree of saturation in P. They increase linearly with the degree of saturation when P is undersaturated and plateau at a value higher than in the P-free system when P is saturated (Equations 7 and 9 in Hopfe and Goldstein 2001). The interdiffusion coefficients also depend on the Ni concentrations (Equations 6 and 8 in Hopfe and Goldstein 2001; note that there is a sign error in Equation 6 before 116.112). Another parameter that comes into play is the degree of undercooling that affected the meteorite. Given the bulk Ni and P concentrations, it is possible to calculate the temperature at which the meteorite enters the stability field of kamacite and to specify a temperature below this point where kamacite is allowed to nucleate. In the following, an undercooling of ~27 °C is used for Toluca, corresponding to a nucleation temperature of 700 °C. This is the value used by Saikumar and Goldstein (1988) and Hopfe and Goldstein (2001) in their models.

The ratio of the diffusivities of two isotopes ($i$ and $j$) is often parameterized as follows:

$$\frac{D_i}{D_j} = \left(\frac{M_j}{M_i}\right)^\beta$$

where $M_i$ and $M_j$ are the masses of the two isotopes and $\beta$ is an empirical parameter. Isotopic fractionation during diffusion in metal has been extensively studied because it is useful in elucidating diffusion mechanisms (e.g., Schoen 1958; Tharmalingam and Lidiard 1959; Mullen 1961). The $\beta$-values calculated for diffusion of Fe in pure α (bcc, <910 °C), (fcc, 910 to 1390 °C), δ (bcc 1390 to melting at 1534 °C) iron, pure...
V, Cu, Ag, Pt, and equiatomic Fe-Co (Mullen 1961; Coleman et al. 1968; Heumann and Imm 1968; Graham 1969; Walter and Peterson 1969; Fishman et al. 1970; Oviedo de González and Walsöe de Reca 1971; Imer and Feller-Kniepmeier 1972; Iijima et al. 1988; Roskosz et al. 2006) are compiled in Fig. 3. Although the β values of Fe vary with temperature and composition of the alloy, the range is small (0.15 to 0.35). A review of literature data also shows that for a wide range of temperatures and elements, β in metal is within 0.1 to 0.5. It is therefore reasonable to take 0.25 as a starting point for Fe and Ni in order to compute isotopic fractionation associated with the formation of the Widmanstätten pattern. A β of 0.25 corresponds to a difference of ~4‰/amu in diffusion coefficient for adjacent isotopes in the Fe-Ni mass region. Diffusion-driven kinetic isotope fractionation should scale linearly with β (e.g., if β doubles, then the isotopic fractionation that is produced should also double).

There is no constraint on what the equilibrium fractionation between taenite and kamacite might be at the temperatures relevant to the formation of the Widmanstätten pattern. Another complication arises due to the fact that, if resolvable, the equilibrium fractionation will vary with temperature. In the present contribution, an exploratory calculation is presented for Ni with arbitrary constant equilibrium fractionation at the interface of 0.4‰/amu.

**NUMERICAL MODEL**

The problem at hand shares some similarities with the case studied by Dauphas and Rouxel (2006). The task is to develop a numerical model that follows isotopes in a finite system with a moving boundary. In essence, the model presented here follows the front-tracking, fixed finite-difference grid method described by Crank (1984). We consider an infinite system where kamacite plates nucleate at regular intervals. The half-distance between two nucleation sites is denoted as \( \delta_t \) and is called the impingement length (Fig. 4). Because identical patterns are repeated infinitely, one can only consider a subunit comprising half of a taenite-kamacite pattern with no flux-boundary conditions on each side. The general equation governing changes in concentration as a function of time is Fick’s second law:

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) + D \frac{\partial^2 C}{\partial x^2} \tag{3}
\]

The derivative of the diffusion coefficient is included because in taenite it depends on the Ni concentration and hence on \( x \).

The scheme used for differentiating Equation 3 is the Iterated Crank-Nicholson (ICN), which is a popular algorithm in numerical relativity (Teukolsky 2000). Its virtue is that it is easy to implement and yet possesses some of the stability features of implicit methods. The first step in the ICN is the forward time centered space (FTCS) scheme. If \( i \) is a grid point and \( n \) is a time step, Equation 3 translates into:

\[
\frac{C_{i,n+1} - C_{i,n}}{\Delta t} = \frac{1}{4\Delta x^2} (D_{i+1,n} - D_{i-1,n}) + \frac{D \Delta^2 C}{\Delta x^2} (C_{i+1,n} - C_{i-1,n} - 2C_{i,n}) \tag{4}
\]

For kamacite, the first term on the right side of the equation disappears because \( D^\alpha \) is constant at a given temperature. All properties are symmetric along the left and right boundaries \((i = 1 \text{ and } i = I)\), so we have at these grid points:

\[
\frac{C_{1,n+1} - C_{1,n}}{\Delta t} = \frac{2D_{1,n}^\alpha}{\Delta x^2} (C_{2,n} - C_{1,n}) \tag{5}
\]

and

\[
\frac{C_{I,n+1} - C_{I,n}}{\Delta t} = \frac{2D_{I,n}^\gamma}{\Delta x^2} (C_{I-1,n} - C_{I,n}) \tag{6}
\]
For the two grid points located on each side of the interface between kamacite and taenite, the calculation is more involved. The interface is located between \( k \) and \( k + 1 \), with \( k \) and \( p \) the fraction of \( \delta x \) where the interface is located, and \( \xi = (k + p - 1)\delta x \) is the absolute position of the interface. These grid points are used for computation of first and second derivatives at the interface using interpolations of Lagrangian type (Crank 1984; see the Numerical Model section).

For the two grid points located on each side of the interface between kamacite and taenite, the calculation is more involved. The interface is located between \( k \) and \( k + 1 \), at a fraction \( p \) of the distance \( \delta x \) between adjacent grid points \( (0 < p < 1) \) (Fig. 4). Around the interface, the points are unequally spaced and one can use interpolation formulae of Lagrangian type to calculate first and second derivatives (Crank 1984). In this study, the grid points \( k - 2, k - 1, k + p, k + p, k + 2, \) and \( k + 3 \) were used at the left and the right of the interface, respectively (instead of \( k - 1, k, k + p, k + p, k + 1, \) and \( k + 2 \) as in Crank 1984, because otherwise instability problems arose for \( p \) close to 0 and 1). In kamacite (index \( k \)), the interdiffusion coefficient is constant and we have:

\[
\frac{C_{k,n+1} - C_{k,n}}{\delta t} = \frac{2D_{n}^{k}\delta t}{\delta x^{2}} \left[ \frac{C_{k-2,n} - C_{k-1,n}}{p + 2} + \frac{C_{n}^{*}}{(p + 1)(p + 2)} \right]
\]

where \( C_{n}^{*} \) is the Ni concentration in kamacite given by the phase diagram. In taenite (index \( k + 1 \)), other terms must be added because the diffusion coefficient depends on the Ni concentration:

\[
\frac{C_{k+1,n+1} - C_{k+1,n}}{\delta t} = \frac{2D_{n}^{k}\delta t}{\delta x^{2}} \left[ \frac{C_{k+2,n} - C_{k+3,n}}{2 - p} \right]
\]

\[
+ \frac{1}{\delta x^{2}} \left[ \frac{-3}{(p - 2)(p - 3)} \left[ \frac{C_{n}^{*}}{2 - p} \right] + \frac{(1 + p)C_{k+2,n} + pC_{k+3,n}}{p - 3} \right]
\]

\[
\times \left[ \frac{-3}{(p - 2)(p - 3)} \left[ \frac{C_{n}^{*}}{2 - p} \right] + \frac{(1 + p)D_{k+2,n} + pD_{k+3,n}}{p - 3} \right]
\]

At each time step, the displacement of the interface allowed by diffusion is calculated. If we note \( \xi \) the absolute position of the boundary, \( \xi = (k + p - 1)\delta x \), we have:

\[
\frac{\partial \xi}{\partial t} (C^{a} - C^{f}) = D_{n}^{k} \frac{\partial C^{a}}{\partial x} - D_{n}^{k} \frac{\partial C^{f}}{\partial x}
\]

where \( C^{a} \) and \( C^{f} \) are the concentrations at the interface given by the phase diagram (at the interface the two phases are in equilibrium) and the derivatives of the concentration are taken at the right (+) and the left (−) of the interface. These are estimated using Lagrangian interpolations between the grid points \( k - 2, k - 1, k + p, k + p, k + 2, \) and \( k + 3 \):

\[
\frac{\xi_{n+1} - \xi_{n}}{\delta t} (C_{n}^{a} - C_{n}^{f}) = \left( \frac{2p - 5}{p - 2}(p - 3) \right) \frac{D_{n}^{k+p,2}}{\delta x} C_{n}^{f}
\]

\[
+ \left( \frac{p - 2}{p - 3} \right) \frac{D_{n}^{k+p,3}}{\delta x} C_{n}^{f} - \left( \frac{p - 2}{p - 3} \right) \frac{C_{n}^{a}}{p + 2}
\]

For computing isotopic fractionation, one cannot simply independently calculate the concentration profiles of two isotopes and ratio them. Indeed, doing so would result in computing distinct interface positions \( (\xi) \) for the two isotopes while this value is uniquely defined. In addition, the concentrations on both sides of the interface are given by the phase diagram; independently calculating the profiles for two isotopes would artificially anchor the isotopic composition at the interface to 0‰/amu.

In the following, we consider two isotopes referred to as leading (setting the pace for migration of the interface) and trailing (reacting in response to migration of the interface). For all grid points away from the interface \( (1, \ldots, k - 1, k + 2, \ldots, l) \), the calculation for the trailing isotope is identical to that described for the leading isotope (see Equations 4 to 6). At the interface, we use the displacement calculated for the leading isotope (Equation 10) to calculate the concentrations of the trailing isotope at and around the interface. The concentration of the trailing isotope is denoted as \( C^{*} \) and its diffusion coefficient as \( D^{*} \). The ratio of the diffusion coefficients of the two isotopes:
Diffusion-driven kinetic isotope effect during formation of the Widmanstätten pattern

1603

(11)
is given by Equation 2. When \( r = D^* / D \) is equal to 1 (\( \beta = 0 \)), then there is no kinetic isotope fractionation. The equilibrium fractionation at the interface is:

\[
\lambda = \frac{C_{\alpha}^*/C_\gamma}{C_\alpha^*/C_\alpha}
\]

(12)

When \( \lambda \) is equal to 1, then there is no equilibrium fractionation. The objective at this point is to estimate \( C_{\alpha}^* \) and \( C_\gamma^* \) using Equations 10–12. As discussed previously, the position of the interface is uniquely defined. We can therefore apply Equation 10 to the trailing isotope:

\[
\frac{z_{n+1} - z_n}{\delta t} (C_{\alpha}^* - C_\gamma^*) = \frac{r D_{k+p,n}^I}{\delta x} \left[ \frac{(2p-5)C_n^*}{(p-2)(p-3)} \right] + \frac{r D_{k+p,n}^I}{\delta x} \left[ \frac{(p+3)C_n^*}{p+1} \right].
\]

(13)

We have two equations (12 and 13) in two unknowns (\( C_{\alpha}^* \) and \( C_\gamma^* \)) and the system can be solved:

\[
C_{\alpha}^* = \frac{r}{\delta x} \left[ D_{k+p,n}^I \left[ \frac{(2p-5)C_{n}^*}{p-2} + \frac{(p+3)C_{n}^*}{p+1} \right] \right]
\]

(14)

3. New values at \( t + \delta t \) are computed and inserted back into Equation 1.

This iteration can be repeated an infinite number of times and converges to the Crank-Nicholson method. In the present contribution, only two iterations after the FTCS step were performed because Teukolsky (2000) showed that in most cases this is enough to ensure stability of the algorithm. After computation of \( \xi \) at \( t + \delta t \), \( p = z/\delta x + 1 - k \). If it is higher than 1, then \( k \) increases by 1, \( p \) decreases by 1, and the point near the interface that was in taenite moves into kamacite. If \( p \) is lower than 0, then \( k \) decreases by 1, \( p \) increases by 1, and the point near the interface that was in kamacite moves into taenite. Thus, the algorithm allows the interface to move in both directions. At each time step, the concentrations at the interface in taenite and kamacite, which depend on the temperature, are updated. As the temperature decreases, the diffusion coefficients decrease and the parameter that governs stability of the algorithm \( (\propto \delta x^2 / D \delta t) \) increases. This makes it possible to refine the mesh size to a final spatial resolution of \( \delta x \approx 1 \mu m \). The code was written in R and the simulations were performed on a dual 2 GHz PowerPC G5 with 6 GB of RAM.

**TEST OF THE ALGORITHM**

Modeling growth of the Widmanstätten pattern involves following a moving boundary in a finite system with time-dependent conditions at the interface. Few research groups have developed such algorithms (Wood 1964; Goldstein and Ogilvie 1965; Goldstein and Short 1965; Willis and Wasson 1978; Rasmussen 1982; Saikumar and Goldstein 1988), so care was taken to validate the numerical code used in this study. It was tested against Ni profiles given by Hopfe and Goldstein (2001) and also against the analytical solution of a problem that shares similarities with the problem at hand.

The problem treated hereafter has no physical foundation. Its only purpose is to provide a basis for testing the finite difference algorithm (see the Numerical Model section) against a problem that has an exact analytical solution. Let us consider a system with an element present at concentration \( C(x, 0) = C_0 \) in a semi-infinite phase I. At time 0, the concentration at the surface (\( x = 0 \)) is lowered and maintained at a constant value afterward, \( C(0, t) = C_r \). As a result, a second phase (II) grows at the surface. The phase diagram for I and II gives equilibrium concentrations at the interface between the two phases, \( C_{1I} \) and \( C_{2I} \) (in II and I, respectively). After some time, the system converges toward a self-similar asymptotic regime whereby all properties propagate in space with \( t^{1/2} \) (regardless of the initial conditions, if one waits long enough and takes a snapshot of the system at a given time, the concentration plotted as a function of the distance divided by the square root of time will be very similar to the profile shown in Fig. 5). Jost and Wagner (Jost 1952) presented the analytical solution for this
As before, $\xi$ is the absolute position of the interface between the two phases. We have for the concentration in phase II ($0 < x < \xi$):

$$C = C_s - \frac{(C_s - C_{II,I})}{\text{erf}(\gamma D_{II} t)} \text{erf}(\frac{x}{2\sqrt{D_{II} t}})$$  \hspace{1cm} (15)$$

the concentration in phase I ($\xi < x$):

$$C = C_0 + \frac{C_s - C_{II,I}}{\text{erf}(\gamma D_{II} / D_I)} \text{erfc}(\frac{x}{2\sqrt{D_I t}})$$  \hspace{1cm} (16)$$

and the position of the interface:

$$\xi = 2\gamma \sqrt{D_{II} t}$$  \hspace{1cm} (17)$$

where $\gamma$ is the root of the transcendental equation:

$$C_{II,I} - C_{II,I} = \frac{C_s - C_{II,I}}{\sqrt{\pi}\gamma \text{erf}(\gamma D_{II} / D_I)} \exp(-\gamma^2)$$  \hspace{1cm} (18)$$

$$-\frac{C_{II,I} - C_0}{\sqrt{\pi}D_{II} / D_I \gamma \text{erfc}(\gamma D_{II} / D_I)} \exp(-\gamma^2 D_{II} / D_I)$$

Note that Equation 1.315 of Jost (1952) contains an error ($D_{II}/D_I$ was not included in the last term of Equation 18). If one introduces $u = x/\sqrt{D_{II} t}$, the functions given above only depend on this variable. In order to compare these analytical expressions with the numerical treatment described before, one must choose numerical values for the parameters. The following values were adopted: $C_s = 5 \text{ wt}\%$, $C_{II,I} = 10 \text{ wt}\%$, $C_{II,I} = 15 \text{ wt}\%$, $C_0 = 20 \text{ wt}\%$, $D_{II} = 3 \text{ mm}^2/\text{yr}$, and $D_I = 0.3 \text{ mm}^2/\text{yr}$ (the values for $D_{II}$ and $D_I$ correspond to the interdiffusion coefficients in kamacite and taenite at 700 °C in a P-free system). The value of $\gamma$ obtained by solving Equation 18 is 0.446973. The algorithm developed for following the growth of kamacite from taenite was modified to accommodate the conditions set in this section. The analytical solution is compared with that obtained from the ICN after convergence in Fig. 5. As shown, there is perfect agreement between the two approaches, which supports the validity of the code used.

The algorithm was also tested against Ni concentration profiles simulated by Hopfe and Goldstein (2001) for Toluca using a nucleation temperature of 700 °C, an impingement length of 700 μm, and a cooling rate (CR) of 50 °C/Myr (the present best estimate for the cooling rate of this meteorite). The phase diagram and diffusion coefficients used in the present study are identical to those
used by Hopfe and Goldstein (2001), so the results of the two studies can be directly compared. Figure 6 shows snapshots taken at different temperatures during cooling of the meteorite. The simulations in this study were stopped at 450 °C because below this temperature, the diffusion scale is so small that the system is almost frozen, except for variations right at the interface. As can be seen, there is excellent agreement between the two studies. The only noticeable difference lies in the position of the interface, which is shifted toward the right by ~5–25 μm in this study compared to Hopfe and Goldstein (2001). This is due to the fact that in the present work, a fixed-grid method with an initial spacing of 12.5 μm was used and a seed of kamacite comprising 2 grid points (25 μm) was used to initiate the differentiation. Again, the agreement between the present study and Hopfe and Goldstein (2001) supports the validity of the algorithm.

Finally, two consistency checks were performed for all simulations. The no flux-boundary conditions at the left and the right of the system impose that mass conservation must be respected. For all simulations, the total Ni content did not vary beyond 1 part per thousand (given by the area below C_{Ni}) and the Ni isotopic composition of the system remained constant within ~0.01‰/amu (given by the area below F_{Ni} × C_{Ni}).

**RESULTS**

Several computer simulations were performed in order to understand what causes isotopic variations in iron meteorites and to evaluate the potential of Fe and Ni isotopes to refine cooling rate estimates. Because these calculations are computer-intensive, only a small fraction of the parameter space was explored. As discussed previously, the case example and primary focus of this study is Toluca, an IAB iron meteorite (see Choi et al. 1995 and Benedix et al. 2000 for details on the petrogenesis of this type of meteorite).

The influence of cooling rates on isotopic fractionation due to diffusion was explored by fixing the impingement length at 700 μm and varying the cooling rate over an interval (25 to 500 °C/Myr) that encompasses the range of metallographic cooling rates estimated for IAB meteorites by Herpfer et al. in 1994 (30–70 °C/Myr; however, Rasmussen 1989 and Meibom et al. 1995 estimated lower values of 1 to 15 °C/Myr).

**Kinetic Isotope Fractionation of Nickel**

Kinetic isotope fractionation was investigated by setting β = 0.25 (Equations 2 and 11) and λ = 1 (Equation 12). At 650 °C (50 °C after nucleation), the isotopic composition of
Ni in kamacite is almost homogeneous for all cooling rates (Fig. 7). Taenite already shows the imprint of diffusion, with overall light Ni isotopic composition relative to kamacite. At moderately slow cooling rates (25 and 100 °C/Myr), taenite shows zonation from light cores to heavy interfaces. At a high cooling rate (500 °C/Myr), the profile is different. The meteorite cooled so fast that the diffusion signal did not have time to propagate all the way to the center of the crystal. As a result, the center of taenite has undisturbed Ni isotopic composition and the point that shows the largest effect is located ~300 μm off center. The cooling rate also has a strong influence on the magnitude of the fractionation. At 25 °C/Myr, the maximum difference in isotopic composition between taenite and kamacite (0.18‰/amu) is smaller than at 100 °C/Myr (1.10‰/amu) and 500 °C/Myr (0.98‰/amu). At low cooling rates, the system tends toward equilibrium at all time steps with little kinetic isotope fractionation between the two phases.

As the temperature decreases to 550 °C, a new feature becomes apparent. At 650 °C, the isotopic composition of kamacite was homogeneous due to high diffusivity at 550 °C, transport of Ni in kamacite becomes diffusion-limited; this phase shows a gradient in Ni isotopic composition. The center of kamacite becomes enriched in the light isotopes relative to the interface. This is due to the fact that as the temperature decreases, the Ni concentration of kamacite at the interface increases relative to the center, which causes diffusion and hence isotopic fractionation. The fractionations between the center of kamacite and the interface at 550 °C are 0.07‰/amu, 0.15‰/amu, and 0.19‰/amu for cooling rates of 25, 100, and 500 °C/Myr, respectively.

At around 450 °C, the largest isotopic fractionation in taenite does not occur at the center but at some distance away from the boundary. This was already visible at 650 °C for the highest cooling rate (500 °C/Myr), but at 450 °C, all profiles show such a feature on a scale commensurate with the width of the taenite crystal. The isotopic fractionation between the center of kamacite and the interface is higher at 450 °C than it is at 550 °C. For the low cooling rate (25 °C/Myr), the fractionation within kamacite is almost as high as the fractionation within taenite (0.23 and 0.29‰/amu), respectively. For higher cooling rates, kamacite has more homogeneous isotopic composition than taenite. These results show that one cannot directly compare interdiffusion coefficients to argue for diffusion-limited transport in one phase or another. The other parameter that comes into play is the contrast between the interdiffusion coefficients of the two phases. The dimensionless parameter that is relevant for discussing these issues is:

$$\eta = \frac{w^2 cr}{D\Delta T}$$ (19)

where $w$ is the half-width of either taenite or kamacite, $cr$ is the cooling rate, $D$ is the interdiffusion coefficient in taenite or kamacite taken at the interface, and $\Delta T$ is a characteristic temperature interval used for calculating diffusion distances (20 °C following Wood 1964; note that Rasmussen et al. 2001 adopted a slightly higher value of 50 °C). If $\eta << 1$, then diffusion has time to homogenize the phase on the time scale relevant to cooling. If $\eta >> 1$, then the system is frozen because the diffusion signal does not have time to propagate across the phase. For values around unity, diffusion can
produce isotopic fractionation. The values of $\eta$ calculated for Toluca with an impingement length of 700 $\mu$m and a nucleation temperature of 700 °C are reported in Fig. 8. For a cooling rate of 25 °C/Myr, the value of $\eta$ for kamacite is higher or similar to that of taenite for temperatures below ~550 °C. This explains why the two phases show similar isotopic fractionation. At 100 and 500 °C/Myr, $\eta$ in kamacite is always lower than in taenite. As a result, kamacite is more isotopically homogeneous than taenite. Below 450 °C, the diffusion length is significantly reduced at all cooling rates and the system stops evolving.

### Kinetic Isotope Fractionation of Iron

The algorithm developed for calculating Ni isotope fractionation during growth of kamacite out of taenite can easily be modified to investigate Fe isotope fractionation (Fig. 9). A set of simulations were run for Fe for cooling rates of 25, 100, and 500 °C/Myr, assuming that $\beta$ of Fe is identical to that of Ni (0.25) and $\lambda = 1$ (Equation 12). As expected, the calculated Fe concentrations exactly mirror Ni concentrations ($[Fe] + [Ni] = 100$) and the position of the interface based on Fe is the same as that based on Ni (Fig. 9, top panels). The main features that can be identified in Fe isotope profiles are very similar to those already presented for Ni and will not be repeated hereafter. The main differences are the magnitude and sign of the fractionation. Concentration gradients for Fe are similar in magnitude but opposite in sign compared to Ni. For this reason, one would expect Fe to be isotopically light when Ni is heavy and vice-versa. This is what is observed in model results. Also, because the absolute concentration of Fe is higher than that of Ni in both taenite and kamacite, diffusing Fe atoms are diluted to a greater extent by normal Fe than is the case for Ni. This explains why for the most part the isotopic fractionation of Fe is smaller than that of Ni.

The exact relationship between Fe and Ni isotopic fractionation deserves special attention because it is a key observation that may help us distinguish between kinetic and equilibrium isotope fractionation (Fig. 10). At all cooling rates, the isotopic compositions relative to the bulk, taken at the centers of both phases, are more fractionated in absolute values for Ni than they are for Fe. Isotopic fractionation does not only depend on concentration gradients, which are opposite in sign but equal in magnitude, but also on absolute concentrations. For a given concentration gradient, the fractionation will be large for Ni and small for Fe if the Ni concentration is low and the Fe concentration is large (and vice-versa). There are large concentration differences in Ni between taenite and kamacite and within taenite. These dilution effects are the main cause for the non-linearity in the relationship between Fe and Ni isotopic fractionation.

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**Fig. 9.** Iron concentration and kinetic isotope fractionation ($\beta = 0.25$ in Equation 2 and $\lambda = 1$ in Equation 12) for three cooling rates, 25 (left), 100 (center), and 500 °C/Myr (right). The three colored curves correspond to snapshots taken at different temperatures (650 °C, red; 550 °C, orange; 450 °C, blue). The top panels show Fe concentration profiles (wt%). The middle panels show Fe isotope profiles (%/amu deviation relative to the bulk). The bottom panels show the product of the Fe concentrations and isotopic compositions. These curves help to visually evaluate how isotopic compositions are balanced between positive and negative values (the area below the curve must be equal to 0).
The difficulty with equilibrium fractionation is that we do not know what the value is and how it varies with temperature. For illustration purposes, an arbitrary value of +0.4‰/amu between kamacite and taenite was adopted (Fig. 11). Because the outcome of the simulations scales with this value, it is easy to predict what the effect would be if equilibrium fractionation was reduced or increased by a given factor. At a slow cooling rate (25 °C/Myr), taenite and kamacite have almost homogeneous isotopic compositions. If taenite and kamacite were in complete equilibrium, the isotopic compositions of each phase could be calculated by mass-balance:

\[ F' = -\Delta \frac{C'_\alpha - C'_\gamma}{C'_\gamma C'_\alpha - C'_\gamma} \]

\[ F' = \Delta + F' \]

where \( \Delta = \left( \frac{1}{\lambda - 1} \right) \times 10^3 \) is the kamacite-taenite equilibrium fractionation (arbitrary, 0.4‰/amu), \( C' \) is the bulk Ni concentration (8.14 wt% for Toluca), and the other concentrations are equilibrium values given by the phase diagram (Fig. 2). The values calculated at 650, 550, and 450 °C for kamacite in equilibrium with taenite \( (F'_\gamma) \) are 0.23, 0.09, and 0.03‰/amu, respectively. The results of the simulations for 25 °C/Myr taken at the center of kamacite are 0.22, 0.11, and 0.07‰/amu at the same temperatures. These values are very close to the equilibrium values, and it shows that throughout the thermal history of the meteorite, the kamacite-taenite fractionation at each point will remain close to what is expected for bulk equilibrium. As the temperature cools to 450 °C, most of the Ni is in kamacite, the concentration in this phase is close to the bulk concentration \( (C'_\gamma \approx C'_\alpha) \), and it follows from Equation 20 that \( F'_\alpha \approx 0 \) and \( F'_\gamma \approx -\Delta \). This is the primary reason why for 100 and 500 °C/Myr, isotopic fractionation at the interface is expressed predominantly in taenite.

Fig. 10. Fe-Ni isotope correlations in Toluca at 450 °C for diffusion-driven kinetic isotope fractionation \( (\beta = 0.25) \). The points along the curves correspond to individual grid points. Kamacite is in black; while taenite is in red. The centers of the two phases are shown as large squares. The dashed curves are point-to-point linear interpolations and have no other virtue than guiding the eye.

**Fixed Equilibrium Fractionation of Nickel**

The difficulty with equilibrium fractionation is that we do not know what the value is and how it varies with temperature. For illustration purposes, an arbitrary value of +0.4‰/amu between kamacite and taenite was adopted (Fig. 11). Because the outcome of the simulations scales with this value, it is easy to predict what the effect would be if equilibrium fractionation was reduced or increased by a given factor. At a slow cooling rate (25 °C/Myr), taenite and kamacite have almost homogeneous isotopic compositions. If taenite and kamacite were in complete equilibrium, the isotopic compositions of each phase could be calculated by mass-balance:

\[ F' = -\Delta \frac{C'_\alpha - C'_\gamma}{C'_\gamma C'_\alpha - C'_\gamma} \]

\[ F' = \Delta + F' \]

where \( \Delta = \left( \frac{1}{\lambda - 1} \right) \times 10^3 \) is the kamacite-taenite equilibrium fractionation (arbitrary, 0.4‰/amu), \( C' \) is the bulk Ni concentration (8.14 wt% for Toluca), and the other concentrations are equilibrium values given by the phase diagram (Fig. 2). The values calculated at 650, 550, and 450 °C for kamacite in equilibrium with taenite \( (F'_\gamma) \) are 0.23, 0.09, and 0.03‰/amu, respectively. The results of the simulations for 25 °C/Myr taken at the center of kamacite are 0.22, 0.11, and 0.07‰/amu at the same temperatures. These values are very close to the equilibrium values, and it shows that throughout the thermal history of the meteorite, the kamacite-taenite fractionation at each point will remain close to what is expected for bulk equilibrium. As the temperature cools to 450 °C, most of the Ni is in kamacite, the concentration in this phase is close to the bulk concentration \( (C'_\gamma \approx C'_\alpha) \), and it follows from Equation 20 that \( F'_\alpha \approx 0 \) and \( F'_\gamma \approx -\Delta \). This is the primary reason why for 100 and 500 °C/Myr, isotopic fractionation at the interface is expressed predominantly in taenite.
As discussed previously, a principal issue with Fe and Ni isotopic fractionation measured in taenite and kamacite is determining whether it reflects equilibrium, kinetic, or a combination of both processes. Although critical measurements and experiments are missing to definitively answer this question, model results presented here give important clues on which process may dominate. For all measurements available, there are either no constraints on where the material was sampled or the sampling scale is too large and isotopic compositions were integrated over a wide area (Poitrasson et al. 2005; Cook et al. 2006, Forthcoming; Horn et al. 2006).

Kinetic or Equilibrium Fractionation?

One must bear in mind that as far as the magnitude of the isotopic fractionation is concerned, there is some degeneracy between the cooling rate and the relative diffusion coefficients of neighbor isotopes. Thus the discussion that follows critically depends on the value adopted for $\beta$, which is still uncertain (0.25) (Fig. 3) (Mullen 1961; Coleman et al. 1968; Heumann and Imm 1968; Graham 1969; Walter and Peterson 1969; Fishman et al. 1970; Oviedo de González and Walsöe de Reca 1971; Irmer and Feller-Kniepeier 1972; Iijima et al. 1988; Roskosz et al. 2006). While the simulations at 25 °C/Myr and 100 °C/Myr give too small and too large fractionations, respectively, a cooling rate of 50 °C/Myr reproduces the observations for both Fe and Ni (Fig. 12). Using Wood’s method of matching measured and modeled taenite central Ni content and half-width, Hopfe and Goldstein (2001) concluded that Toluca had cooled at a rate of 25 °C/Myr. These authors also concluded that a cooling rate of 50 °C/Myr was within model uncertainties. This speaks strongly in favor of the possibility that the fractionation measured for Fe and Ni in iron meteorites was produced by partial separation of isotopes through diffusion. It also supports the validity of the value of 0.25 adopted for $\beta$.

An additional constraint on whether kinetic or equilibrium effects control the fractionation comes from the difference between the isotopic compositions of kamacite and the bulk. Overall, the general pattern for Fe isotopes is to have taenite heavy relative to kamacite. If this were due to equilibrium, then the taenite-kamacite fractionation should be positive. Simulations with fixed equilibrium isotope fractionation at the interface show that for all points along the profile, the isotopic composition of kamacite and taenite should have light and heavy Fe isotopic compositions, respectively. This is not true for diffusion-driven kinetic isotope fractionation with slow cooling. Indeed, for cooling rates of 25 to 50 °C/Myr, transport of Fe is diffusion-limited in kamacite to the same extent as it is in taenite (Fig. 8). This results in Fe isotope variations within kamacite characterized by a heavy center and a light interface. If kinetic fractionation were the controlling factor, one would expect to find both light and heavy Fe isotopic compositions relative to the bulk.

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![Diagram](image-url)  
Fig. 11. Nickel isotopic fractionation during formation of Widmanstätten pattern in Toluca for an arbitrarily fixed equilibrium fractionation at the interface between kamacite and taenite of +0.4 ‰/amu ($\lambda = 1.004$ in Equation 12). No fractionation due to diffusion was included in this calculation ($r = 1$ in Equation 11). The three columns correspond to different cooling rates (25, 100, and 500 °C/Myr) and the different curves in each panel are snapshots taken at different temperatures (650, 550, and 450 °C). The top panels show Ni isotope profiles (‰/amu deviation relative to the bulk). The bottom panels show the product of the Ni concentrations and isotopic compositions. These curves help to visually evaluate how isotopic compositions are balanced between positive and negative values (the area below the curve must be equal to 0).
Kinetic isotope fractionation associated with the formation of the Widmanstätten pattern is an extension of chemical zoning and cannot be used as an independent thermochronometer. However, it provides additional constraints that may help remove degeneracy in model parameters (if these are not perfectly known) and reveal problems that had not been appreciated before. Figure 13 shows, using a thought experiment, how isotopic fractionation is not redundant with chemical zoning. Let us consider a system whereby a finite phase II grows at the expense of a semi-infinite, well-mixed phase I. The concentration in II at the interface is noted $C_{II,I}$. The left graph in the two panels shows two possible time evolutions for $C_{II,I}$ (governed by a hypothetical phase diagram and time-temperature evolution). In the top panel, $C_{II,I}$ does not change much and the diffusion coefficient in II is very small. In the bottom panel, $C_{II,I}$ increases dramatically, but this is mitigated by diffusion in II. The two scenarios would create similar chemical profiles ($C$ versus $x$) but very distinct isotopic profiles ($F$ versus $x$).

Fig. 12. Comparison between predicted (diffusion-driven kinetic isotope fractionation with $\beta = 0.25$) and measured Fe and Ni isotopic fractionation in Toluca for a cooling rate of 50 °C/Myr and an impingement length of 700 μm. The top two panels show Ni and Fe isotope profiles at 450 °C (for the Ni concentration profile, see Fig. 6). The bottom panel shows the Fe-Ni isotopic correlation. The values taken at each grid point along the profile are shown. The symbols and notations are identical to Fig. 10. The range of measured values is reported as hatched regions relative to the bulk Fe and Ni isotopic compositions of all iron meteorites measured so far (thin horizontal and vertical lines). As illustrated, there is good agreement between measured and calculated isotopic fractionations for both Fe and Ni in taenite and kamacite.

in a single phase. As shown in Fig. 1, available data suggests that this may be the case.

**Perspectives in Stable Isotope Thermometry**

Kinetic isotope fractionation associated with the formation of the Widmanstätten pattern is an extension of chemical zoning and cannot be used as an independent thermochronometer. However, it provides additional constraints that may help remove degeneracy in model parameters (see the Discussion section for details). Phase II grows at the expense of semi-infinite, well-mixed phase I. The concentration in II at the interface is noted $C_{II,I}$. The left graph in the two panels show two possible time evolutions for $C_{II,I}$ (governed by a hypothetical phase diagram and time-temperature evolution). In the top panel, $C_{II,I}$ does not change much and the diffusion coefficient in II is very small. In the bottom panel, $C_{II,I}$ increases dramatically, but this is mitigated by diffusion in II. The two scenarios would create similar chemical profiles ($C$ versus $x$) but very distinct isotopic profiles ($F$ versus $x$).
CONCLUSIONS

Isotopic fractionation of Fe and Ni associated with formation of Widmanstätten pattern was modeled. Two sets of simulations were computed, one with arbitrarily fixed equilibrium fractionation at the interface and the other with kinetic isotope fractionation driven by diffusion. Using a β of 0.25, which corresponds to a difference in diffusivities of adjacent isotopes of 4‰/amu in the Fe-Ni mass region, the taenite-kamacite isotopic fractionation measured by several workers in Toluca can be reproduced with a cooling rate of 50 °C/Myr. This is in the range of values previously estimated for Toluca (Hopfe and Goldstein 2001). Other methods are available for testing the validity of the assumptions and parameters used in models of formation of the Widmanstätten pattern, including analysis of trace highly siderophile element distribution (Goldstein 1967; Watson and Watson 2003; Righter et al. 2005). The main virtue of Fe and Ni isotopes is that they provide a direct test that only involves the determination of an extra parameter, β. If this value is known for Fe and Ni, then calculating isotopic fractionation follows in a straightforward way from modeling concentration profiles. Obvious targets for study are IVA iron meteorites, where simulations indicate that meteorites from this group cooled at different rates, which contradicts the idea that they formed from differentiation of an asteroid core. This may reflect a complex thermal evolution such as breakup-reassembly of a planetary core or removal of the overlying mantle. It may also be due to inaccuracies in the assumptions and parameters used in the simulations; this could be tested using isotopes.

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Editorial Handling—Dr. Edward Scott

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1988). The present study shows that Toluca, the meteorite for which the largest database of isotope measurements exists, has passed this test. An obvious extension of this work is the analysis of meteorites from the group IVA of iron meteorites. These meteorites are related genetically by a trend of magmatic differentiation (Wasson and Richardson 2001). If all IVA meteorites were derived from a single core, one would expect isothermal cooling (e.g., Haack and Scott 1992). The reason is that thermal conductivity in a metallic core is much higher than in the overlying silicate mantle, so one would not expect large temperature gradients between samples from the central and peripheral regions of the core. However, several groups have shown that for IVA, the computed cooling rates vary from one meteorite to another and correlate with bulk Ni concentrations (Goldstein and Short 1967; Moren and Goldstein 1979; Rasmussen 1982; Rasmussen et al. 1995; Yang et al. 2007). Haack et al. (1996a) suggested that after crystallization, the core was disrupted by impact and the resulting debris were reassembled by gravitation. According to this model, the correlation between cooling rates and Ni concentrations would be purely fortuitous, reflecting limited sampling of this asteroid. More recently, Yang et al. (2007) argued that the core preserved its integrity but that the parent body of IVAs was stripped of part of its mantle by collisions. Others (Willis and Wasson 1978; Wasson and Richardson 2001) have argued that the correlation between computed cooling rates and Ni concentrations must reflect systematic errors in model assumptions or parameters. If the later interpretation is correct, then one may find that the Fe and Ni isotopic compositions that are predicted based on models of growth of Widmanstätten pattern in IVA are inconsistent with measured compositions.

At this stage, several experiments and analyses must be performed to put the study of Fe and Ni isotope fractionation on solid foundations. The equilibrium fractionation between taenite and kamacite must be documented. This can be done experimentally, but one could also resort to natural samples. If there is equilibrium fractionation, then the compositions immediately at the left and at the right of the interface should show a jump corresponding to the equilibrium fractionation at the time when the system was frozen to diffusion. Mesosiderites, which cooled at a slow rate (0.2 °C/Myr) (Powell 1969; Haack et al. 1996b; Hopfe and Goldstein 2001) and achieved close to equilibrium growth conditions through most of their thermal history, may also be good targets for study. For kinetic isotope fractionation, the β value must be determined experimentally as a function of temperature and composition of the alloy.
Diffusion-driven kinetic isotope effect during formation of the Widmanstätten pattern 1613


