Relationship between cooling rate and cooling age of a mineral: Theory and applications to meteorites

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Abstract—We reviewed here the recent development on the mathematical formulation of closure temperature of a cooling geochronological system, which permits direct retrieval of cooling rate from cooling age when the diffusion parameters, grain size and initial temperature are known. This formulation is used to show how the cooling rate can be retrieved by comparing the core and bulk age of a mineral determined by a single decay system. The cooling rates of seven H chondrites of the metamorphic types H4, H5 and H6 were retrieved from the available data on the Pb-Pb model ages of the phosphates and the diffusion kinetic data of Pb in apatite. The results are in excellent agreement with the metallographic cooling rates and show an inverse relation with the metamorphic grade of these chondrites. We also addressed the problem of ~90 Ma younger Sm-Nd mineral isochron age, defined by orthopyroxene, phosphate and plagioclase, of the Morristown mesosiderite compared to the Pb-Pb age of the Estherville mesosiderite. It is shown that this younger age could have been a consequence of resetting during cooling instead of an "impulsive heating" event, as suggested earlier.

INTRODUCTION

The cooling age of a mineral for a specific geochronological system is defined to be the time since the closure of diffusive exchange of the system between the mineral and the matrix during cooling. The temperature below which the diffusive exchange becomes insignificant is called the closure temperature ($T_c$) of the system. A knowledge of the cooling ages and the corresponding closure temperatures of two or more minerals in a rock permits calculation of the temperature drop within a specific time interval, and hence of an average cooling rate within that interval. This procedure has been applied widely to both terrestrial rocks and meteorite samples (e.g., Spear and Parrish, 1996; Zipfel et al., 1995, respectively). However, the $T_c$ of a specific decay system in a mineral is not a unique quantity but depends, in principle, on the grain size and the cooling rate itself, especially when it is slow (e.g., Ganguly et al., 1998). Thus, retrieval of the cooling rate from the above procedure is based on the implicit assumption that the effects of cooling rate and grain size are insignificant within their usual range of variation in natural samples.

Dodson (1973, 1986) formalized the concepts of closure temperature and cooling age through rigorous mathematical analyses. However, his classic formulation is restricted to minerals in which diffusion during cooling has completely erased any signature of the initial homogeneous composition of the mineral that was established at the peak metamorphic temperature, $T_0$. Dodson's formulation has recently been modified by Ganguly and Tirone (1999) to include systems with arbitrarily small amount of diffusion. Also, Ganguly et al. (1998) showed that the cooling rate of a rock can be directly retrieved from the cooling age, that is without requiring any knowledge of $T_c$ of the specific geochronological system, if the grain size, initial temperature ($T_i$) and the extent of resetting of the age upon cooling from $T_i$ are known. Part of the objectives of the present paper is to briefly review the development of the analytical relation between the cooling rate and the cooling age of a mineral, provide the numerical data on the behavior of a function that are required to calculate $T_c$ from the analytical relation, and then apply the analytical relation to selected meteoritic problems. In addition, expanding on the ideas of Dodson (1986) and Ganguly and Tirone (1999), we would present a method of "single crystal chronometry" by which the cooling rate can be retrieved from the difference between the bulk age and the average age at the central segment of a mineral.

RESETTING OF AGE DURING COOLING: THEORY

Review

During cooling from a peak temperature $T_0$, a mineral would develop compositional zoning if the rate of homogenization
of composition by diffusion within the mineral fails to keep up with the rate of change of the interface composition resulting from component exchange with the surrounding matrix in response to decreasing temperature. In this case, the mineral would not have a single closure temperature, but a closure temperature profile, \( T_C(x) \), of the diffusing species, decreasing progressively from core to rim. Dodson (1986) derived an expression of \( T_C(x) \) for a mineral in which the component of interest has undergone sufficient diffusive exchange with the matrix so that its initial concentration is not preserved in any part of the mineral. This formulation has been modified by Ganguly and Tirone (1999) in order that it is applicable to a mineral with arbitrary extent of diffusion. The modified formulation is as follows:

\[
\frac{E}{RT_C(x)} = \frac{E}{RT_o} + \ln M + G(x) + g(x) \tag{1}
\]

where \( E \) is the activation energy of diffusion, \( M \) is a dimensionless parameter, as defined below, \( G(x) \) is a geometric term that depends only on the shape of the crystal and position within it, and \( g(x) \) is a term which depends on the parameters governing \( G(x) \) and \( M \). The term \( g(x) \) is negligible when \( M \geq 1 \).

The quantity \( G(x) \) is called the "closure function" by Dodson (1986). The analytical expression for \( G(x) \) can be found in Dodson (1986) and Ganguly and Tirone (1999), and that of \( g(x) \) can be found in the latter. In developing the above expression, it was assumed that the reciprocal temperature changes linearly with time, that is,

\[
\frac{1}{T} = \frac{1}{T_o} + \eta t \tag{2}
\]

where \( \eta \) is a cooling time constant with dimension of K\(^{-1}\)t\(^{-1}\), and \( t \) is the elapsed time between \( T_o \) and \( T \).

Dodson (1973, 1986) defined the dimensionless quantity \( M \) as equal to \( D(T_o)\tau \alpha^2 \), where \( D(T_o) \) is the diffusion coefficient at \( T_o \), \( \alpha \) is characteristic dimension of the crystal (e.g., radius of a spherical or cylindrical grain and half thickness of a plane sheet), and \( \tau \) is a characteristic time taken for \( D \) to diminish by a factor \( e^n \) (i.e., by about two-thirds) during cooling (note that since \( D = D_o e^{-E/RT} \), we have, according to the above cooling model, \( D(t) = D_o e^{-E/RT} \)). From this definition, one can see that \( \sqrt{M} \) is of the order of average distance that the diffusing species would travel within the time \( \tau \) at \( T_o \), that is, \( (D(T_o)\tau)^{1/2} \), relative to the characteristic dimension of the crystal, \( \alpha \). Ganguly and Tirone (1999) showed that the above definition of \( M \) is equivalent to the following identity, which is convenient for our present purpose:

\[
M = \frac{RD(T_o)}{\eta^2} \tag{3}
\]

Combining Eqs. (1) and (2), we then have

\[
t(x) = \frac{R}{E\eta} \left[ \ln M + G(x) + g(x) \right] \tag{4}
\]

This expression allows us to recover the cooling time constant, \( \eta \), from the extent of resetting of the mineral age at any given point within the crystal, without requiring any knowledge of \( T_C \), and vice versa (note that \( t \) in Eqs. (2) and (4) are the same as \( \Delta t \) in Ganguly and Tirone, 1999). Of course, the solution for \( \eta \) has to be obtained numerically since it appears both outside the square brackets and as part of the dimensionless term \( M \).

Commonly, one determines the bulk age of a mineral by isotope dilution and thermal ionization mass spectrometry. In that case, \( G(x) \) and \( g(x) \) in Eq. (4) are simply replaced by their corresponding weighted averages, \( G \) and \( g \) respectively. The values of \( G \) are given by Dodson (1986; also see later) for spherical, cylindrical and plane sheet geometries, whereas Ganguly and Tirone (1999) presented the variation of \( g \) as a function of \( M \) for the three geometries in graphical form.

**Cooling Rate from the Central and Bulk Age of a Mineral**

Ganguly and Tirone (1999) calculated the cooling age profile, \( t(x) \), of crystals of different geometries as function of the normalized distance, \( x \), and the dimensionless parameter \( M \), so that the cooling rate of a mineral can be recovered if one can determine its cooling age profile. Determination of age profile of a mineral, however, does not seem to be a realistic goal within the near future. A more practical goal is the determination of the bulk age of a mineral and the age preserved in a central domain of specified dimension. From Eq. (4), the difference between these two ages, \( \Delta t \) (which equals \(-\Delta t\)) is given by

\[
\Delta t = -\frac{R}{E\eta} \left[ \Delta G + \Delta g \right] \tag{5}
\]

where \( \Delta \) stands for the difference of the specified quantity between its weighted average values at a central domain and for the bulk crystal. \( G \) is a function of only the normalized position \( x \) in the crystal, whereas \( g \) is a function of both \( x \) and \( M \). For \( x = 0.25 \), 0.50 and 1.00, the weighted average values of \( G \) are as follows, as obtained from the expression of \( G(x) \) in Dodson (1986).

<table>
<thead>
<tr>
<th>( G )</th>
<th>Sphere</th>
<th>Cylinder</th>
<th>Plane sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>2.0169</td>
<td>1.6517</td>
<td>1.0289</td>
</tr>
<tr>
<td>0.50</td>
<td>2.1985</td>
<td>1.8149</td>
<td>1.1570</td>
</tr>
<tr>
<td>1.00</td>
<td>4.0082</td>
<td>3.2951</td>
<td>2.1584</td>
</tr>
</tbody>
</table>

(The \( G(1.00) \) values for sphere and plane sheet given above are slightly, but not significantly different from those in Dodson (1986), which are 4.0066 and 2.1382, respectively, and are probably due to the differences in the computational techniques.) The corresponding average values of \( g \), as calculated from the expression given in Ganguly and Tirone (1999), are listed in Table 1. In order to get enough sample for mass spectrometric analysis, it may be necessary to use a number of grains together. The above method of retrieval of
cooling rate from the central and bulk ages of a mineral would still be applicable if each central segment has the same or closely similar value of $x$.

Because of the nature of Eq. (5), the cooling time constant $\eta$ has to be calculated by successive approximations from a measured $\Delta \Gamma$ value. That is, one would have to calculate $\Delta \Gamma$ from a guessed value of $\eta$ and the corresponding value of $M$ (Eq. (3)), and see if it matches the measured value. The quantity $\Delta \Gamma$ is illustrated as a function of $\eta$ and $M$ for different geometries in Fig. 1, which can be used to graphically retrieve $\eta$ from the measured value of $\Delta \Gamma$ by successive approximations, following the same procedure. When $g \approx 0$ corresponding to a given value of $M$ (Table 1), $\eta$ can be calculated directly from $\Delta \Gamma$, using Eq. (5) and the $G$ values given above. Unfortunately, the appropriate age data are not available as yet from either terrestrial or planetary samples to apply this method, but it is hoped that this type of core and bulk age data would be available in the near future, especially with the increasing use of the sensitive high-resolution ion microprobe (SHRIMP) and multicollector inductively coupled mass spectrometer (ICP-MS) with coupled UV laser for microsampling.

**APPLICATIONS TO METEORITE SAMPLES**

**Cooling Rates of Selected H Chondrites**

The nature of the parent body of ordinary chondrites has been a debated issue. Taylor *et al.* (1987) did not find any
correlation between the metallographic cooling rates and metamorphic grades of 27 H, 10 L and 4 LL chondrites, which led them to reject any model of the layered or "onion skin" structure for the parent body in which the depth of burial of the samples is supposed to correlate positively (and hence the cooling rates negatively) with their metamorphic grades. Lipschutz et al. (1989), on the other hand, concluded that the metallographic and fission-track cooling rates and $^{39}$Ar/$^{40}$Ar systematics of unshocked meteorites do support an "onion skin" structure for the parent body of H and LL chondrites. However, the samples studied by Taylor et al. (1987) are either unshocked or had suffered only mild shocks (Haack et al., 1990).

Göpel et al. (1994) determined the Pb-Pb model ages of phosphates from seven H chondrites (Forest Vale, H4, Ste Marguerite, H4, Nadiabondi, H5, Richardson, H5, Allegan, H5, Kemouvé, H6 and Guareña, H6), and found that these ages become progressively younger with the increasing metamorphic grade of the host chondrites. They also noted that the available metallographic cooling rates of the H chondrites show a direct correlation between the age and the cooling rate; the metamorphic age, on the other hand, has an inverse correlation with metamorphic grade (Fig. 2). Thus, taken at face value, these data support the layered parent body structure of at least the H chondrites. Göpel et al. (1994), however, noted that the

FIG. 1. The difference between the average age of core with specified normalized radius and of the bulk crystal, $\Delta \Gamma$, as a function of the cooling time constant, $\eta$, and the dimensionless variable $M$ (Eq. (3)) for (a) spherical, (b) cylindrical and (c) plane sheet geometries. The solid and dashed lines apply to $\Delta \Gamma$ with core ages averaged over $x = 0.5$ and 0.25, respectively. There is no significant difference between these two ages for $M \leq 0.05$. 

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Fig. 2. Comparison of the metallographic cooling rates vs. cooling ages of phosphates in H chondrites (diamonds) with the cooling rate vs. age relation (solid line) calculated from the theoretical formulation and the diffusion kinetic data in apatite. All cooling rates are at 550 °C. Meteorite types: Forest Vale (H4 FV), Ste Marguerite (H4 SM), Nadiabondi (H5 Na), Richardson (H5 Ri), Allegan (H5 Al), Kemouvé (H6 Ke), and Guareña (H6 Gu).

metamorphism of the H4 chondrites took place between ~375 and 675 °C, which may be lower than the closure temperature for Pb diffusion in phosphates, as calculated using Dodson’s formulation for spherical geometry and cooling rates of 1 to 100 °C/Ma. Thus, they suggested that the U-Pb closure in the phosphates might not have been related to their cooling history, and consequently, the interpretation of the observed correlation between the age and metallographic cooling rates of the H chondrites remains uncertain. In the following discussion, we will present a revised calculation of the closure temperature of Pb diffusion in the phosphates and then present direct derivation of cooling rates of the H chondrites from their ages.

Cherniak et al. (1991) determined the Pb diffusion in apatite, which yielded the Arrhenian relation $D = 1.27 \times 10^{-4} e^{-Q/RT} \text{cm}^2/s$, with the activation energy $Q = 54.6 \pm 1.7 \text{kcal/mol}$. For an initial temperature of 550 °C (which is an intermediate temperature within the range of metamorphic temperatures of the H4 chondrites), the mean closure temperatures for spherical, cylindrical and plane sheet geometries are illustrated in Fig. 3 as a function of the dimensionless variable $M$ according to the formulation of Dodson (1973) and its modification by Ganguly and Tirone (1999). For a cooling rate of 100 °C/Ma at 550 °C (i.e., $\eta = 1.48 \times 10^{-4} \text{K}^{-1} \text{Ma}^{-1}$), and phosphate grains of radii between 25 and 65 μm, as given by Göpel et al. (1994), the value of $M$ determined according to Eq. (3) is 0.50–0.07, so that $\log \sqrt{M} = -0.15$ to $-0.57$. Thus, as is obvious from Fig. 3, the reason that Göpel et al. (1994) concluded that $T_C$ for Pb diffusion in the phosphates in the H4 samples might have been greater than $T_p$, lies in their application of Dodson’s formulation to a domain of $M$ values (i.e., $M < 1$) where it is no longer valid. The correct $T_C$, as obtained from the modified formulation of Ganguly and Tirone (1999), is less than $T_p$ for all geometries.

Having removed the objection to accepting the Pb-Pb ages of the H chondrites as their cooling ages, we would now determine the cooling rates of these samples from the age data, and compare the results with the metallographic cooling rates. Using Eq. (4) and the spatially weighted average values of the functions $G(x)$ and $g(x)$ for the whole grain (i.e., $G(1)$ and $g(1)$ respectively, as given above and in Table 1), we calculated the average elapsed time, $t$, until the closure of Pb diffusion in apatite as a function of the time constant $\eta$. Göpel et al. (1994) gave the peak metamorphic temperatures ($T_p$) of 950–1200 K for the type 5 and 6, and 650–950 K for the type 4 H chondrites. We have arbitrarily chosen the upper limits of these peak metamorphic temperatures for our calculations. The characteristic grain size was chosen to be 40 μm, which is within the specified range of grain diameter of 25–65 μm. The shape of apatite, which crystalizes in the hexagonal system, is, however, more akin to cylindrical than spherical geometry. Thus, unlike Göpel et al. (1994), who assumed the latter geometry, we used a cylindrical geometry to solve for $t$ from specified value of $\eta$ in Eq. (4). As noted by these workers, the metallographic cooling rate is valid at temperature ~550 °C. Thus, we calculated the cooling rate from $\eta$ at this temperature (according to $dT/dt = -\eta T^2$). The results of calculation of cooling rate at 550 °C vs. time to $T_C$ (i.e., $t$) from the formation

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age of ordinary chondrites, using $T_p = 1200$ K, have been superimposed on the data for metallographic cooling rate vs. $t$ in Fig. 3; using $T_p = 950$ K for the H4 chondrites does not materially affect the results. It is obvious from Fig. 3 that the cooling rates of the H chondrites calculated directly from the model cooling ages are in excellent agreement with their metallographic cooling rates. According to the calculation of Wood (1979), the inferred cooling rate of the H6 chondrites imply a parent body of at least 200 km diameter, in which the depth of burial of these chondrites should be ~50 km.

Inasmuch as the cooling rates of the seven H chondrites calculated by two independent methods agree with each other and are inversely correlated with their metamorphic grade, it is tempting to endorse the model of layered parent body for the chondrites. However, the fact that Taylor et al. (1987) did not find any correlation between metallographic cooling rates and metamorphic grades of a much larger suite (41) of samples might imply that the inverse correlation deduced in this work is a special property of the chosen set of samples rather than a statistically meaningful global characteristic of the chondrites. On the other hand, the metallographic method has been undergoing significant modifications recently (Hopfe and Goldstein, 2001), and has also been shown to lack sufficient accuracy to be able to always uncover, by itself, cooling rate systematic in a suite of samples (Ganguly and Stimpfl, 2000).

**Morristown Mesosiderite**

**Problem with the Sm-Nd Age**—The mesosiderites are stony-iron meteorites with nearly equal amounts of silicates and metals, and represent a small fraction (~1.6%) of the total meteorite abundance. Bogard et al. (1990) presented a critical overview of the various hypotheses concerning the origin and evolution of mesosiderites. Prinzhofer et al. (1992) carried out detailed studies of the Sm-Nd evolution of meteorites including the Morristown mesosiderite. The mineral isochron defined by the Sm-Nd isotopic compositions of plagioclase, phosphate and orthopyroxene yielded an age of $4470 \pm 20$ Ma for the Morristown mesosiderite, which is ~90 Ma younger than the U-Pb age of $4560 \pm 31$ Ma for the Estherville mesosiderite, as determined by Brouxel and Tatsumoto (1991).

In order to explain this age difference, Prinzhofer et al. (1992) appealed to an "impulsive" disturbance model. In this scenario, the Sm-Nd isotopic composition of plagioclase, which had the lowest rare earth element (REE) concentration, was assumed to have been disturbed by a very short duration metamorphic event after closure of the system in all minerals. It was also assumed that the Sm-Nd composition of orthopyroxene remained unaltered during this event since, according to the data of Sneeringer et al. (1984), Sm diffusion in clinopyroxene is very slow, and the diffusion kinetic properties of the clinopyroxenes may not be substantially different. Prinzhofer et al. (1992) argued that the compositions of the phosphates, which exchanged REE with plagioclase, had remained essentially unaffected as these were the principal hosts of Sm and Nd because of their much larger mass abundance. Thus, as a consequence of the "impulsive" disturbance of REE concentration in plagioclase, there would be, within the resolution of the analytical data, an apparent Sm-Nd mineral isochron defined by plagioclase, phosphate and orthopyroxene (with increasing Sm/Nd ratio) which had a smaller slope than that without the disturbance, thus giving the false impression of an younger age.

Stewart et al. (1994) presented a detailed analysis of the Sm-Nd chronology of mesosiderites and addressed the question of disturbance of the Sm-Nd system in pyroxene and plagioclase by cooling under metal and regolith blankets on the basis of the inferred Sm-Nd diffusion data in plagioclase and making the same assumption as Prinzhofer et al. (1992) concerning the Sm-Nd diffusion in orthopyroxene. They concluded that in order to escape significant resetting of the Sm-Nd system during cooling, the mesosiderite clasts must have been buried no deeper than 10–20 m in metal or 1 m in regolith. In the following sections, we present an evaluation of the Sm-Nd diffusion data in pyroxene and plagioclase, and explore the younger age of the Morristown mesosiderite could have been due to the resetting of the Sm-Nd system during cooling rather than an impulsive disturbance.

**Sm-Nd Diffusion in Pyroxene**—Sneeringer et al. (1984) determined Sm diffusion in synthetic diopside at 8, 14 and 20 kbar, 1100–1250 °C, but their data are internally inconsistent. For example, the activation energy of diffusion parallel to the c crystallographic axis at 14 kbar is ~531 kJ/mol, whereas at 8 kbar is ~238 kJ/mol. The activation volume varied (unsystematically) between 0.3 to 61.5 cm$^3$/mol in the temperature range 1100 to 1250 °C. The erratic nature of the data notwithstanding, Sneeringer et al. (1984) mentioned that "comparison of Sr and Sm high pressure data shows very similar activation energies and D$_p$'s at each pressure". They suggested that the Arrhenian relation for Sr diffusion in natural diopside, which was derived from experimental data at 1 bar without buffering the O$_2$, and is characterized by an activation energy of 406 kJ/mol, could also be used for Sm diffusion in diopside. This recommendation seems to have been accepted by Prinzhofer et al. (1992). In addition to the potential problems with this recommendation, as should be evident from the above discussion, there could also be a change of diffusion mechanism at lower temperature. Thus, even granting that Sm diffusion in orthopyroxene is not significantly different from that in clinopyroxene, there seems to be ample reason for concern about the approximate validity of the assumed Sm diffusion data in orthopyroxene, at least at temperatures much lower than 1100 °C.

No REE diffusion data are yet available for the orthopyroxene. We have carried out one diffusion experiment using $^{154}$Nd tracer isotope on a gem quality orthopyroxene crystal from Sri Lanka with composition En$_9$Fs$_1$ and a small amount of Ca and Al. (Ca = 0.01, $^{IV}$Al = 0.04 and $^{VI}$Al = 0.04

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on six oxygen basis.) The tracer isotope was dissolved in a very dilute (≤2 N) HCl solution and deposited on a polished crystal surface of orthopyroxene, which was oriented normal to the c-axis. The crystal was pre-annealed for 7.5 h at 827 °C under a flowing mixture of CO and CO₂ gas with a mixing ratio of CO/CO₂ = 0.537, providing an fO₂ = 18 bars, which is equivalent to that defined by wüstite-iron (WI) buffer at this temperature. The preparation of the isotope solution and polishing of crystal surface to a mirror finish by a combination of chemical-mechanical polishing (which removes the surface layer weakened by mechanical polishing action) are described by Ganguly et al. (1998). After the diffusion-anneal of the sample at 827 °C for 103.25 h, log fO₂ = 18 bars, the sample was analyzed by depth profiling in an ion probe, as described by Ganguly et al. (1998). The measured concentration profile of 145Nd, and the model fit to the data, assuming a fixed surface concentration, are illustrated in Fig. 4 (use of a variable surface concentration yields a significantly worse fit to the data). The data in the first 200 Å segment were ignored as simultaneous analyses 30Si, shown in the inset, indicate analytical instability within this region (which seems to be a typical problem with ion probe analyses). The modeling procedure including the coupled determination of the surface concentration through an optimization technique has been described in Ganguly et al. (1998).

The fitted profile to the experimental tracer diffusion data yields D(Nd) = 1.1 × 10⁻¹⁷ cm²/s for orthopyroxene at 1 bar, 827 °C, and fO₂ corresponding to that of WI buffer (10⁻¹⁸ bars). This value is similar to that of 27Mg tracer diffusion in orthopyroxene (X_Fe = 0.1) parallel to the c-axis, D(Mg) = 2 × 10⁻¹⁷ cm²/s, as determined experimentally by Schwandt et al. (1998) at 1 bar, 800–900 °C, and fO₂ corresponding to that of WI buffer. It is also similar to the average Fe-Mg interdiffusion value, D(Fe-Mg) = 1.2 × 10⁻¹⁷ cm²/s, which is calculated from the theoretical relation of Ganguly and Tazzoli (1994) at fO₂ corresponding to WI to 0.8 log unit above WI buffer and orthopyroxene of the same Fe content (X_Fe = 0.01) as used in the Nd tracer diffusion experiment. This similarity between the Nd and divalent cation diffusion in orthopyroxene may seem surprising, but analogous behavior was also found in garnet (Ganguly et al., 1998). In view of the diffusion-compensation law which implies that log D vs. 1/T relations for different diffusing species in a given phase should intersect at a point at some high temperature, T* (e.g., Lasaga, 1998), the species which have similar diffusivities in a given phase at T < T* should have similar activation energies, Q. It is then reasonable to assume that in orthopyroxene, Q(Nd) ≈ Q(Fe-Mg), which is ~57–61 kcal/mol (Ganguly and Tazzoli, 1994; Schwandt et al., 1998).

Sm-Nd Diffusion in Plagioclase—There are no experimentally determined diffusion data for REE in plagioclase. In evaluating the extent of resetting of Sm-Nd system in plagioclase in mesosiderite clasts as a function of burial depth beneath either a metal or a regolith layer, Stewart et al. (1994) assumed that in plagioclase D(Nd) is a factor of 10 smaller than D(Sr), for which they used the available data of Giletti (1991) for albite. However, the plagioclase in mesosiderites has ~90% anorthite (An) component (e.g., Rubin and Mittlefehdlt, 1992; Ruzicka, 1998). Giletti and Casseley (1994) found strong dependence of the Sr diffusion coefficient on the anorthite content. According to their data, Sr diffusion in a plagioclase with ~90% An content is ~3 orders of magnitude slower than that in pure albite. Thus, the Nd diffusion in plagioclase in mesosiderites should be ~3 orders of magnitude slower than what was assumed by Stewart et al. (1994) if we accept their assumption about the relative diffusivities of Nd and Sr in plagioclase. This yields D(Nd) = 2.5 × 10⁻⁶ cm²/s with Q = 59 kcal/mol for the mesosiderite plagioclase. The Arrhenian expression is the same as used by Stewart et al. (1994) except that the pre-exponential factor is smaller by a factor of 100.

Closure of Sm-Nd System in Orthopyroxene and Plagioclase During Cooling—Ganguly et al. (1994) developed an integrated model of the cooling history of mesosiderites between 1150 and 250 °C using cooling rates obtained from modeling compositional zoning across the core–overgrowth interface and Fe-Mg ordering in orthopyroxenes, and reconciling the results with the metallographic cooling rates and Ar-Ar age data. Haack et al. (1996) presented a model of the thermal and shock history of mesosiderites which is consistent with the cooling model of Ganguly et al. (1994). In the latter model, the mesosiderites cooled very rapidly at a rate of ~1 °C/1000 years from ~1150 to 850 °C, and subsequently cooled very slowly. The slow cooling regime, which started somewhere between 850 and 500 °C was modeled using the formal T−t relation given by Eq. (2). A value of time constant η = 1.8 × 10⁻⁶ K⁻¹ Ma⁻¹, which corresponds to a cooling rate of 0.5 °C/Ma at 250 °C, yielded a T−t path that satisfied the restrictions on the cooling rate reflected by the Fe-Mg ordering state in orthopyroxene and the metallographic data, and the mean black body temperature of an object in the asteroidal belt. Using this two step cooling model, we can now calculate the time lapse from the initial temperature of ~1150 °C to the closure of the Sm-Nd system in pyroxene and plagioclase according to Eq. (4).

Following Ganguly et al. (1994), we assume that the change from the very rapid to very slow cooling regime took place at ~727 °C, which lies well within the temperature limits within which this change was likely to have taken place. Stewart et al. (1994) also argued that the slow cooling regime began at a temperature ~700 °C. The total time lapse in the high-temperature rapid cooling regime (1 °C/100 years) from ~1150 to 700 °C is insignificant from the standpoint of resetting the Sm-Nd age of orthopyroxene. Thus, we need only to evaluate the time lapse in the slow cooling regime at the lower temperature until the Sm-Nd system becomes closed in orthopyroxene and plagioclase. Prinzhofer et al. (1992) gave the grain size of the silicates in the Morristown mesosiderites.
as 75–150 μm. We, thus, assume that the average radius (or half thickness) of the silicates were 50 μm. This is also the average value used by Stewart et al. (1994) in their calculation of resetting of the Sm-Nd system in mesosiderite as a function of the depth of burial.

Using now the Sm-Nd diffusion data, as discussed above, we get from Eq. (3) \( M = 2 \) and 7 for orthopyroxene and plagioclase, respectively, which make the function \( g \) vanishingly small (Table 1). The spatially weighted averages of \( G \) for the whole crystal of plane sheet and spherical geometries are 3.2951 and 4.0082, respectively. Thus, from Eq. (4), we get ~90 and 50 Ma for spherical and plane sheet geometries, respectively, as the time lapse before closure of the Sm-Nd system in orthopyroxene. The corresponding values for plagioclase are ~110 and 80 Ma. These results compare well with the 90 ± 20 Ma younger Sm-Nd mineral age of the Morristown compared with the Pb-Pb age of the Estherville mesosiderite, as noted by Prinzhofer et al. (1992). The closure temperature of the Sm-Nd system in orthopyroxene is ~600–650 °C, and that in plagioclase is ~560–600 °C, depending on whether these minerals have spherical (first number) or plane sheet (second number) geometries (the properties for cylindrical geometry are intermediate between the limits defined by spherical and plane sheet geometries; see Ganguly and Tirone,
1999). It is likely that orthopyroxene grains conform more to the spherical and the plagioclase grains conform more to the plane sheet geometries, in which case the above calculations imply a resetting of ~80–90 Ma and closure temperature of ~600 °C for the Sm-Nd system in both orthopyroxene and plagioclase.

In principle, it is possible that orthopyroxene, phosphates and plagioclase had closed at different times and the linearity of their $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in the Sm-Nd evolution plot is coincidental, especially since the $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of the phophates and orthopyroxene do not differ very much (this ratio is largest in orthopyroxene and smallest in plagioclase). However, the fact that the model calculations suggest ~50–110 Ma time lapse for the closure of the Sm-Nd decay system in orthopyroxene and plagioclase from the onset of cooling provides an alternative explanation of the ~90 Ma younger Sm-Nd mineral age in the Morristown compared to the Pb-Pb model age of the Estherville mesosiderite. This explanation appears particularly attractive when one recognizes that the assumption made by Prinzhofer et al. (1992) about the Sm-Nd diffusion kinetics in orthopyroxene does not match the direct experimental data at 1 bar, 827 °C.

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