

Conditions in the protoplanetary disk as seen by the type B CAIs

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Abstract-Type B coarse-grained calcium-aluminum-rich inclusions (CAIs) are the oldest known materials to have formed in the solar system and are a unique source of information regarding conditions and processes in the protoplanetary disk around the young sun. Recent experimental results on the crystallization and evaporation of type B-like silicate melts allow us to place the following constraints on the conditions in the protoplanetary disk during the formation of type B CAIs. 1) Once type B CAIs precursors have been condensed from a solar composition gas, they were reheated at 1250-1450 °C, as is indicated by their igneous texture. 2) The melilite mantles characteristic of type B1 CAIs could be formed by crystallization of magnesium- and silicon-depleted melt in the outer part of the partially molten droplets. Such depletion can arise when evaporation is fast compared to chemical diffusion in the melt. This requires the pressure of the surrounding solar composition gas to be at least 10⁻⁴ bars during the initial crystallization of melilite mantle. Type B2 CAIs with uniform distribution of melilite are expected to form at pressures less than 10^{-5} bars. 3) Evaporation calculations are used to place bounds on the thermal history of the type B CAIs. Observed compositional zoning in melilite suggests that the temperatures in the protoplanetary disk where the type B CAIs resided after crystallization could not have exceeded ~1000 °C for more than a few tens of thousands of years. A recent calculation of the physical conditions associated with nebular shocks produced transient temperatures and gas pressures very much like what we find is required to melt reasonable CAI precursors and evaporate these sufficiently quickly to make a type B1 CAI.

INTRODUCTION

Our understanding of how the solar system formed derives from a combination of astronomical observations, theoretical considerations, and the physical and chemical properties of solar system materials. Astronomical observations provide direct evidence of young stars developing at the centers of planar disks of dust and gas; however, these observations are severely limited by their spatial resolution. Theoretical models (see, for example, the recent review by Boss 2003) provide a more detailed picture of possible conditions surrounding a growing young star, but the dynamical regimes involved are complex and there are significant uncertainties in specifying the key parameters. These limitations make interpretations based on the physical and chemical properties of materials formed and processed during the earliest stages of solar system evolution especially important. The best materials for this purpose are small refractory inclusions in primitive meteorites that have remained relatively unchanged since they were formed in the solar nebula at the birth of the solar system.

We will focus on calcium-aluminum-rich inclusions (CAIs) in chondritic meteorites, and especially the type B CAIs, to infer conditions in the early solar system. These CAIs are the oldest known materials to have formed in the solar system, and their age, 4.567×10^9 years (Amelin et al. 2002), is generally taken to be that of the solar system as well. The type B CAIs are made of four main minerals: magnesium spinel (MgAl₂O₄); melilite, a solid solution of åkermanite (Ca₂MgSi₂O₇), and gehlenite (Ca₂Al₂SiO₇); anorthite (CaAl₂Si₂O₈); and an aluminum- and titanium-rich clinopyroxene called fassaite (a solid solution of CaMgSi₂O₆, $CaAl_2SiO_6$, $CaTi^{+3}AlSiO_6$ and $CaTi^{+4}Al_2O_6$). These are the minerals predicted by thermodynamic calculations to condense during the early stages of cooling of an initially hot gas of solar composition (Grossman 1972; Yoneda and Grossman 1995), suggesting a close connection between the type B CAIs and materials that condensed from an initially



Fig. 1. False-color X-ray images of natural type B CAIs and laboratory-produced analogues emphasizing the distribution of melilite. The major phases are melilite (dark blue), fassaite (light blue), anorthite (pink) and spinel (red). a) Allende type B1 CAI TS23, showing a well-developed surface layer (mantle) of melilite crystals. The very thin outer rim of spinel (also seen along the unbroken edge of the CAI in [c] is the "Wark-Lovering rim" and is generally believed to have been produced by a separate later exchange between the solidified CAI and surrounding gas. The black regions in the interior of the sample are voids resulting from the polishing done to produce the thin section. b) Melilite mantle produced in the laboratory by cooling a type B CAI-like melt in a very reducing hydrogen atmosphere that results in rapid evaporation of magnesium and silicon (i.e., $\varepsilon_{Mg} > 1$; see text for detail). This particular experiment was quenched while melilite was still crystallizing in order to demonstrate that the mantle is made up of the early-crystallizing melilite. The interior of this sample is spinel and quench glass (colored light blue in this image). c) Allende type B2 CAI TS33 showing a relatively random distribution of melilite. d) Randomly distributed melilite produced in the laboratory by cooling a type B CAI-like melt in air, in which case evaporation is negligible ($\varepsilon_{Mg} <<1$).

hot, well-mixed protoplanetary nebula. Beckett (1986) provided added support for this view by showing that the high Ti^{3+}/Ti^{4+} ratio (~0.5) in CAI fassaite requires extremely reducing conditions consistent with equilibrium with a surrounding gas of solar composition. There are, however, several important differences between the predictions of a simple one-stage condensation model and the actual properties of the type B CAIs:

1. The typical coarse-grained textures of the type B CAIs (Fig. 1) are entirely different from what one expects for condensation of solids from a gas as implied by the thermodynamic calculations, and indicate instead that the various minerals crystallized from a melt. The implication is that after condensing, the type B CAIs must have been reheated and partially melted to a high

degree, which requires temperatures several hundred degrees higher than original condensation temperature of melilite (Stolper 1982).

- 2. There are significant differences between recent estimates of the bulk composition of the type B CAIs and that calculated for equilibrium condensates from a gas of solar composition (Grossman et al. 2000). The most likely explanation for the depletion of type B CAIs in MgO (and very likely, SiO₂ as well) compared to compositions along the condensation trajectory shown in Fig. 2 is that a measurable fraction of these more volatile components were lost by evaporation while the inclusions were partially molten.
- 3. Many type B CAIs are surrounded by thin compositionally distinct refractory rims.

4. Type B CAIs are often found to be enriched in the heavy isotopes of silicon and magnesium by several parts per thousand per atomic mass unit relative to the bulk solar system (Clayton et al. 1988), and this is typical of evaporation residues of molten silicates due to the lighter isotopes of a given element evaporating slightly faster than the heavier ones (Davis et al. 1990).

Ironically, it is the discrepancies between the properties of natural type B CAIs and the predictions of equilibrium condensation models that allow for the most quantitative constraints on nebular conditions. We will use the results of laboratory experiments to interpret the texture and bulk chemical properties of the type B CAIs in terms of the temperature, pressure, and gas composition required to partially melt their precursors and produce sufficient evaporative loss of magnesium and silicon to explain their observed elemental and isotopic composition. Our focus is on the effects of evaporation while the inclusions are partially molten and thus we will not discuss the origin of thin refractory rims, which we believe formed at a later stage once the inclusions had crystallized. Stolper and Paque (1986) carried out a series of crystallization experiments that showed that, in order for the particular type B CAI-like composition that they studied to produce large melilite crystals such as those shown Figs. 1a and 1c, the run products had to be heated to about 1420 °C, sufficient to dissolve any of the preexisting melilite, and that the subsequent cooling rate could be no greater than 50 °C hr⁻¹ to avoid producing distinctly dendritic crystals. Figure 3 expands on this by showing the temperature required to begin crystallizing melilite in a type B CAI-like melt as a function of the bulk composition of the system characterized in terms of the molar ratio of the more volatile components MgO and SiO₂ to the refractory ones CaO and Al₂O₃. Type B CAIs typically have $(MgO + SiO_2)/$ $(CaO + Al_2O_3)$ in the range 0.8 to 1.2, which corresponds to melilite crystallization temperatures of about 1250-1450 °C. Figure 3 also shows the åkermanite content of the first melilite to crystallize, which can be used as a measure of the initial crystallization temperature of melilite in a refractory inclusion. The melilite in type B CAIs commonly has a minimum åkermanite content of about 20 mole% (Åk₂₀), implying that crystallization began at about 1400 °C, but in some inclusions the initial åkermanite content is as low 10 mole%, which would require crystallization to have begun at a temperature close to 1500 °C.

Richter et al. (2002a) studied the elemental and isotopic fractionations produced at the high temperatures implied by the textures and åkermanite content of melilite in typical type B CAIs. Laboratory experiments were used to determine the evaporation rate of MgO from a type B CAI-like melt and the relationship between the magnesium isotopic fractionation of the residue and the amount of magnesium volatilized. The experimental results were used to constrain the duration of the high temperature event that led to the partial melting and



Fig. 2. The solid curve gives the MgO and SiO₂ contents of solid condensates in equilibrium with a solar composition gas of 10^{-5} bars total pressure at different temperatures (Grossman et al. 2000). Bulk compositions of type B CAIs are shown as circles (Grossman et al. 2000; Simon and Grossman 2004). The reason two of the compositions fall on the Mg-enriched side of the condensation curve is not known. The open circles labeled χ and δ represent two assumed precursor compositions for type B CAIs that we use to evaluate how particular thermal histories shift the composition of these precursors into the field of the type B CAIs by evaporating SiO₂ and MgO. The circle labeled δ_e is the composition that results from subjecting material of composition δ to the thermal history calculated by Desch and Connolly (2002) for the passage of a "canonical" nebular shock.

heavy isotope enrichment of magnesium of typical type B CAIs. They found that a broad range of thermal histories are allowed, mainly because the evaporation rate of MgO from a type B CAI-like melt depends not only on the temperature but also on the pressure and composition of the surrounding gas, as shown in Fig. 4. The existing estimates of the pressure in the solar nebula in the region where silicates were first forming come from model calculations, giving values of 10⁻⁴ to 10^{-7} bars (Boss 1996), which translate into an uncertainty of more than factor of thirty in the evaporation rate and a similarly large range in the allowable duration of the high temperature event required to produce a given amount of elemental and isotopic fractionation. Tighter constraints on the thermal history of the type B CAIs will require more specific estimates of the pressure that prevailed in those regions of the protoplanetary disk where type B CAIs were made.



Fig. 3. Experimentally determined equilibrium crystallization temperature (or equivalently, dissolution temperature) of melilite in a CaO-MgO-SiO₂-Al₂O₃ melt plotted as a function of the molar ratio of the sum of the more volatile oxides MgO and SiO₂ to the sum of the much more refractory oxides CaO and Al₂O₃, after Mendybaev et al. (2004). The mole fraction of åkermanite in the first melilite to crystallize is also given. Data are from relevant experiments reported by various groups (Stolper 1982; Beckett 1986; Stolper and Paque 1986; Mendybaev et al. 2003).



Fig. 4. Evaporation rate of magnesium from a type B CAI-like melt as a function of temperature and pressure of a surrounding hydrogendominated gas. The curves are based on the experimentally calibrated evaporation kinetics given in Richter et al. (2002a). The rate of evaporation of Mg is proportional to the saturation vapor of Mg over the melt. The rate increases with increasing pressure of a hydrogendominated surrounding gas because of the effect of the associated reduction in f_{O} on the saturation vapor pressure of Mg. At sufficiently high pressures of the surrounding gas, the evaporation rates increase more slowly with pressure, or even decline, due to recondensation becoming important as the evolved gas has increasing difficulty leaving the vicinity of the surface (for details see Richter et al. 2002a).

PRESSURES IN THE PROTOPLANETARY DISK

In this section we will develop the argument that the distribution of melilite in the type B CAIs can be used as a constraint on the surrounding gas pressure during crystallization. Figure 1 shows two type B CAIs with distinctively different distributions of melilite. TS23, the CAI shown in Fig. 1a, has a distinctive outer layer (mantle) of almost pure melilite surrounding an interior with more

randomly distributed melilite. The well-developed melilite mantle of TS23 makes it a good example of type B1 CAI. We classify the CAI shown in Fig. 1b, TS33, as a type B2 CAI, defined as a type B CAI without a distinct melilite mantle or obvious concentric zoning (Wark and Lovering 1982). A question that will lead us to an estimate of pressure is what caused the outside parts of the type B1 CAIs to become so obviously different from their interiors? We can almost certainly rule out temperature gradients as a likely cause,



Fig. 5. MgO content as a function of radius in a molten sphere at a time such that 50% of the initial magnesium has evaporated for various choices of ε_{Mg} , which is defined in the text and provides a measure of whether the time scale for chemical homogenization by diffusion is fast ($\varepsilon_{Mg} < 1$) or slow ($\varepsilon_{Mg} > 1$) compared to the time scale for evaporating the magnesium. For details, see Richter et al. (2002a).

because thermal diffusion in silicate melts is sufficiently fast that the temperature gradients within cm-size objects would be miniscule even at the fastest allowable cooling rates of $50 \,^{\circ}\text{C}$ h⁻¹. The fact that the type B2 CAIs did not preferentially nucleate melilite at the gas-liquid interface would seem to rule out surface effects as being important. The most likely choice for establishing conditions that would make the near-surface the preferred place to crystallize melilite is that the evaporation rate was sufficiently fast that chemical diffusion was not able to maintain chemical homogeneity of the melt. During diffusion-limited evaporation the near-surface parts of a molten drop will become depleted in SiO₂ and MgO relative to the interior, with the effect of raising the crystallization temperature there (see Fig. 3). Melilite will then crystallize first and grow in the more volatile depleted near surface parts of the molten droplet, producing a mantle like that of the type B1 CAIs.

A good measure of whether evaporation is fast or slow relative to the ability of chemical diffusion to maintain the homogeneity of an evaporating molten sphere is given by the nondimensional number ε_{Mg} , the ratio of the time scale for chemical homogenization by diffusion, τ_{diff} , to the time scale for evaporation, τ_{evap} , defined in terms of how long it would take under the prevailing conditions to evaporate all of the element of interest:

$$\varepsilon_{Mg} = \frac{\tau_{diff}}{\tau_{evap}} = \frac{\left(\frac{r^2}{D_{Mg}}\right)}{\left(\frac{r\rho_{Mg}}{3J_{Mg}}\right)} = \frac{3rJ_{Mg}}{D_{Mg}\rho_{Mg}}$$
(1)

where r is the radius, J_{Mg} is the evaporation flux of MgO in moles per unit surface area per unit time, D_{Mg} is the effective

chemical diffusion coefficient, and ρ_{Mg} is the molar density of MgO. For $\varepsilon_{Mg} > 1$, chemical gradients will arise, with the near-surface parts being more depleted in MgO than the interior. The results of a set of evaporation calculations for different values of ε_{Mg} taken from Richter et al. (2002a) are shown in Fig. 5 and confirm that the near-surface becomes significantly depleted in MgO relative to the interior when $\varepsilon_{Mg} > 1$. Because depletion of MgO promotes the crystallization of melilite at higher temperature (Fig. 3), regimes with $\varepsilon_{Mg} > 1$ and depletion of MgO at the surface would be expected to produce type B1 CAI-like textures. When $\varepsilon_{Mg} < 1$, a molten sphere will remain effectively homogeneous despite evaporation from its surface and one would expect randomly distributed melilite as in type B2 CAIs like TS33. We have confirmed these expectations through laboratory experiments in which melilite was crystallized from CAI-like melts for different evaporation rates of SiO₂ and MgO (see Mendybaev et al. 2003 and 2004 for details). Type B1-like melilite mantles were produced in experiments with $\varepsilon_{Mg} \ge 1$ (Fig. 1b), while randomly distributed melilite crystals (Fig. 1d) are the norm for ε_{Mg} < 0.3. Intermediate textures with thin partial melilite mantles were produced in experiments in which ε_{Mg} was in the range 0.3-1.

The requirement that $\varepsilon_{Mg} \ge 1$ in order for melilite mantles to develop can be used to constrain nebular conditions at the time melilite began to crystallize. ε_{Mg} can be estimated using typical type B CAI values of r = 0.25 cm and $\rho_{Mg} =$ 0.01 moles cm⁻³ together with the evaporation rates given in Fig. 4 and appropriate values for the chemical diffusivity of magnesium, D_{Mg} , in a type B CAI-like melt. For a temperature of 1400 °C, we will use $D_{Mg} = 10^{-6}$ cm² s⁻¹, which is the value obtained by extrapolation of the



Fig. 6. The time required for the evaporation of 25% of the initial magnesium content of a molten sphere of type B CAI-like composition 0.25 cm in radius. Our estimate of the pressure regimes for making type B1 versus type B2 CAIs is also shown. 25% loss of magnesium from the precursors to the type B CAIs is fairly typical, according to Fig. 2, and for this to be the case, the length of time the type B CAIs can have been at temperatures of the order 1400 $^{\circ}$ C is only a few hours.

experimentally measured diffusion coefficients in type B CAI-like melts at slightly higher temperatures (Richter et al. 2002b). This value of the diffusion coefficient is also consistent with that obtained from the empirical models for multicomponent diffusion given in Liang et al. (1997). The diffusivity of magnesium in the melt will be much less sensitive to the pressure of the surrounding gas than the evaporation rate, and therefore a constraint on ε_{Mg} at a given temperature will translate into a constraint on the pressure. For r = 0.25 cm, $\rho_{Mg} = 0.01$ moles cm⁻³, and $D_{Mg} =$ $10^{-6} \text{ cm}^2 \text{ s}^{-1}$; ε_{Mg} will be ≥ 1 when $J_{Mg} \ge 1.3 \times 10^{-8}$ moles cm² s⁻¹, which, given how J_{Mg} depends on pressure (Fig. 4), will require $P_{H_2} \ge 10^{-4}$ bars. The values of $\varepsilon_{Mg} < 0.3$, which result in texture with homogeneous distribution of melilite such as in type B2 CAIs, can be transformed into $P_{H_2} \le 10^{-5}$ bars. At intermediate pressures, type B CAIs with incomplete melilite mantles would form. This bound on the hydrogen pressure will be relatively insensitive to temperature (less than a factor of two for a 200 °C change in temperature) because the activation energy for evaporation ($E_{evap} \approx 300 \text{ kJ}$ mole⁻¹) (Richter et al. 2002a) and that of chemical diffusion in silicate melts ($E_{diff} \approx 225 \text{ kJ mole}^{-1}$) (Liang and Davis 2002) are similar. It is worth noting that the values of P_{H_2} we calculate based on experimentally determined evaporation kinetics in a hydrogen-dominated gas and cation diffusion in silicate melts are well within the range of P_{H_2} in the protoplanetary disk derived from astrophysical models. Having determined bounds on the pressures required to make type B1 and type B2 CAIs, we can make better estimates of how long it would take to evaporate a given amount of magnesium from a type B CAI-like melt. Figure 6 shows the time it would take to evaporate 25% of the magnesium from a

type B CAIs precursor as a function of pressure and temperature. At $P_{H_2} \ge 10^{-4}$ bars, required for formation of type B1 CAIs, it would take less than 20 hours to evaporate 25% of the magnesium at 1300 °C and only a few hours at 1500 °C. Because of the slower evaporation kinetics at the lower pressures required to form type B2 CAIs, the times necessary for them to lose a similar fraction of their initial magnesium could have been considerably longer.

THERMAL HISTORIES

In this section we use model calculations to establish bounds on thermal histories that can account for typical elemental and isotopic fractionation of the type B CAIs. Figure 7a illustrates the change in the composition of the possible type B CAI precursor (labeled δ) as it evaporates in a hydrogen-dominated gas while being heated to 1300 °C, 1450 °C, and 1550 °C. The composition labeled χ is that from which melilite with $Åk_{20}$, which is typical for type B CAIs, will crystallize. The melt composition from which $Åk_{10}$ melilite (also sometimes found in type B CAIs) crystallizes is also shown. The evaporation kinetics used for allowable trajectories in temperature-composition space shown in Fig. 7a assumes that the pressure of the surrounding hydrogen-dominated gas is 10⁻³ bars. The usual assumption has been that the melilite in type B CAIs crystallized during cooling (Stolper 1982; Stolper and Paque 1986; Grossman et al. 2002), and that the maximum cooling rate allowed is 50 °C h⁻¹ in order to form blocky rather than dendritic melilite. However, as we show in Fig. 7, given sufficient evaporation of silicon and magnesium from a type B CAI-like melt, isothermal trajectories or even trajectories with



Fig. 7. a) Temperature-composition trajectories calculated for model precursor compositions χ and δ (see Fig. 2) when these are subjected to rapid heating (solid or dashed heavy arrows) followed by cooling or heating at a constant rate until melilite begins crystallize at the intersection of the trajectory with the crystallization curve (taken from Fig. 3). The evaporation kinetics are based on the experimentally calibrated parameterizations of Richter et al. (2002a) with a pressure of 10^{-3} bars. The isotopic fractionation of the residue is calculated using the kinetic isotopic fractionation factor for magnesium evaporating at 1500 °C given in Richter et al. (2005). The time to complete each trajectory is given, along with the calculated magnesium isotopic fractionation and the åkermanite content (interpolated using the data given in Fig. 3) for the first melilite to crystallize. The peak temperature allowed is that which results in a cooling rate of 50 °C h⁻¹. Higher peak temperature would result in faster cooling rates, which would produce unacceptably dendritic textures. The pressure in this case (10^{-3} bars) is such that we expect the early crystallizing melilite to form a continuous layer at the surface that will stop further evaporation of the melt and thus the subsequent evolution will be that of a closed system with no further isotopic fractionation. b) The same as above, except that only the precursor δ is considered and the pressure of the surrounding gas is now taken to be 10⁻⁵ bars. The slower evaporation kinetics at this pressure compared to the previous case increases the time along the trajectories and also results in somewhat higher allowable peak temperatures. In this example, we continued to calculate trajectories even after melilite would have begun to crystallize under the assumption that when $P = 10^{-5}$ bars, no continuous melilite layer will develop at the surface and thus the partial melt would continue to evaporate. In the case of continued rapid cooling after the initial crystallization of melilite (50 °C h^{-1}) there will be very little additional evaporation; however, for cooling rates of a few °C h⁻¹, there will be enough additional evaporation that the melilite will be zoned both in åkermanite content and magnesium isotopes. The range of expected Åk and the associated isotopic fractionation of the crystallized melilite are indicated.



Fig. 8. Time in years required to homogenize a 200 μ m melilite crystal that was initially zoned in åkermanite content. The binary diffusion coefficient for Al + Al versus Mg + Si exchange in melilite (Nagasawa et al. 1999, 2001) is quite sensitive to the åkermanite content, and for this reason we show times calculated using both the diffusion coefficient for Åk₂₀ and that for Åk₅₀.

increasing temperature can result in crystallization of the melilite. The figure illustrates that it would take only about an hour in order to change the melt composition from δ to χ , when Åk₂₀ starts to crystallize, by evaporation of Mg and Si from a molten droplet heated to 1450 °C and 1550 °C, and 3.5 hours if droplet started to evaporate at 1300 °C while the temperature was rising. Figure 7a also shows the calculated fractionation of ²⁵Mg/²⁴Mg in the first melilite to crystallize (expressed as δ^{25} Mg, defined as $1000 \times [\{^{25}$ Mg/ 24 Mg} $_{melilite}/$ {²⁵Mg/²⁴Mg}_{precursor}-1] and measured in ‰). The isotopic fractionation associated with a given amount of magnesium evaporated was calculated using the Rayleigh equation $({^{25}Mg/^{24}Mg}_{sample}/{^{25}Mg/^{24}Mg}_{precursor} = f_{24}^{\alpha - 1})$, where f_{24} is the fraction of ²⁴Mg remaining in the residue and $\alpha = 0.988$ is the kinetic isotopic fractionation factor reported by Richter et al. (2005) as being appropriate for evaporation at 1500 °C. The isotopic fractionation calculated using $\alpha = 0.988$ is appropriate for evaporation from a chemically homogeneous melt (i.e, $\varepsilon_{Mg} < 1$). For finite ε_{Mg} , Richter et al. (2002a) show that the isotopic fractionation of Mg in the residue will be reduced by a factor of $e^{-0.09 \varepsilon_{Mg}}$ (i.e., ~10% reduction for ε_{Mg} = 1, 60% for ε_{Mg} = 10), which can be taken into account when the need arises for more precise calculations. Figure 7b shows the trajectories that would produce melilite with an initial åkermanite content of Åk₂₀ when the pressure of the surrounding gas is 10⁻⁵ bars. As one would expect from the effect of pressure on the evaporation kinetics (Fig. 4), the time scale over which the evaporation takes place is considerably longer for the case shown in Fig. 7b compared to that in Fig. 7a.

We have argued that the evaporation of a molten sphere with a radius of 0.25 cm and type B CAI-like composition will produce a melilite mantle typical of a type B1 inclusion if the pressure of the surrounding hydrogen-dominated gas is greater than 10⁻⁴ bars. We expect that once the solid melilite mantle forms, melt will stop evaporating and further crystallization of melilite at lower temperatures will take place in an effectively closed system. That being the case, one would predict that the melilites in type B1 inclusions should have essentially uniformly fractionated magnesium isotopic composition. This could be, depending on the cooling rate, in marked contrast to what we would expect for evaporation at lower pressures, such as the case shown in Fig. 7b, where evaporation from the interstitial melt could very well continue as melilite crystallizes. The effect of this will be to produce melilite crystals that are zoned with increasing magnesium isotopic fractionation from cores to the edge of the crystals. We have illustrated this in Fig. 7b by showing trajectories that allow for evaporation even after the first melilite has begun to crystallize at 1400 °C. If the cooling rate is sufficiently fast (e.g., 50 °C h⁻¹) the additional loss of silicon and magnesium will be negligible and the melilite will be compositionally zoned but isotopically uniform. At slower cooling rates, there will be sufficient evaporation to produce continuous isotopic fractionation of the partial melt, which will result in the melilite being also isotopically zoned. Figure 7b gives an example showing that if the cooling rate during melilite crystallization is 3 °C h⁻¹, the melilite will be zoned in ²⁵Mg/ ^{24}Mg from 3‰ at the core to about 9‰ at the edge.

Once a melilite mantle has formed, or in the case of the type B2 CAIs when only a very small amount of melt remains, the evaporation kinetics can no longer be used to constrain the duration of high temperatures. The best one can do under these circumstances is use the fact that the melilite



Fig. 9. The same as Fig. 7, except that the thermal history (shown as an inset) and pressure ($P = 5 \times 10^{-4}$ bars) are those calculated by Desch and Connolly (2002) for the reheating of condensed solids by the passage a "canonical" nebular shock.

crystals in the type B inclusion are zoned in åkermanite content, which together with the diffusion coefficient for Al + Al \Leftrightarrow Mg + Si exchange as a function of temperature, to place bounds on how long a given temperature could have persisted without erasing the chemical zoning. Figure 8 gives the annealing time (proportional to l^2/D , where l is a typical dimension and D is the binary diffusion coefficient for Al + Al \Leftrightarrow Mg + Si exchange in melilite) of a typical 200 µm melilite crystal as a function of temperature, and shows that the region of the protoplanetary disk where the type B CAIs resided after crystallizing could not have had temperatures in excess of 1000 °C for more than a few tens of thousands of years.

PROCESSES AND CONDITIONS IN THE PROTOPLANETARY DISK

We now turn to the question of what process or processes in the early protoplanetary nebula could give rise to temperature-composition trajectories such as those shown in Fig. 7. Theoretical models of midplane temperatures at distances greater than 1 AU in a gravitationally collapsing protoplanetary disk struggle to achieve temperatures as high as 1200 °C (Boss 1998), which is several hundred degrees lower than what is required to partially melt plausible type B CAI precursor compositions and crystallize melilite with $Åk_{20}$. This suggests that the reheating was either a local event (e.g., lightning or a nebular shock) or that precursors to the type B CAIs were processed along trajectories that took them very close to the young sun, heated them there, and later ejected back to ~2.5 AU where the meteorite parent bodies are believed to have formed. A key test for any proposed process for reheating the type B CAI precursors is that the duration of high temperatures be reasonable in terms of producing the

right textures and the degree of elemental and isotopic fractionation. The fact that cooling rates have to be less than 50 °C h⁻¹ in order to produce coarse-grained melilite crystals rules out reheating by lightning and subsequent free radiative cooling (which will be of the order of one second) (Tsuchiyama et al. 1980). Shu and coworkers (see Shu et al. 1996, 2001) have developed models in which CAIs are heated to high temperatures as they are brought very close to the young star and then cooled as they are flung back out onto the protoplanetary disk by what they refer to as an X-wind. Once these models are developed to the point that they provide quantitative temperature and pressure histories, they could be tested in terms of the elemental and isotopic fractionations that would be produced. For the moment, however, the only proposed process for reheating condensed materials for which sufficiently detailed temperature and pressure histories have been calculated is that associated with the passage of a nebular shock. Desch and Connolly (2002) recently calculated the temperature and pressure history of condensed silicate materials that are heated by what they refer to as a "canonical" nebular shock (7 km s⁻¹ shock, preshock temperature and pressure of 300 K, and 10⁻⁵ bars). The temperature history, shown as an inset to Fig. 9, consists of an initial rise in the temperature due to radiation from the hot shock front prior to the actual arrival of the shock, a very short duration spike in the temperature due to gas drag as the shock arrives, and a final phase as the solids and surrounding gas cool over a period of hours. The pressure increases rapidly from 10^{-5} bars in front of the shock to 5×10^{-4} bars after passage of the shock. The calculation is not specifically for CAIs and a more appropriate calculation for our purposes would have involved a somewhat larger object (e.g., 5 mm diameter typical of type B CAIs rather than the 0.5 mm used in the calculation) and a preshock temperature closer to the condensation temperature of reasonable precursors for the type B CAIs. We do not expect that assuming a larger size object and a higher starting temperature would have a major effect on the calculated temperature history above 1200 °C, which is the relevant temperature range where melting and evaporation become important.

Figure 9 shows the calculated trajectory in temperaturecomposition space for a type B CAI subjected to the temperature and pressure history given by Desch and Connolly (2002) for their "canonical" shock. The precursor in this example started with the same composition δ used in Fig. 7a and now results in the first melilite to crystallize at 1380 °C with Åk₂₅ and δ^{25} Mg of 2.6‰. The evaporation rate associated with a post-shock pressure of 5 \times 10⁻⁴ bars is sufficiently high to make a melilite mantle and therefore a type B1 CAI. Assuming that there is no significant further evaporation of silicon and magnesium once the melilite mantle forms, the calculated bulk composition falls in the middle of the range of actual type B CAIs as shown by the point δ_e in Fig. 2. The calculated δ^{25} Mg also falls in the middle of the range of values observed in natural type B CAIs.

SUMMARY

The conditions in the protoplanetary nebula inferred from the texture and composition of the type B CAIs involve various stages. The disk material must have first become sufficiently hot and well-mixed for the precursors of the type B CAIs to condense from a gas not much different from the solar composition. The temperature dropped to a point where about 5% of the rock-forming material in the disk condensed, some of it making mm- to cm-sized objects, which are the precursors to the type B CAIs. The condensed material must have been reheated and melted by some local process to temperatures of at least 1400 °C for the first melilite to crystallize to have $Åk_{20}$, which is the commonly found value. We argued that in order to make the mantled type B1 CAIs, the pressure of the solar gas must have been of the order 10^{-4} bars or greater, in which case the duration of the hightemperature event (or events, if they were recurring) could not have been more than a few hours. The canonical nebular shock of Desch and Connolly (2002) produced transient pressure and temperature conditions that are remarkably similar to those we infer for making the type B1 CAIs. We interpret the random distribution of melilite in the type B2 CAIs as indicating that there were no significant core to rim chemical gradients in the melt droplet from which melilite crystallized, and that this would require relatively slow evaporation in order for chemical diffusion to maintain a homogeneous melt. Such slow evaporation relative to diffusion would be the case when the surrounding hydrogendominated gas pressure is less than about 10⁻⁴ bars. The time along evaporation trajectories that could make a typical type B2 CAI will be of the order of five to several tens of hours

when the pressure is 10^{-5} bars. Once a melilite mantle has formed at the surface of a typical type B1 CAI ($T \sim 1400$ °C), or once most of the melilite has crystallized in a type B2 CAI ($T \sim 1250$ °C), evaporation kinetics of the sort we have been discussing here gives no further insight into subsequent cooling rates. The fact that melilite crystals in type B CAIs are zoned in åkermanite content can be used as a constraint on how long they could have been at a given temperature by requiring that solid state chemical diffusion not have erased the zoning: measured diffusion coefficients imply that temperatures in excess of 1000 °C could not have lasted for more than a few tens of thousands of years.

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