

THE SEARCH FOR SUPERNOVA GRAINS IN AN ICE CORE

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Received 2005 December 20; accepted 2006 January 27

ABSTRACT

A search was conducted for grains of the potential core-collapse supernova (SN) condensate minerals corundum (Al_2O_3), hibonite ($\text{CaAl}_{12}\text{O}_{19}$), and spinel (MgAl_2O_4) among grains filtered from the 308.6 m Guliya ice core recovered from the Qinghai-Tibetan plateau in China. Simple models are developed and calculations are presented to estimate the number of Al_2O_3 grains that would be deposited per cm^2 on the Earth by a nearby core-collapse SN and to estimate the number of presolar oxide grains that could be contained in micrometeorite (MM) grains that are accreted by the Earth. A total of 698 candidate SN condensate grains were identified in six Guliya ice core grain samples from the following time periods: ~ 2 – 10 , ~ 25 – 27 , ~ 34 – 36 , ~ 53 – 57 , ~ 59 – 62 , and ~ 68 – 72 kyr. A procedure developed at the University of Chicago to identify presolar grains in meteoric samples was used to find these candidate grains. Nanometer-scale secondary ion mass spectrometry (NanoSIMS) analysis, performed at Washington University on 37 grains from the ~ 34 – 36 , ~ 53 – 57 , and ~ 59 – 62 kyr samples, indicated that none possessed the extreme oxygen-16 enhancements expected from a SN source. However, nine of the 37 grains did possess the oxygen-16 enhancements consistent with calcium-aluminum-rich inclusions (CAIs).

Subject headings: dust, extinction — supernovae: general

1. INTRODUCTION

Signatures of celestial influences on our planet's evolution are easily destroyed or masked by terrestrial processes that constantly reform the Earth's surface, e.g., volcanic eruptions, seismic activity, erosion, vegetation growth, plate tectonics, and anthropological activity. Tree rings, lacustrine sediments, deep sea sediments, and ice cores are geological archives capable of preserving some of these signatures in a stable, sequential, and datable manner. Beryllium-10 abundance peaks of approximately twice the background over a period of 1–2 kyr at ~ 35 and ~ 60 kyr have been discovered in an Antarctic ice core by accelerator mass spectrometry (AMS) (Raisbeck et al. 1987). In addition, the ~ 35 kyr peak has been observed in core samples from Greenland (ice), the Mediterranean Sea (sediment), and the Pacific Ocean (sediment) (Ellis et al. 1996). Analysis of the Guliya ice core, and also of the Greenland Ice Core Project ice core, has revealed a ^{36}Cl peak, approximately twice the background, with an age estimate of 35–40 kyr (Thompson et al. 1997; Baumgartner et al. 1997). At ~ 2.8 Myr before the present, enhancements of ^{60}Fe have been observed in layers from deep-sea manganese crust (Knie et al.

2004). In addition to these three radioisotopes, Ellis et al. (1996) proposed ^{26}Al as a potential signature of a nearby core-collapse SN.

In the Ellis et al. (1996) hypothesis, ^{10}Be and ^{36}Cl enhancements on the Earth are produced primarily by SN cosmic rays emitted in a burst, lasting a few thousand years, while ^{26}Al and ^{60}Fe enhancements are the result of the direct deposit of SN ejecta on the Earth. The large atmospheric cosmic-ray production of ^{10}Be and ^{36}Cl radioisotopes makes it difficult to distinguish SN enhancements from those produced by other processes that also modulate the Earth's cosmic-ray flux. However, the radioisotope ^{26}Al is likely produced and ejected primarily by core-collapse SN as suggested by the Galactic distribution of the 1809 keV gamma-ray signal produced from its decay (Diehl et al. 1995). Observations from SN 1987A indicate that refractory grains, Al_2O_3 , MgSiO_3 , and Fe_3O_4 , form 1–2 yr after the SN (Kozasa et al. 1991; Lingenfelter et al. 1998). While ^{60}Fe is also likely a core-collapse supernova product (Knie et al. 2004), Fe_3O_4 grains (along with MgSiO_3 grains) are relatively abundant, compared to the terrestrially rare Al_2O_3 in the pre-industrial age. Thus, we have searched among grains filtered from the 308.6 m Guliya ice core recovered from the Qinghai-Tibetan plateau in China (Thompson et al. 1997) for potential core-collapse SN condensate grains composed of the Aluminum-rich minerals corundum

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(Al₂O₃), hibonite (CaAl₁₂O₁₉), and spinel (MgAl₂O₄) (Ebel & Grossman 2001). These minerals are rare among terrestrial rocks and fine-grained atmospheric dust of terrestrial origin. Furthermore, they are insoluble in the acids used in the sample preparation process and are therefore separable from other minerals, such as silicates, that have high terrestrial abundances. The preparation process employed to identify candidate SN condensate grains among their terrestrial diluents was developed at the University of Chicago for detecting presolar grains in meteoritic samples (Amari et al. 1994). In this approach, size sorting and targeted chemical dissolutions eliminate grains that are most likely not of a SN origin. On the order of 10³ grains are mounted onto high-purity gold and examined with a Scanning Electron Microscope by Energy Dispersive Spectroscopy (SEM-EDS) for candidate grains (Amari et al. 1994).

We prepared the following six Guliya grain samples for analysis, identifying corundum, hibonite, and spinel grains in each: ~2–10, ~25–27, ~34–36, ~53–57, ~59–62, and ~68–72 kyr. These refractory oxide grains primarily possess three possible origins: terrestrial, meteoritic, or supernova. The oxygen isotope ratios of 37 grains from the ~34–36, ~53–57, and ~59–62 kyr samples were measured with the nanometer-scale secondary ion mass spectrometry (NanoSIMS) at Washington University to assess the potential grain origin. Preliminary results of this work were presented by Cole et al. (2005); they indicated that while the grains are not likely from a SN source, 1/4 of the grains are likely high-temperature condensates formed in the solar nebula and accreted by the Earth. In this work, a simple model, developed in greater detail in § 2, is presented along with calculations to estimate the number of Al₂O₃ grains that could have been deposited per cm² on the Earth by a core-collapse supernova and the number of presolar oxide grains (corundum, spinel, hibonite) contained in micrometeorite grains accreted by the Earth.

2. GRAINS

A theoretical study by Ellis et al. (1996) presents an expression to estimate the expected number of atoms per gram of ice (Λ) for various radioisotopes deposited on the Earth from a distance of $D = 20$ pc by a $10 M_{\odot}$, core-collapse supernova. By analogy to the work of Ellis et al. (1996), we present an expression for the number of grains of mineral composition, i , deposited per cm² on the Earth

$$\sigma_i = \frac{M_i/m_g}{4\pi R_{\oplus}^2}, \quad (1)$$

where M_i is the total mass of grains composed of mineral i , m_g is the average mass per grain, and $4\pi R_{\oplus}^2$ is the surface area of the Earth.

2.1. Supernova Grains

For the mass, M_i , of grains deposited on the Earth we adapt the expression from Ellis et al. (1996) to yield

$$M_i = f_i \left(\frac{R_{\oplus}}{2D} \right)^2 M_i^{\text{ej}}, \quad (2)$$

where M_i^{ej} is the mass of grains with mineral composition i , condensed from the SN ejecta, D represents the mean Earth-supernova distance, and f_i accounts for the fraction of grains of mineral i , in the size range of interest. The total mass of grains

TABLE 1
GRAIN ESTIMATES

Composition (i)	σ_i (grains cm ⁻²)
SN 1987A Al ₂ O ₃ ($D = 20$ pc).....	<95
SN 1987A refractory ($D = 20$ pc).....	<2400
MM Presolar oxides ($\Delta t = 1000$ yr).....	~110

NOTES.— Estimates for the number of supernova grains and presolar oxide grains in micrometeorite (MM) deposited per cm² (σ_i) of the Earth.

formed from SN ejecta, M_i^{ej} , is a function of the grain composition and mass of the SN progenitor. The expression for σ_i becomes

$$\sigma_i = 4.2 \times 10^{-8} \left(\frac{10 \text{ pc}}{D} \right)^2 \left(\frac{M_i^{\text{ej}}}{M_{\odot}} \right) \frac{f_i}{m_g}, \quad (3)$$

after substituting M_i into equation (1), expressing D in units of pc and M_i^{ej} in solar mass units, M_{\odot} . The fraction of grains in the size range of interest, f_i , is assumed to be 1 so that the resulting estimates are upper limits. The mass of ejected grains, M_i^{ej} , is based on the observations of refractory grains formed after SN 1987A (see § 2.1.2). The average grain mass, m_g (in grams), is estimated in § 2.1.1.

2.1.1. Supernova Grain Size

To zeroth order, the solar gravity and radiation forces acting on a dust grain traveling through the heliosphere impose a lower limit on the infalling dust grain diameter of $d_g \sim 1 \mu\text{m}$ (Frisch et al. 1999; Kortenkamp & Dermott 1998). We fixed the size separation procedure to select grains between this $1 \mu\text{m}$ minimum and a $2 \mu\text{m}$ maximum diameter. For a density of 2.5 g cm^{-3} , which is typical of terrestrial material and which will be assumed for the remainder of this work, this corresponds to a range of particle masses of 1–10 pg. We focused on these small grains for two reasons. First, small grains, due to efficient cooling on atmospheric entry, are not heated to as high a temperature as larger grains (Love & Brownlee 1991) and hence experience little oxygen isotopic exchange with the Earth's atmosphere. Second, we expect, based on the observed size distributions of the surviving presolar grains in meteorites, that grains larger than the $2 \mu\text{m}$ cutoff would be much less abundant; so the grains would be both less likely to be found and more likely to be diluted with terrestrial contaminants.

2.1.2. Supernova Grain Model Estimates

The estimates of the number density of core-collapse supernova grains of composition, i , deposited on Earth, σ_i , are based on grains of mass $m_g = 1$ pg and assumed grain compositions of corundum ($i = \text{Al}_2\text{O}_3$) and all expected refractory mineral species ($i =$ refractory grains). We have assumed the fraction of grains in the size range of interest, f_i , to be 1; the resulting estimates are therefore upper limits. The mass of grains that formed, M_i^{ej} , is equated to the mass of refractory grains that condensed from SN 1987A ejecta: $\sim 0.031 M_{\odot}$ of Fe₃O₄, $\sim 0.19 M_{\odot}$ of MgSiO₃, and $\sim 0.009 M_{\odot}$ of Al₂O₃ (Kozasa et al. 1991). Table 1 displays the expected number of grains cm⁻², σ_i , from a core-collapse supernova at a mean Earth-SN distances, $D = 20$ pc, as calculated with equation (3).

2.2. Presolar Grains in Micrometeorites

Presolar, isotopically anomalous grains may be contained in micrometeorite grains accreted by the Earth. Employing equation (1), the number of presolar grains of composition i , deposited per cm^2 of the Earth during the time period Δt can be estimated by

$$\sigma_i = \frac{M_i^{\text{ac}} \Delta t / m_g}{4\pi R_{\oplus}^2}, \quad (4)$$

where M_i^{ac} is the mass of micrometeorites (MMs) of composition i , accreted per year. The model estimates assume a grain deposition duration of $\Delta t = 1000$ yr, the order of magnitude time period spanned by the Guliya grain samples, and a grain mass of $m_g = 1$ pg, the mass used in our SN grain model. The estimate for the mass of presolar oxide grains accreted per year, $M_{\text{oxide}}^{\text{ac}}$, is described below.

Recent work by Yada et al. (2006) indicates that presolar silicate grains from Antarctic micrometeorites (AMMs) represent ~ 50 parts per million (ppm). The fraction of presolar oxide grains in the ALH 77307 meteorite is $\sim 36\%$ based on the discovery of 9 presolar silicates and 5 presolar oxide grains (Nguyen et al. 2005). We assume the same proportions for MMs and estimate an abundance of ~ 28 ppm for presolar oxide grains in MMs. Given the Earth's total accretion rate of $20 \times 10^9 \text{ g yr}^{-1}$ (Engrand & Maurette 1998), the accretion rate of presolar oxide grains in MMs is $M_{\text{oxide}}^{\text{ac}} = 5.6 \times 10^5 \text{ g yr}^{-1}$. For a grain mass of 1 pg and a deposition time $\Delta t = 1000$ yr, this corresponds to 5.6×10^{20} grains or $\sigma_{\text{oxide}} \sim 110$ grains cm^{-2} deposited on the Earth (see Table 1).

3. THE GULIYA ICE CORE SAMPLES

The 308.6 m Guliya ice core was drilled on the Qinghai-Tibetan plateau in China (Thompson et al. 1997). The investigators of the core performed grain concentration measurements on 12,480 grain samples that were extracted from ice with dimensions, of 1 cm \times 3 cm \times 2.5 cm (Thompson et al. 1997). We have obtained Guliya grain samples from the epochs corresponding to the previously discovered ^{10}Be and ^{36}Cl enhancements, ~ 34 – 36 and ~ 59 – 62 kyr, and additional samples from the following epochs: ~ 2 – 10 , ~ 25 – 27 , ~ 53 – 57 , and ~ 68 – 72 kyr. The grains ranged in size from 0.63 to 80 μm and were stored on filter sheets.

Before sample preparation, the grains represented a surface area $A = 1 \text{ cm} \times 3 \text{ cm} = 3 \text{ cm}^2$ (based on the dimensions of the samples) of ice core exposed to the atmosphere at the time of precipitation; the total area of the ~ 2 – 10 kyr sample was $A/4 = 0.75 \text{ cm}^2$ as only 1/4 of the original filter sheets were used to prepare the sample. Assuming uniform distribution of grains throughout the original ice samples, the total area is also effectively reduced by the fraction of grains removed from each sample during preparation. We define an effective ice sample surface area, A_{eff} , as the product of the total ice sample surface area, A , and the fraction of grains in the size range of interest from each sample that were mounted for the SEM-EDS search. Consequently, the effective area, A_{eff} , accounts for all of the sample reductions that occurred during the preparation procedures described in § 3.1.

3.1. Sample Preparation

All of the sample preparations and treatments were performed at the University of Chicago. The six grain samples were paired to form three groups: group 1 (~ 34 – 36 and ~ 53 – 57 kyr), group 2 (~ 25 – 27 and ~ 68 – 72 kyr), and group 3 (~ 2 – 10 and ~ 59 –

62 kyr). While the samples within each group received the same treatments, the different groups of samples did not experience the same treatments. A qualitative inspection of SEM-EDS images from a sampling of the ~ 59 – 62 kyr grains suggested a mass distribution dominated by diameters $\geq 20 \mu\text{m}$ and a composition dominated by silicates. In the first stage the grains were recovered by dissolving the filters on which they were stored with acetone and rinsing the insoluble grains with clean acetone until the mass of dissolved filter was less than the minimum expected mass of a potential supernova grain, 1 pg. Concurrently, the grains were size sorted into a coarse fraction, $> 2 \mu\text{m}$ in diameter, and a fine fraction $\leq 2 \mu\text{m}$ in diameter. The fine fraction grains were suspended in a solution of $\sim 70\%$ isopropanol and $\sim 30\%$ distilled water and divided in half by transferring $\sim 1/2$ of the solution volume into a test tube; an ultrasonic bath was used to distribute the grains throughout the solution just prior to the volume transfer. We assumed that the fraction of grains transferred was equal to the fraction of solution volume transferred. The entire coarse fraction and $\sim 1/2$ of the fine fraction were dried and saved to preserve them for possible analysis in the future. The following fractions of the fine-grained samples were prepared for analysis: 49% of the ~ 34 – 36 kyr grains, 48% of the ~ 53 – 57 kyr grains, 49% of the ~ 25 – 27 kyr grains, 49% of the ~ 68 – 72 kyr grains, 54% of the ~ 2 – 10 kyr grains, and 47% of the ~ 59 – 62 kyr grains. An optical microscope was used to estimate the number of fine fraction grains as being on the order of $\sim 10^8$ for the ~ 34 – 36 and ~ 53 – 57 kyr samples.

Following the size sorting, targeted chemical dissolutions of unwanted minerals were used to reduce the number of grains to a quantity, on the order of 10^3 , that could be mounted and examined by SEM-EDS for candidate grains (Amari et al. 1994). Based on the SEM-EDS results from the ~ 59 – 62 kyr grains, we assumed that all of the samples had a similar composition and treated them with hydrofluoric acid to dissolve silicates, which have a high terrestrial abundance. Other dissolution treatments were applied based on additional SEM-EDS analysis of the samples. Each treatment stage was followed by a series of rinses to reduce the mass of the treatment agent to less than the mass of a potential SN grain, 1 pg. Each sample was then suspended in an isopropanol ($\sim 70\%$), distilled water ($\sim 30\%$) solution from which approximately 2000 to 5000 grains were transferred onto high-purity gold foil mounts; higher grain counts make it difficult to perform the SEM-EDS analysis to search for candidate supernova grains.

For the group 1 samples the fraction of ~ 34 – 36 and ~ 53 – 57 kyr grain samples mounted onto gold corresponded to effective areas of $A_{\text{eff}} \sim 0.5 \text{ cm}^2$ and $A_{\text{eff}} \sim 0.2 \text{ cm}^2$, respectively. In the group 2 samples, $A_{\text{eff}} \sim 0.7 \text{ cm}^2$ of the ~ 25 – 27 kyr and $A_{\text{eff}} \sim 1.5 \text{ cm}^2$ of the ~ 68 – 72 kyr were mounted onto gold. Two gold mounts were made for the ~ 59 – 62 kyr sample. The grains of the first mount, comprising $\sim 1/3$ of the sample, were not dispersed enough to make an SEM-EDS search for potential supernova grains possible. The remaining ~ 59 – 62 kyr sample and the ~ 2 – 10 kyr sample were rinsed several more times to remove any residual, high-viscosity substance that could restrict grain dispersion. Approximately $A_{\text{eff}} \sim 0.05 \text{ cm}^2$ of the ~ 59 – 62 kyr grains were deposited on a second gold mount, and $A_{\text{eff}} \sim 0.0024 \text{ cm}^2$ of the ~ 2 – 10 kyr grains. The initial sample area, A , and the effective area, A_{eff} , mounted for analysis are displayed in Table 2.

3.2. Detection Limits

The upper limit for the mean Earth-SN distance, D , is constrained by the minimum detection requirement that at least one

TABLE 2
SAMPLE ANALYSIS

Sample	A_{eff} (cm^2)	$D_{\text{Al}_2\text{O}_3}^{\text{max}}$ (pc)
~2–10 kyr.....	0.0024	~10
~25–27 kyr.....	0.7	~160
~34–36 kyr.....	0.5	~140
~53–57 kyr.....	0.2	~90
~59–62 kyr.....	0.05	~40
~68–72 kyr.....	1.5	~240

NOTES.—The columns display the sample, the effective area, A_{eff} , of each sample after preparation, and the maximum Earth-SN distance, $D_{\text{Al}_2\text{O}_3}^{\text{max}}$, from which a SN corundum grain can be detected in the ice core samples.

SN grain of composition, i (i.e., Al_2O_3) reside in the ice core sample. This minimum detection constraint is defined as

$$\sigma_i^{\text{min}} \equiv \frac{1}{A_{\text{eff}}}, \quad (5)$$

where A_{eff} is the effective surface area (see § 3.1) of the ice core sample exposed to the atmosphere at the time of precipitation. Hence, $\sigma_{\text{Al}_2\text{O}_3}^{\text{min}}$ is the minimum detection constraint for finding one SN Al_2O_3 grain in the effective area of the ice core sample. Substituting σ_i^{min} for σ_i in equation (3) and solving for D yields an expression for the maximum distance from which a SN can deposit one grain of mineral composition, i , in the ice core sample:

$$D_i^{\text{max}} = 2.0 \times 10^{-3} \left(\frac{A_{\text{eff}} M_i^{\text{ej}} f_i}{1 M_{\odot} m_g} \right)^{1/2}, \quad (6)$$

where M_i^{ej} is the total mass of grains of composition i , m_g is the mass per grain, and f_i is the fraction of grains that possess the mass m_g . Given the effective areas, A_{eff} , we estimate the maximum distance, $D_{\text{Al}_2\text{O}_3}^{\text{max}}$ from which one SN Al_2O_3 grain can be detected in the mounted area of the samples. These estimates use $M_{\text{Al}_2\text{O}_3}^{\text{ej}} = 0.009 M_{\odot}$ (Kozasa et al. 1991) for the total mass of corundum grains, $m_g = 1$ pg as the mass per grain and $f_{\text{Al}_2\text{O}_3} = 1$ as all of the grains are assumed to 1 pg. Table 2 displays maximum distance for each sample.

A lower limit mean Earth-SN distance, $D = D_i^{\text{min}}$, is established by considering the effect that a near-Earth supernova would have on terrestrial life. A study by Ellis & Schramm (1995) establishes a distance of $D \sim 10$ pc. Hence, we assume that any supernova grains deposited on Earth originate from a mean Earth-SN distance $D > 10$ pc. Due to the small effective area mounted for the ~2–10 kyr sample, the maximum distance from which a SN can be detected is approximately equal to this 10 pc lower limit.

3.3. Sample Mapping and NanoSIMS Analysis

Each gold foil sample mount was imaged and X-ray mapped with a photomosaic composed of about 300 frames with dimensions of $100 \mu\text{m} \times 125 \mu\text{m}$. The resulting elemental maps were used to identify the refractory minerals spinel, hibonite, and corundum. The results of the sample elemental mapping are as follows: ~2–10 kyr, 102 frames with corundum; ~25–27 kyr, 211 frames with corundum and one spinel grain; ~34–36 kyr, 69 frames with corundum; ~53–57 kyr, 134 frames with corundum; ~59–62 kyr, 70 frames with corundum, three spinel grains

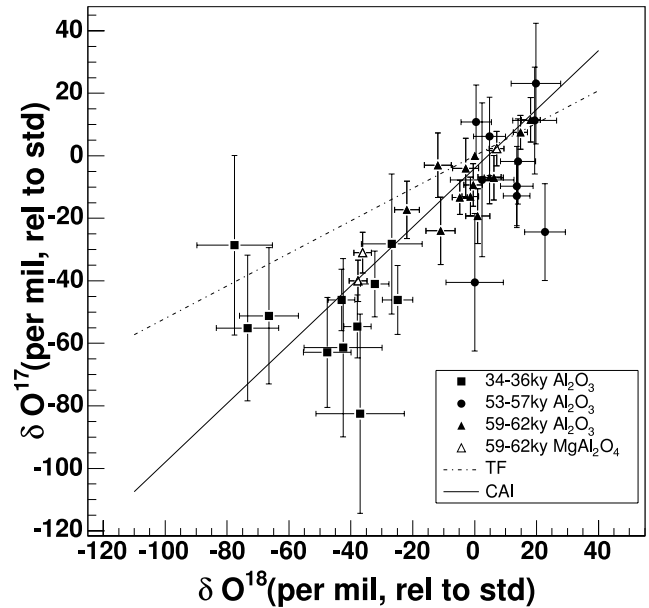


FIG. 1.—NanoSIMS used to measure the $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values for 37 refractory oxide grains from the Guliya ice core grain samples ~34–36, ~53–57, and ~59–62 kyr. These values are compared to the terrestrial fractionation (TF) line and the calcium-aluminum-rich inclusion (CAI) mixing line. The displayed error bars are 1σ . Nine grains, seven corundum (Al_2O_3) and two spinel (MgAl_2O_4), from the ~34–36 and ~59–62 kyr samples, respectively, reside within 1σ of or more than 1σ below the CAI mixing line.

and one hibonite grain; and ~68–72 kyr, 105 frames with corundum and two spinel grains. The estimate for the corundum grain number fraction is a lower limit of 1%, as some of frames possessed corundum grain aggregates of order 10^2 that were difficult to enumerate. Elemental X-ray spectra were taken of all of the spinel and hibonite grains and of a sampling of the corundum grains to verify the visual inspections in preparation for NanoSIMS analysis (see Zinner et al. 2003 for description of NanoSIMS).

The origin of the 37 grains from three samples, ~34–36, ~53–57, and ~59–62 kyr, were assessed by measuring the oxygen isotopic ratio and comparing them to standards, synthetic Al_2O_3 grains placed on each mount. The resulting $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ values for each grain performed via NanoSIMS analysis and first reported by Cole et al. (2005) and displayed in Figure 1 indicate that nine grains, seven corundum and two spinel, are likely calcium-aluminum-rich inclusions (CAIs) formed in the solar nebula. The seven corundum grains are all from the ~34–36 kyr sample and reside either within 1σ of the CAI mixing line or more than 1σ below the mixing line. The two spinel grains are from the same $100 \mu\text{m} \times 125 \mu\text{m}$ frame of the ~59–62 kyr sample; these grains may be pieces of a larger grain that was fragmented during mounting onto the gold. The remaining grains from these samples and all grains from the ~53–57 kyr reside within approximately 2σ of the terrestrial fractionation (TF) line also displayed in Figure 1.

4. DISCUSSION

The results of the model calculations presented in Table 1 indicate that <100 grains cm^{-2} of Al_2O_3 would be deposited on the Earth if a core-collapse supernova of similar mass to SN 1987A occurred at a distance of 20 pc. The results of the model calculations for presolar grains in MMs presented in Table 1 estimate that 110, 1 pg, presolar oxide grains could be deposited per cm^2

Earth over 1000 yr. Our samples represented an area of $<1.5 \text{ cm}^2$ (see § 3.1). Based on the effective areas mounted, the three analyzed samples (see Table 2), provide sensitivity to supernovae with a mean Earth distance of $\sim 140 \text{ pc}$. The NanoSIMS analysis indicates that none of the 37 analyzed grains from the time periods $\sim 34\text{--}36$, $\sim 53\text{--}57$, and $\sim 59\text{--}62 \text{ kyr}$ possessed the ^{16}O and ^{18}O enhancements relative to the standard expected for corundum and spinel grains originating from a core-collapse SN source (Nittler et al. 1998; Nittler 2003; Messenger et al. 2005). Thus, the NanoSIMS results do not support the hypothesis of a SN-induced cosmogenic source for the observed ^{10}Be and ^{36}Cl enhancement peaks. Furthermore, none of the analyzed grains are presolar in origin. However, the ^{16}O enrichments of seven corundum and two spinel grains from the $\sim 34\text{--}36$ and $\sim 53\text{--}57 \text{ kyr}$ samples, respectively, are consistent with CAIs typically found in carbonaceous chondrites (Clayton 1993). Selected from the fine fraction, diameter $\leq 2 \mu\text{m}$, these grains, due to efficient cooling on atmospheric entry, are not heated to as high a temperature as larger grains (Love & Brownlee 1991) and hence experience little oxygen isotopic exchange with the Earth's atmosphere during

atmospheric entry. The nine grains possessing ^{16}O enrichments are likely high-temperature condensates formed in the solar nebula and accreted by the Earth.

The 37 refractory oxide grains analyzed from three Guliya ice core samples represent $<15\%$ of candidate supernova grains identified via the SEM-EDS analysis. Future NanoSIMS analysis of additional grains from all six samples will improve the statistics and yield information about the time dependence of the CAI grains accreted by the Earth for periods extending to $\sim 68\text{--}72 \text{ kyr}$ before the present. Finally, based on the effective areas mounted (see Table 2), analysis of the $\sim 68\text{--}72 \text{ kyr}$ sample will extend the sensitivity to supernovae with a mean Earth distance of $\sim 240 \text{ pc}$.

The authors acknowledge the assistance of S. Amari in sample preparation. This work is supported in part by NSF grants PHY-0110253 and PHY-0099476 and by NASA grants NAG5-12997, NAG5-11903, and NAG5-11545.

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