It has been suggested that ice cores may preserve detectable enhancements of some terrestrially rare radioisotopes, \(^{10}\text{Be}\), \(^{26}\text{Al}\), \(^{36}\text{Cl}\), resulting from a near-Earth core-collapse supernova (SN) [1]. Both \(^{10}\text{Be}\) and \(^{36}\text{Cl}\) are also produced by atmospheric cosmic ray spallation and hence are influenced by processes that modulate the Earth’s cosmic ray flux. Previous studies [2], [3] have suggested that enhancements occurred in the \(^{10}\text{Be}\) and \(^{36}\text{Cl}\) fluxes at \(\sim 35\) ky and at \(\sim 60\) ky for \(^{10}\text{Be}\). Thus we have searched for potential SN condensates with \(^{26}\text{Al}\) amongst grains filtered from the 308.6m Guliya ice core recovered from the Qinghai-Tibetan plateau in China [3].

We searched for potential core-collapse SN condensate grains corundum (\(\text{Al}_2\text{O}_3\)), hibonite (\(\text{CaAl}_{12}\text{O}_{19}\)) and spinel (\(\text{MgAl}_2\text{O}_4\)) (see [4]) in Guliya grain samples from the following time periods: \(\sim 2-10\) ky, \(\sim 25-27\) ky, \(\sim 34-36\) ky, \(\sim 53-57\) ky, \(\sim 59-62\) ky and \(\sim 68-72\) ky. These minerals are rare among terrestrial rocks and fine-grained atmospheric dust of terrestrial origin. Furthermore, they are insoluble in the acids employed in the sample preparation process and therefore separable from other minerals, such as silicates, that have high terrestrial abundances. Candidate SN condensate grains were identified among their terrestrial diluents employing a procedure developed at the University of Chicago for detecting presolar grains in meteoritic samples [5]. A set of 37 grains from the \(\sim 34-36\) ky, \(\sim 53-57\) ky and \(\sim 59-62\) ky samples were analyzed with the NanoSIMS at Washington University to measure their oxygen isotopic ratios. The preliminary results indicate that...
the analyzed grains, representing < 15% of those identified, do not possess the extreme O isotopic ratios expected to characterize a SN source [6], [7].

1. Sample Preparation

The six Guliya grain samples were size sorted into a coarse fraction, > 2µm diameter, and a fine fraction, ≤ 2µm. Approximately half of the fine fraction, representing ~ 10⁸ grains per sample, was employed in the analysis, with the remaining grains being saved to preserve the archive and the prospect of future analysis. 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 10⁵, that could be mounted and examined by Scanning Electron Microscope (SEM) Energy Dispersive Spectroscopy (EDS) for candidate grains [5]. Finally, the grains were transferred from suspension onto high purity gold foils with the aim of mounting no more than 2,000 to 5,000 grains. We focused our analysis on grains of diameter ≤ 2µm, for two reasons. First, the majority of grains in the fine fraction size distribution would have diameters less than < 10µm, which is the size capable of surviving descent through the Earth’s atmosphere with a speed of 20 km/s as described in [8]. Second, smaller grains experience less atmospheric heating and oxygen isotopic exchange during entry than larger grains.

2. Elemental Mapping

Each of the sample mounts was covered by a grid composed of approximately 300 100µm×125µm frames. Elemental X-ray maps were made of each frame of the samples to identify the refractory grains spinel, hibonite and corundum. The number of frames with corundum and other refractory grains identified among the six samples were: ~2-10 ky, 102 frames with corundum; ~25-27 ky, 1 spinel grain and 211 frames with corundum; ~34-36 ky, 69 frames with corundum; ~53-57 ky, 134 frames with corundum; ~59-62 ky, 3 spinel grains, 1 hibonite grain and 70 frames with corundum; ~68-72 ky, 2 spinel grains and 103 frames with corundum. We present the number of frames that possessed Al₂O₃ grains, as some of these frames contained multiple corundum grains and/or aggregates of on the order 10² corundum grains that were difficult to enumerate.

3. NanoSIMS

The oxygen isotopic compositions of 37 grains from the ~34-36 ky, ~53-57 ky and ~59-62ky samples were measured with the NanoSIMS at Washington University; a more detailed description of NanoSIMS analysis can be found in [9]. Figure 1 displays the measured δ¹⁸O, δ¹⁷O ratios for each sample, the associated 1σ errors, the terrestrial fraction (TF) line, and the calcium aluminum inclusion (CAI) mixing line. Before the analysis, terrestrial Al₂O₃ grains were placed on each of the three gold mounts to serve as standards. Following the method of [9], we assume that the oxygen isotope ratios of these terrestrial Al₂O₃ grains are equivalent to standard mean ocean water (SMOW) values.

As shown in Figure 1, five of the eleven Al₂O₃ grains from the ~34-36 ky sample are within 1σ of the CAI mixing line with δ¹⁸O~ − 40 per mil and δ¹⁷O~ − 60 per mil. Two of the eleven grains reside below the CAI mixing line by more than 1σ. All ten ~53-57
ky grains are roughly within 2σ of the TF line and near δ¹⁸O~0 per mil and δ¹⁷O~0 per mil. Finally, the isotopic ratios of 13 Al₂O₃ and three MgAl₂O₄ grains from the ~59-62 ky sample were measured. Two of the spinel grains reside within 1σ of the CAI mixing line at δ¹⁸O~−40 per mil and δ¹⁷O~−40 per mil. These two spinel grains are located in the same 100µm×125µm frame and may represent two pieces of a single grain that was fractured during the mounting procedure.

4. Discussion

Previous studies [2], [3] have indicated that enhancements occurred in the ¹⁰Be and ³⁶Cl fluxes at ~35 ky and at ~60 ky for ¹⁰Be. None of the analyzed corundum and spinel grains from the time periods ~34-36 ky, ~53-57 ky, ~59-62 ky possessed the anomalous, non-CAI values of δ¹⁸O, δ¹⁷O indicative of ¹⁶O enhancements expected from a core-collapse SN source [6], [7]. However, the 37 grain set represents < 15% of the total number identified from the elemental maps. The NanoSIMS results indicate that seven corundum grains from the ~34-36 ky sample and two spinel grains from the ~59-62 ky sample possess δ¹⁸O, δ¹⁷O values that suggest ¹⁶O enhancements consistent with CAIs which are typically found in carbonaceous chondrites [10]. These grains are likely high temperature condensates from the solar nebulae. As the grains are in the fine fraction < 2µm, they are unlikely to have experienced significant size alteration during the atmospheric entry. The detected CAI grains represent ~1/3 of the 37 grains analyzed and the number detected differs between the three samples with the majority residing in the ~34-36 ky epoch. Additional analysis of grains from the above samples, ~34-36 ky, ~53-57 ky, ~59-62 ky, and of the remaining three samples, ~2-10 ky, ~25-27 ky, ~68-72 ky, is needed to determine if the variation is the result of the small number of grains sampled or an indication of a time variation in the number of CAI grains accreted by the Earth.

REFERENCES

Figure 1. The oxygen isotope ratios and $1\sigma$ errors of refractory oxide grains from three Guliya ice core grain samples measured with a NanoSIMS.