

The Episodic Influx of Tin-rich Cosmic Dust Particles During the Last Ice Age

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Abstract. This paper presents evidence of the first detection of interstellar dust in ice age polar ice. Neutron activation analysis (NAA) results are reported for 15 elements found in dust filtered from eight samples of Camp Century Greenland ice dating from 40 to 78 kyrs BP. High concentrations of Sn, Sb, Au, Ag, Ir, and Ni were found to be present in three out of these eight samples. One compositionally anomalous dust sample from an ice core depth of 1230.5 meters (age ~49 kyrs BP, near the beginning of D/O stadial No. 13) was found to contain tin with an average weight percent of 49% as determined by energy dispersive x-ray analysis (EDS). This sample was also found to contain high concentrations of Pb with an average weight abundance of 8.4% and matching the Sn:Pb ratio observed in interstellar spectra. Dust particles in this sample generally have a platy morphology and range from submicron size up to a size as large as 120 μm , a particle consisting almost entirely of SnO_2 and being the largest monomineralic extraterrestrial dust particle so far discovered. One porous aggregate tin-bearing particle was found to contain nanometer sized chondrules indicating an extraterrestrial origin. The extraterrestrial origin for the tin is also indicated by the presence of isotopic anomalies in the ^{114}Sn , ^{115}Sn and ^{117}Sn isotopes. Follow up isotopic measurements of this tin-rich dust need to be performed to improve confidence in the anomalies reported here. High abundances of the low melting point elements Ag, Au, and Sb are also present in this tin-rich sample along with elevated abundances of the siderophiles Ir, Ni, Fe, and Co, the latter being present in chondritic proportions and indicating that about 9% of the dust has a C1 chondrite component. Measurements indicate that about 97% of this dust is of extraterrestrial origin with a 3% residual being composed of terrestrial wind blown dust. EDS analysis of another tin-rich Camp Century ice core dust sample dating to ~130 kyrs BP was found to contain tin-rich particles with a similar platy morphology and to have Sn and Pb weight abundances averaging 39% and 7.5% respectively, again approximating the interstellar Sn:Pb ratio. The relative absence of cosmic microspheres and the unmelted appearance of the tin-rich particles in both of these samples suggests that these particles entered the Earth's atmosphere at low velocity, implicating a gradual accumulation of dust from a dispersed state in the near Earth space environment. The unusual enhancement of Sn and Pb could be explained if these dust particles were originally present in the solar system's interstellar environment in a superconducting native metal state and were preferentially concentrated through Meissner effect forces by the passage of cosmic ray driven hydromagnetic shocks which may also have transported them into the solar system. The 49 kyrs BP event is estimated to have lasted over 6 years and to have deposited dust onto the Earth at a rate 10^4 - 10^5 times higher than present rates. This had a significant cooling effect on climate and resulted in a transient 33 fold increase in snow accumulation. Future discovery of this event in ice cores at other locations should void any lingering thoughts that this heavy metal enhancement may be due to sample contamination.

Keywords: cosmic dust; superconductive particles; tin; lead; trace elements; ice age climate

1. INTRODUCTION

Polar ice records provide a valuable account of the composition of the Earth's atmosphere during past millennia. In particular, the polar ice sheets provide an ideal medium for assessing past influxes of extraterrestrial dust due to their remoteness from sources of continental dust. The Camp Century, Greenland deep ice core, retrieved in 1966, was the first polar ice core to penetrate to ice deposited during the last ice age and previous interglacial. It was followed in 1968 by the final retrieval of the Byrd Station ice core in Antarctica, which penetrated to depths corresponding to the last glacial period.

Lonnie Thompson, one of the early researchers of these deep ice cores, studied the size distribution and concentration of microparticles in the ice using a Coulter counter method and also used a scanning electron microscope (SEM) and EDS analysis to determine the morphology and compositions of individual dust particles he had filtered from his samples (Thompson, 1977a, pp. 45, 56, 1977b). One of the perplexing findings of his study was that 3 out of the 13 ice core samples he had analyzed from the Camp Century ice core contained high concentrations of heavy metals such as Sn, Cu, Zn, and Mo. All of these were found in the ice age portion of the core. Tin was most abundant in two of these samples: G962-1 filtered from an ice core depth 1230.5 meters (49.2 kyrs BP) and G1038-1 filtered from a 1342.2 meter depth (~130 kyrs BP). In G962-1, he reported that 6 out of 7 particles contained Sn in abundances ranging from 2 to 30%, and that 4 out of 6 particles contained molybdenum in abundances ranging from 14 to 22%. In G1038-1, he found that 3 out of 5 particles contained Sn and 1 out of 5 contained Mo.¹ However, the results of the present study suggest that Thompson's report of Mo in these samples may be a misidentification as the molybdenum $L\alpha$ line (2.29 keV) has approximately the same X-ray energy as the Pb $M\alpha$ line (2.35 keV). Also in a sample he filtered from a depth of 1162 meters (~17 kyrs BP), Thompson found that one particle out of the eight he had studied contained Sn at an abundance of 46%. In the Byrd Station core, of the 14 ice core samples he analyzed, he found only one tin bearing particle, this one being in a sample from a depth of 700 meters dating ~7400 BP.

It is unlikely that these tin-rich particles represent environmental contamination since Thompson processed his ice core samples in a class-100 clean room and took precautions to remove a layer of ice from the outside of each core sample prior to processing, as is discussed below. The possibility that these metal-rich particles may be windblown material coming from some atypical source is also unlikely since during the ice age, the Camp Century site was at least 3000 km from any ice free continental surface. So it would be expected to receive only an average sampling of airborne dust from many locations. But the composition of these anomalous particles differs radically from the average composition of the Earth's crust. Volcanic sources may be ruled out as the source of these tin-rich particles, since SEM investigation showed that volcanic shards were not present in his samples (Thompson (1977a, 1977b).

Thompson (1977a) has suggested that the anomalous particles may be bedrock scrapings introduced into the ice as the glacier moved over the Greenland bedrock. However, this is unlikely for several reasons. First, these heavy-metal-rich particles were found at distances ranging from 41 to 220 meters above bedrock, and it is doubtful that bedrock scrapings would have migrated upward such a great distance. Second, ice containing bedrock debris has been

¹ These depths specify actual ice core depths such as those used by Johnsen et al. (1972) in plotting the Camp Century isotope profile. Thompson (1977a, 1977b) instead provided log book depths for his samples, listing these two depths respectively as 1234.7 m and 1345.4 m.

found to be present in the lower 16 meters of the Camp Century core, as indicated by the presence of relatively large-size particle aggregates measuring up to 3 cm in size. But coarse debris indicative of bedrock scrapings is absent in the compositionally anomalous sections found at higher elevations in the ice core. The dust samples from these anomalous sections instead are populated by microparticles most of which are less than a few microns in size. He found none to be larger than about 50 microns. Third, whereas the basal 16 meters of the ice core has a homogenized $\delta^{18}\text{O}$ record indicative of mixing and melting of the ice as it traversed the bedrock, ice above that section has an intact isotope profile suggesting that it experienced no mechanical disturbance (Herron and Langway, 1979, Johnsen, et al., 1972). Finally, the composition of these tin particles differ from that of tin ore found in Greenland. The sorensonite deposits, $\text{Na}_4\text{SnBe}_2\text{Si}_6\text{O}_{18} \cdot 2(\text{H}_2\text{O})$, which have been found at the Kvanefjeld and Ilimaussaq locations in southern Greenland, for example, have a Sn:Si ratio of 0.7 as compared with a ratio of between 4 and 8 for the two Camp Century tin-rich polar ice samples.

The present paper reports evidence indicating that these heavy-metal-rich particles may instead have an extraterrestrial origin. As part of an exploratory study to determine the influx of cosmic dust during the last ice age, the author performed nondestructive neutron activation analysis (NAA) on eight Camp Century ice core dust samples, three of which he had processed from ice core repository samples and five of which were dust samples donated by Thompson from his archived sample collection. Of the five from Thompson's study, one was the above mentioned tin-bearing sample from the 1230.5 meter depth which was purposely selected to investigate its cosmic dust content using NAA.

The present study reports NAA results on the abundances of 15 elements in these 8 samples. These include the cosmic dust indicators Ir, Ni, and Au, as well as Fe, Co, Ag, Sn, Sb, Ba, Sc, Cs, La, Ce, Tb, and Hf. These measurements had been previously documented (LaViolette, 1983a) and summarized (LaViolette, 1983b); also see LaViolette (1985).^{*} In addition, new results of EDS analysis and SEM imaging are reported here for both tin-rich Camp Century ice core samples donated by Thompson (G962-1 and G1038-1). In addition, this paper reports evidence that the tin present in sample G962-1 has anomalous abundances for three of its isotopes, another indication that these tin-rich particles have an extraterrestrial origin. The author also had performed NAA analysis on four of Thompson's dust samples from the Byrd Station ice core (LaViolette, 1983a), but those results will be discussed in a separate paper.

2. ANALYTICAL PROCEDURE AND RESULTS

2.1. Neutron Activation Analysis.

Eight Camp Century ice core dust samples spanning depths 1212 to 1275 meters (40.2 - 74.7 kyrs BP), were analyzed. Five of these had been donated by L. Thompson who had filtered them in a class 100 clean room at Ohio State University as part of his earlier microparticle

^{*} Ages previously reported for these eight samples (LaViolette, 1983a, 1983b, 1985) were overly young and have been here substantially revised by correlating the Camp Century oxygen isotope profile with the more recent and better dated GISP2 Greenland ice core isotope profile with additional corrections applied to bring the dating into correspondence with the Cariaco Basin-Hulu speleo-therm chronology (Weninger, 2007). Also the sample depths in the present paper are more correctly given as actual core depths whereas drilling log book depths had been previously published for these samples which were greater by 3 to 4 meters.

concentration study (Thompson, 1977a, 1977b). The other three dust samples, G959, G960, and G962-2, which came from depths 1226.2 m, 1227.7 m, and 1231.5 m, were filtered by the author in a dust-free microbiological laboratory at Portland State University. Thompson's samples were filtered from quarter-core ice samples cut from the 10.8 cm diameter Camp Century ice core. The author's samples were half core samples from the same ice core; see Table 1a for a listing of ice core depths, corresponding ages, and sample lengths.

Thompson cut his core samples into approximately 2 cm lengths and subsequently processed his samples to remove external contamination that may have resided on their exterior due to the core drilling or sample cutting processes. By rinsing each sample with high quality deionized and filtered reagent grade water, he removed about 2 mm of ice from the outer surface of each sample, or about 25% of his sample volume; see Thompson (1977a). Ng and Patterson (1981) have shown that the ice core cleaning technique used by Thompson is able to substantially reduce contamination on the sample's surface. Based on their findings, it may be roughly estimated that Thompson would have reduced surface contamination by one hundred fold using the ice cleaning technique he employed. In current practice it is advisable to remove at least 40% of the outer surface of each ice sample. After cleaning each of his ice samples, Thompson melted the sample, measured its particle concentration by passing it through a Coulter counter, and the effluent was filtered onto a 25 mm diameter Millipore filter having a 0.45μ pore size to collect the sample's insoluble dust fraction. Usually, multiple meltwater samples were filtered onto a given filter, for example, one tin-rich dust sample was comprised of dust filtered from 3 successive meltwater samples. To check the purity of the particle counting system, filtered purified water blanks were run through the Coulter counter.

In the case of the three samples processed by the author, the author removed any surface contamination by performing three successive washings with acetone followed by a rinse of distilled water that had been prefiltered through 0.45μ pore size Millipore filter paper. Approximately 3 mm of the core exterior of samples 3 and 6 were removed in this manner, or about 20% to 23% of the sample volume. In the case of sample number 4, about 12 mm of the core exterior was removed, or about 50% of the sample volume. This cleaning procedure is estimated to have reduced potential surface contaminants by 10^2 - 10^4 fold, hence a negligible amount of contamination should have entered the ice samples. As in Thompson's study, after cleaning each ice core sample, the author melted the sample and filtered the insoluble dust fraction onto a 25 mm diameter Millipore filter having a 0.45μ pore size.

All eight filters, the five donated by Thompson and the three filtered by the author, were prepared in the same fashion for irradiation. Each filter membrane was rolled up and inserted into a clean high-purity quartz irradiation vial. The vial was then slowly heated to 170°C in a vacuum oven to carbonize the filter, and was then sealed shut under a vacuum. Blank filter papers were put through the same procedure. The samples, filter blanks, and standards were irradiated at the Missouri University Research Reactor in two separate irradiations. The first batch (sample Nos. 1, 5, and 8 of Table 1a) were irradiated in July 1981 for 1000 hours at a neutron flux of $6.8 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The second batch, which included samples (Nos. 2, 3, 4, 6, 7, and a split of sample No. 5 (No. 5')), was irradiated in December 1981 for 100 hours at a neutron flux of $2.7 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$.

The first batch included two USGS PCC-1 standards as well as several standards made consisting of powdered gold and iridium diluted in a silica base. The second batch included two W-1 standards, five P6304-7 sediment standards, nine 6609-7 sediment standards, two Sn standards made from slivers of pure tin foil (20 μg and 24 μg), one Au standard made from a 21

µg sliver of pure gold, an Sb standard made from a 55 µg grain of antimony metal, and four blank Millipore filter papers. Chromium was not determined in the irradiations due to background interference and sodium was not analyzed in Thompson's sample since Thompson had previously spiked his meltwater samples with spec pure NaCl to make the conductive for his Coulter counter study.

After each irradiation, the contents of the vials were transferred to clean plastic polyvials for gamma ray counting. About 6 - 7 days after the irradiation, the samples were each counted for one hour on a Ge-Li gamma ray spectrometer to determine their Au content. About three weeks later, they were recounted to determine their content of the 14 other measured elements: Co, Ni, Ag, Sn, Sb, Ba, Ir, Sc, Fe, Cs, La, Ce, Tb, Hf. Sample counting times during this late count ranged from 6 hours to one day. Elemental weights found in each of the samples were divided by the respective sample meltwater volume to yield weight concentrations relative to the ice meltwater volume. The element concentrations for the 8 samples are listed in Table 1b and plotted in figures 1-a and 1-b.

The numerical values given in Table 1b are considered to be accurate to $\pm 20\%$, except for bracketed numbers which have a greater margin of error, e.g., $\pm 25\%$ to $\pm 45\%$. The bracketed values are less accurate because for those particular element determinations the filter substrate makes a sizable contribution, and hence the uncertainty of the filter substrate composition, which is based on analyses of blank control filters, begins to dominate the other measurement uncertainties. Finally, for some elements only upper limit concentrations are given. The limitations in those cases are due either to excessive contributions from the filter substrate, which make it difficult to accurately judge the sample contribution, or to the fact that the element was present in such small quantities that its gamma ray peaks were undetectable above the background count level. The latter was the case for some of the Ir measurements.

The dust weights of the samples that were analyzed are presented in Table 1-a, column 7. Net weights for dust samples Nos. 3, 4 and 6 were determined to an accuracy of 2 - 3 percent by microbalance weighing the filters before and after filtration. Net weights for the other five dust samples, which were filtered by Thompson could not be gravimetrically determined since he had not obtained tare weights for his filters prior to filtration. Weights for four of these five samples (1, 2, 7, and 8) are estimated here by assuming that their dust contained Fe at a concentration of $5 \pm 1\%$, comparable to Fe concentrations found in the gravimetrically assayed dust samples, a value very close to the crustal abundance value for Fe. These sample weights were estimated by dividing their NAA-determined Fe weights by 0.05. The tin-rich sample (No. 5) could not be determined in this way since it was anomalously low in Fe and anomalously high in Sn and other heavy metals. In this case, the dust weight of this tin-rich sample was estimated by dividing the sample's NAA-determined Sn weight (48 µg) by 0.49 ± 0.05 , the Sn weight abundance determined by EDS analysis (see next section), yielding a total sample dust weight of 98 ± 15 µg.

Dust weight meltwater concentrations for the eight samples were calculated by dividing the sample dust weights by the sample meltwater volume. These dust concentrations are listed in the last column of Table 1a and plotted in Figure 2 for comparison with the Camp Century oxygen isotope profile. The two sigma error limits listed for these values reflect the precision with which the corresponding sample dust weights could be determined. The position of this anomalous sample is indicated by the middle arrow in figure 2.

Elemental abundances relative to the dust fraction found in each sample are listed in Table 2. They were calculated by dividing the element weights by the total weight of the dust sample given in Table 1-a. Abundances for most of the samples have an accuracy of $\pm 20\%$ while the

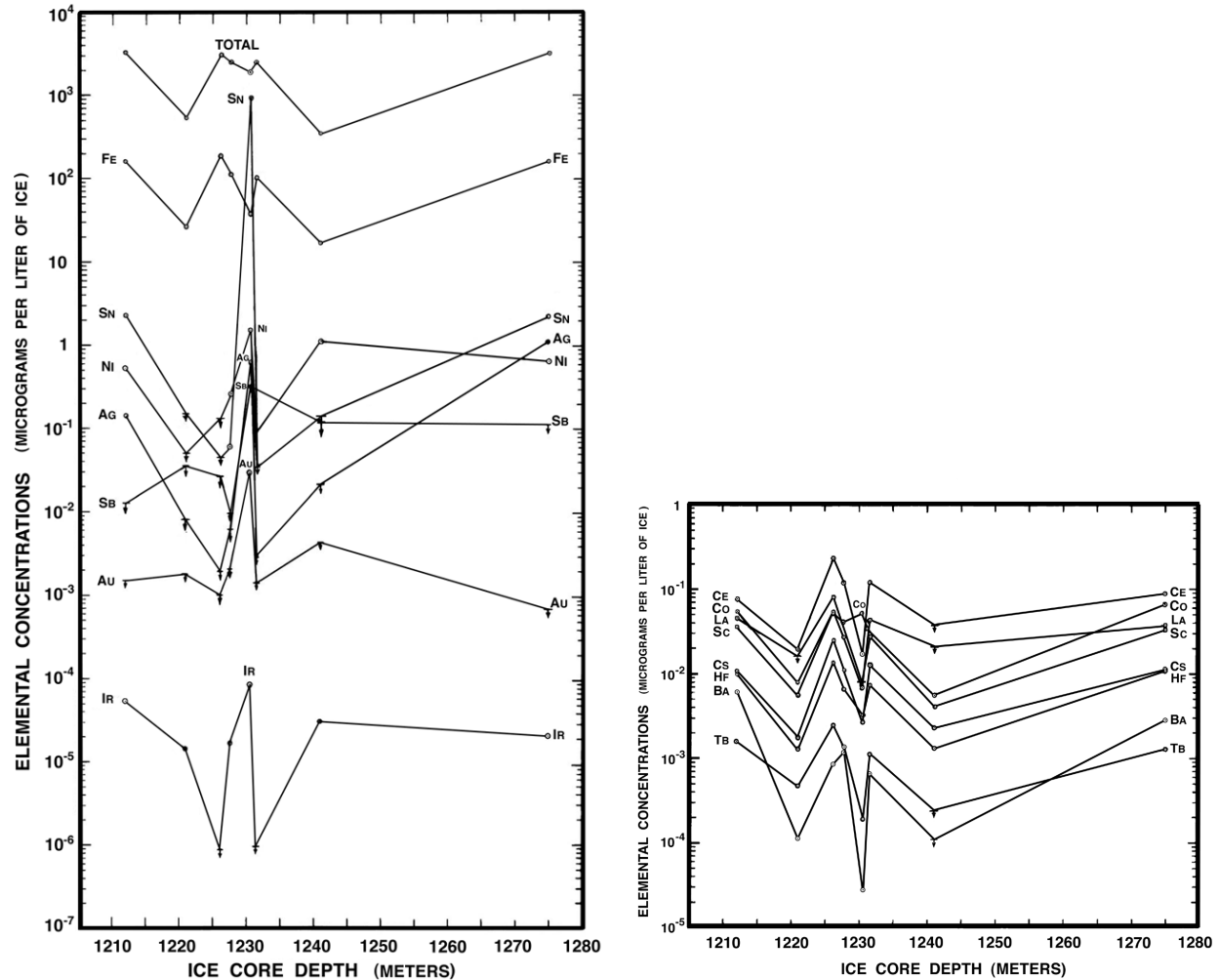


Figure 1. Elemental concentrations found in the Wisconsin section of the Camp Century ice core spanning the period 40,200 - 78,200 years BP. Elements include: a) Fe, Ba, Sn, Ni, Ag, Sb, Au and Ir; b) Ce, Co, La, Sc, Cs, Hf and Tb.

bracketed values have accuracies of $\pm 25\%$ to $\pm 45\%$. Enhancement factors for the 15 elements in these samples are plotted in figure 3. These were determined by dividing the sample abundances listed in Table 2 by the average earth crustal abundances (row EC of Table 2).

Elemental enhancement factors calculated in this way for the compositionally anomalous sample No. 5 are listed in row EF-1 of Table 2. Another way to estimate the elemental enhancement factors relative to crustal abundances for this anomalous sample is to divide the elemental abundance for sample No. 5 (Table 2) by the sample aluminum abundance, which for that sample which was measured by EDS analysis to be $1.34 \pm 0.29\%$, and to compare this to the ratio of the crustal abundance of the corresponding element to that of aluminum, 8.3%, for example,

$$\frac{(\text{measured abundance of element X} \div \text{measured abundance of Al})}{(\text{crustal abundance of element X} \div \text{crustal abundance of Al})}$$

The enhancement factors calculated in this way for sample No. 5, listed in row EF-2 of Table 2, are about 6.2 fold higher than those in row EF-1 and should more accurately reflect the elemental enhancements for this anomalous sample.

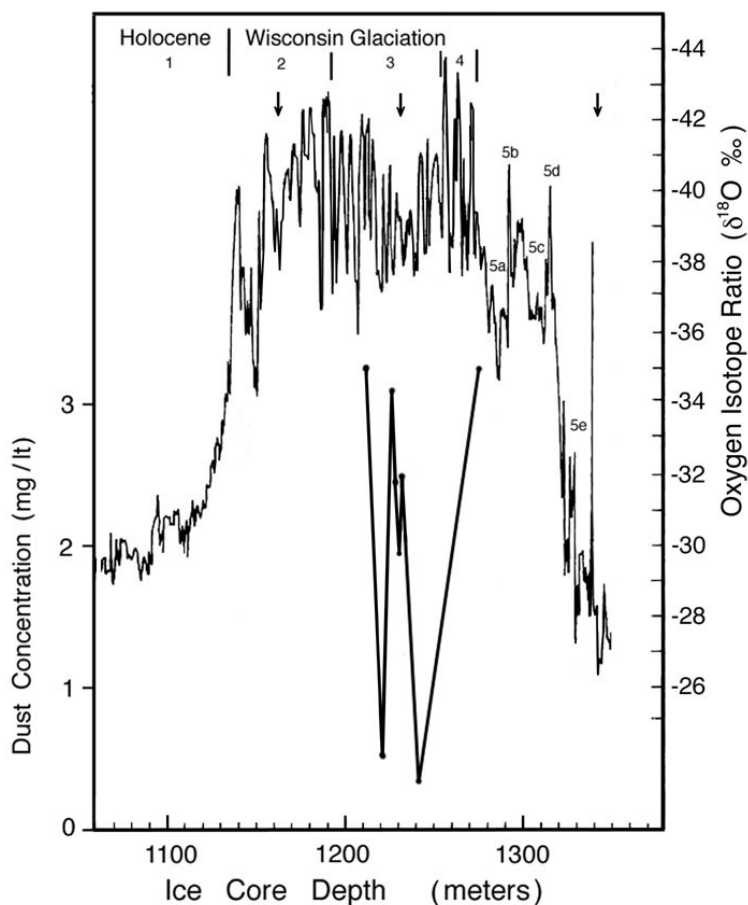


Figure 2. Upper curve: Camp Century, Greenland oxygen isotope profile (after Dansgaard et al., 1982); more negative $\delta^{18}\text{O}$ values indicate cooler climate and greater ice sheet extent. Lower curve: Total dust weight concentrations derived for the 8 samples that were analyzed in this study (LaViolette, 1983a).

2.2. Energy Dispersive X-ray Analysis.

Four filter paper fragments were selected for EDS analysis and for SEM imaging which was performed at Rensselaer Polytechnic Institute. These included three sample fragments from tin-rich sample G962-1, which were sample splits not analyzed in the NAA study, and a filter paper fragment from tin-rich sample G1038-1 (1-6). After carbon was vapor deposited on the dust samples, their composition was analyzed using a Bruker XFlash 5010 SEM/EDS detector with a 15kV beam accelerating voltage and a 20nA probe current. Spectral acquisition times were usually 300 seconds (live time) to ensure sufficient sensitivity for detection. Using the Bruker Quantax 200 software, standardless ZAF corrections were applied. Residuals were carefully inspected to ensure that all elements had been accounted for. The resulting compositional data for these dust samples, which are assumed accurate to at most two significant figures, are given in Table 3.

The EDS detector utilized a beryllium window which absorbed the k-alpha lines of low Z elements such as carbon, nitrogen, and oxygen. This benefited the sample measurement process by reducing the excess signal background coming from the underlying MCE nitrocellulose Millipore® filter membrane substrate. As a result, the oxide compositions needed to be

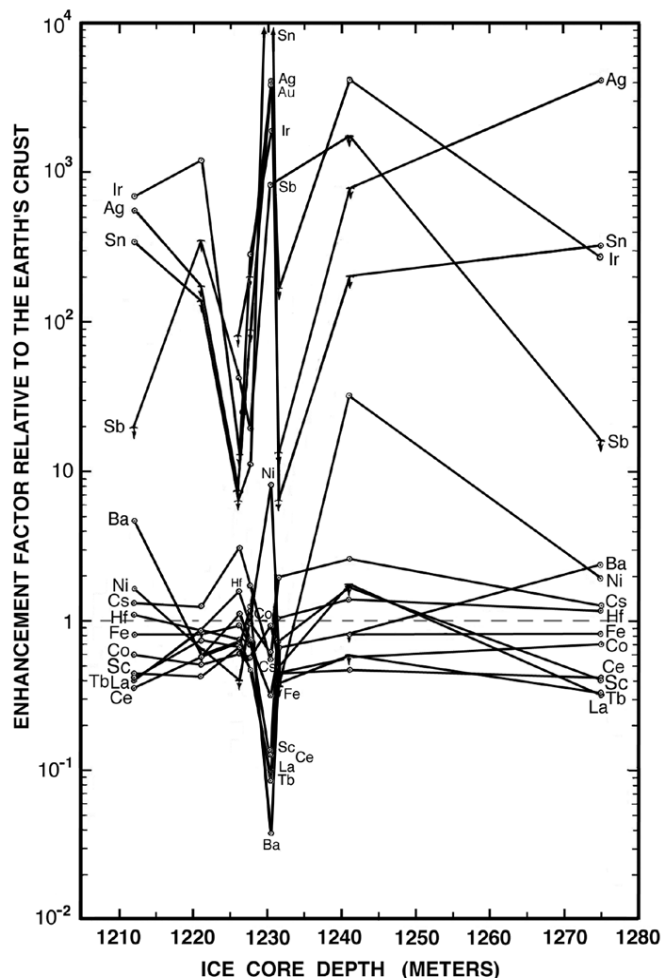


Figure 3. Enhancement factors relative to the Earth's crust for 14 elements found in the 8 Wisconsin stage dust samples filtered from the Camp Century ice core.

artificially reconstructed using the Quantax software with the assumption being made that most of the elements were in an oxide form. This may not necessarily accurately reflect the actual situation as for example some sulfur may be compounded as sulfides rather than as sulfates and some of the sodium may be configured as carbonates rather than as an oxide.

In the case of tin, comparison to a metallic-tin reference by EDS confirmed that Sn is not present in a metallic state. As a further check, X-Ray diffraction (XRD) was carried out on two G962-1 dust sample fragments by means of a Panalytical X'Pert Pro using Cu K-alpha radiation from 15 to 90 degrees two theta. XRD signals were weak due to the small particle size of the material, and the powder patterns for definitive phase ID were incomplete because large particles are rare in the sample. However the resulting incomplete patterns did match some peaks for SiO_2 , and SnO_2 , while no matches were found for metallic tin. So, it was concluded that tin was most likely present as stannic oxide. Nevertheless, when these tin-rich particles were formerly in the reducing environment of space, they were likely present in a metallic state.

Since Thompson (1977a) had spiked his meltwater samples with filtered NaCl solution to make them conductive for microparticle counting, there was residual NaCl left on his dust samples, and this "contaminant" needed to be adjusted out of the EDS analysis. To correct the

data, the chlorine signal was entirely attributed to come from NaCl and its abundance was used to stoichiometrically calculate the corresponding amount of Na (present as NaCl) to subtract from the measured sodium abundance value. Except, in the case of one tin-rich particle, S2-1, a chlorine abundance excess of 1.8% remained even after all the Na had been stoichiometrically nulled out. So in this case, Cl was entirely omitted from the abundance calculation on the assumption that the excess was NaCl associated, its corresponding sodium signal in this case being shielded by the high atomic mass tin particle being examined. Also there were three instances, one field analyzed in sample fragment S3 and two areas analyzed in sample fragment S4 in which the Na and Cl signals were disproportionately high and in which an unreasonably large sodium excess remained after the above described stoichiometric adjustment process. The EDS results for these three samples were omitted from consideration and are not reported.

The present EDS results are of a qualitative nature since they were not made with standards. It was determined that a standardless analysis of the samples was most appropriate since the dust as retained on its filter paper substrate presents a non-ideal geometry for analysis due to the wide range of particle sizes. A more accurate analysis with standards would be useful if particles >0.5 microns in size are selectively picked off the filter samples and ideally dispersed on a graphite substrate. This should be possible to do in a future study.

Particles were randomly selected for this EDS analysis with a preference that they be at least 10 μ m in size to ensure that the electron beam would be targeting the selected particle and not the background. In overview, Sn was found to be a major constituent in both polar ice dust samples. In sample fragments S2 and S3 of G962-1, tin oxide was the most abundant element in 6 out of 7 particles surveyed, ranging in abundance from 60% to 98%. The frequency of finding tin-rich particles compared favorably with Thompson's (1977a) results. However, the average Sn concentrations found here are approximately three fold higher than he reports. Three particles were viewed in fragment S4 of G1038-1, and of those two were found to have a tin oxide abundance of 54%.

Lead was found to be a prominent constituent in particles having high Sn concentrations, although its abundance varied from particle to particle. If present as an oxide, the lead abundance ranged from 0.2% to 12% in particles studied in filter fragments S2 and S3 (G962-1) and was 7% in the two tin-rich particles studied on filter fragment S4 (G1038-1).

The 2.34 keV M line for Pb lies very close to the 2.31 keV K line for sulfur. Hence to make a proper identification, higher energy peaks for Pb were checked for. In some samples, where S was also present, the two peaks were deconvolved using software. None of the particle spectra were found to fit the 2.29 keV $L\alpha$ line for molybdenum. Hence it is likely that Thompson's (1977a) EDS detection of high concentrations of Mo, 2% to 22%, in 4 out of the 6 particles in sample G962-1 were a misidentification of the Pb peak. Molybdenum also was looked for in the neutron activation analysis of dust sample No. 5 and was not found to be present above the 11 ppm threshold of detection.

One of the reasons for doing a qualitative EDS elemental composition analysis on filter membrane fragments of dust sample G962-1 (sample splits) was to approximately assess the sample's tin abundance in order to infer the tin abundance for the main portion of this dust sample previously analyzed in the NAA study (sample No. 5). This was felt to be a reasonable method given that the tin-bearing particles, being the major component of the dust and ranging widely in particle size, should be relatively homogeneously distributed on the filter membrane. Hence the Sn abundance on the smaller fragments was felt to be a reasonable indicator of the Sn abundance on sample No. 5.

To get a reasonable average composition of the sample on the various filter membrane fragments of this 962-1 dust sample, the EDS electron beam was defocused to cover an area of 50 μm diameter and was moved around over the surface of each sample fragment to sum the compositional results from various locations over the 300 second collection time. This "moving beam" measurement was done separately for fragments S1, S2, and S3 of dust sample G962-1. The resulting data are displayed in Table 3. Averaging together the abundances from these three measurements yields an average tin oxide abundance for G962-1 of $62.1 \pm 2.3\%$. In addition, three 50 μm diameter stationary beam field areas were measured on sample S3, designated in Table 3 as measurements S3-3, S3-4. These yielded an average SnO_2 abundance of $56 \pm 13\%$, which compares favorably with the above moving beam measurement average.

The average tin oxide abundance of $62.1 \pm 2.3\%$ for dust sample G962-1 indicates an average elemental Sn abundance in this sample of $48.9 \pm 1.8\%$. Adopting this value of $49 \pm 2\%$ to represent the approximate tin abundance in the much larger area dust sample (No. 5), and knowing that this sample was determined by NAA to contain $48 \pm 5 \mu\text{g}$ of tin, we estimate the total dust weight for sample No. 5 to be $98 \pm 10 \mu\text{g}$. This estimated total dust weight is then used in computing the abundances for sample No. 5 given in Table 2.

The average lead oxide abundance found by averaging the three moving beam measurements for G962-1 comes to $9.0 \pm 1.5\%$, which indicates an average elemental Pb abundance in this sample of $8.4 \pm 1.4\%$. The average ratio of elemental lead to tin in sample G962-1 is then calculated to be 0.17 ± 0.03 ($8.4\% \div 49\%$). This ratio is 8 fold lower than the Pb:Sn weight abundance ratio for C1 chondrites which is found to be 1.4 (Anders and Grevesse, 1989). But it falls very close to the average interstellar Pb-to-Sn weight abundance ratio of 0.22 ± 0.14 seen along the line of sight to the nearby stars 1 Sco and ζ Oph which lie in the direction of the Galactic center. According to Welty, et al. (1995), the gaseous Pb abundance measured towards those stars has a substantial average logarithmic depletion of -0.97 ($+0.22$, -0.48) relative to the meteoritic atom abundance of Pb, while gaseous Sn measured towards those stars shows only a minimal logarithmic depletion of -0.15 relative to its meteoritic atom abundance. The atomic lead-to-tin abundance ratio in interstellar space towards these two stars is found to be 12%, and in terms of weight abundance the ratio becomes 22%. So, based on the lead-tin abundance ratio reported here for sample G962-1, it is reasonable to conclude that an interstellar origin for its tin-rich dust is more likely than a solar system origin.

Iron had a relatively low abundance in sample G962-1, averaging $1 \pm 0.3\%$ in the three moving beam measurements if present as FeO, or $0.8 \pm 0.2\%$ in terms of its elemental Fe abundance. This is over two fold lower than the 2% abundance indicated by the NAA results which assessed a much larger area of this dust sample, perhaps 50 fold greater. The deviation in values can perhaps be ascribed to the inhomogeneous distribution of iron in the sample. Iron is not consistently associated with Sn, the main component of the sample and likely comes from both a C1 chondrite component present in the sample as well as from the small amount of terrestrial windblown dust present in the sample. This elemental iron abundance of 2% falls far short of the C1 chondrite Fe abundance of 19%. But it is noted that interstellar gaseous iron-to-hydrogen ratio is observed to be depleted by almost two orders of magnitude relative to solar system abundances (Savage and Bohlin, 1979; Snow, et al. 2002). While much of the observed interstellar depletion is likely due to a substantial fraction of the interstellar iron being condensed as cosmic dust, these observations leave open the possibility that the iron abundance present in interstellar dust is much lower than that observed in meteorites.

In ice core sample G1038-1, both the incidence of tin-rich particles and their individual

abundances were found to be lower. Of two particles analyzed in filter fragment S4, tin oxide was found to be the main element in one particle. The incidence of tin-rich particles in this sample fragment was lower than what Thompson had reported. However, only a small number of particles were measured in this sample. With an expanded sample size, it is possible that the ratio reported by Thompson would be more closely approached. A better comparison of the composition of this ice core sample with that of G962-1 is afforded by the moving beam EDS measurement described below.

A 50 μm moving beam measurement was performed on sample S4 of G1038-1 in the same fashion as was performed on fragments S1, S2, and S3 of sample G962-1. This yielded an average SnO_2 abundance of 50%, which is roughly 80% of the value found in G962-1. Lead in G1038-1, if present as an oxide, was found to have an abundance of 8%, somewhat lower than the abundance found in G962-1. The lead-to-tin elemental weight ratio in sample G1038-1 then calculates to be 0.19 ($7.5\% \div 39\%$) which again falls very close to the interstellar Pb:Sn abundance ratio while widely deviating from the solar system abundance ratio. The moving beam average measurement for sample S4 yielded an iron oxide measurement of 3%, or an elemental iron abundance of 2.3%. This is three fold higher than that found in the moving beam average for the G962-1 sample fragments, but interestingly falls close to the 2% abundance value determined by NAA for sample G962-1.

In summary, the finding of significant enhancements of both tin and lead in both ice age Greenland ice core samples studied here and in elemental proportions similar to those seen in interstellar space is striking and lends support to the interstellar dust origin scenario originally suggested in 1983 (LaViolette, 1983a) and discussed further in section 3.4.

2.3 SEM Results

Micrographs were made of a number of dust particles observed in samples S2, S3, and S4; see figures 4 -9. These were imaged using a JEOL JSM - 6335FE scanning electron microscope operating at high vacuum mode with a 15 kV accelerating voltage. Figures 4 through 8 show micrographs from filter fragments S2 and S3 corresponding to the tin-rich sample G962-1, and figure 9 shows micrographs from filter fragment S4 corresponding to tin-rich sample G1038-1.

The SEM micrograph in figure 4a, which is imaged in secondary electron (SE) mode, shows a rather large particle measuring 120 X 65 μm . It is found to be composed almost entirely of tin oxide (98%); see EDS spectrum S2-1 in Table 3. Of all the particles examined, this one was the largest, and also the only one to have such a high tin content. It likely holds the world size record for being the largest unmelted monomineralic cosmic dust particle yet found. It is seen to have a flat, plate-like morphology. The pitting seen on its otherwise smooth upper surface was caused by the electron beam during EDS analysis which surprisingly caused reactive displacement of the tin oxide. Figure 4b shows a view of this same particle made at an angle of 33° from the normal. The particle's thickness appears here to range from a few microns to roughly 6 to 8 μm . If its average thickness is taken as 5 μm , its observed size suggests a particle volume of about $3 \times 10^{-8} \text{ cm}^3$ and mass of about 200 ng. While the upper surface of the particle appears quite smooth, its edge in places appears quite porous. This submicron granularity can be seen in figure 4c which shows an additional 40 fold magnification of the mid facing edge displayed in figure 4b. This particle likely formed in space as a result of gaseous tin condensation. There is no indication that the particle has undergone any melting due to passage through the Earth's atmosphere.

The SEM micrograph in figure 4d shows, in backscattered electron (BSE) mode, a 15 X 23 μm particle comprised almost entirely of tin oxide (91%) with a small percentage of lead oxide,

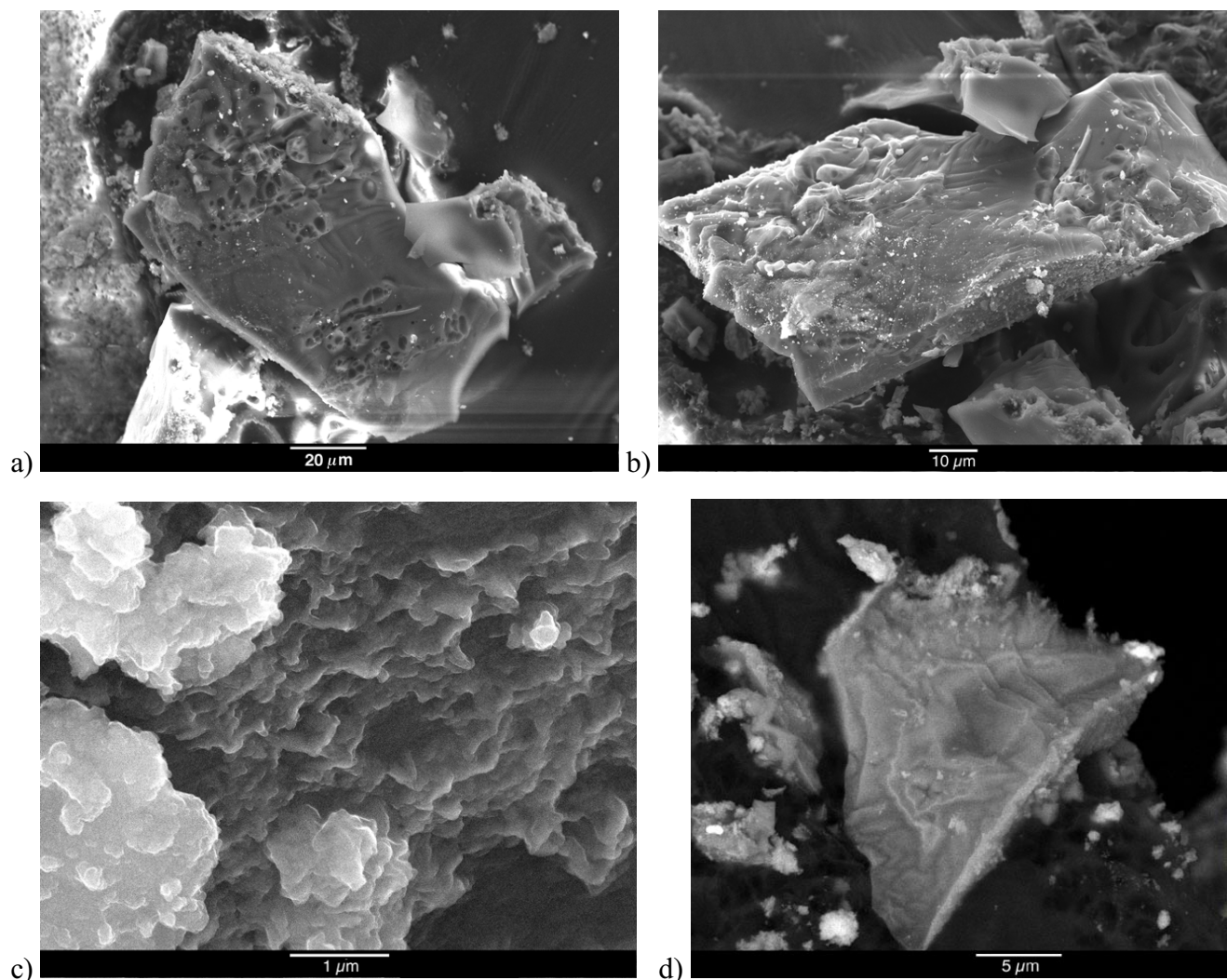


Figure 4. Scanning electron microscope micrographs of two tin-rich particles from Camp Century ice core sample G962-1 (sample fragment S2). (a) and (b) show two views in SE mode of a 120 μm long tin oxide particle and (c) an additional 40 fold magnification of the particle's front edge seen in (b). (d) An image of a triangular tin-rich particle measuring 23 μm in size (BSE mode).

sulfur possibly as sulfate or sulfide, and traces of copper, zinc and other elements; see EDS spectrum S2-2. As elsewhere, the lead is inferred to be present in an oxide state.

Figure 5a shows a tin-rich porous aggregate particle measuring 15 X 27 μm , left image in BSE mode and right image in SE mode. It consists predominantly of tin oxide (60%) and a considerable amount of lead oxide (12%), the remaining elements being aluminum and silicon with traces of iron, nickel, copper, and other elements; see EDS spectrum S2-3. The nickel-to-iron ratio is about twice as high as that found in C1 chondrites, but similar to that found in certain micrometeorites. The BSE mode shows higher Z elements as lighter areas making apparent the presence of a multitude of submicron cosmic spherules possibly of iron-nickel composition. A ten fold magnification in BSE mode of a region on the particle's surface located left of center is shown in figure 5b. This reveals a proliferation of cosmic nanospheres ranging in size from about 20 to 120 nanometers which could amount to literally hundreds of thousands when considering the entire particle volume. Some of the larger ones are seen toward the top of the image as white

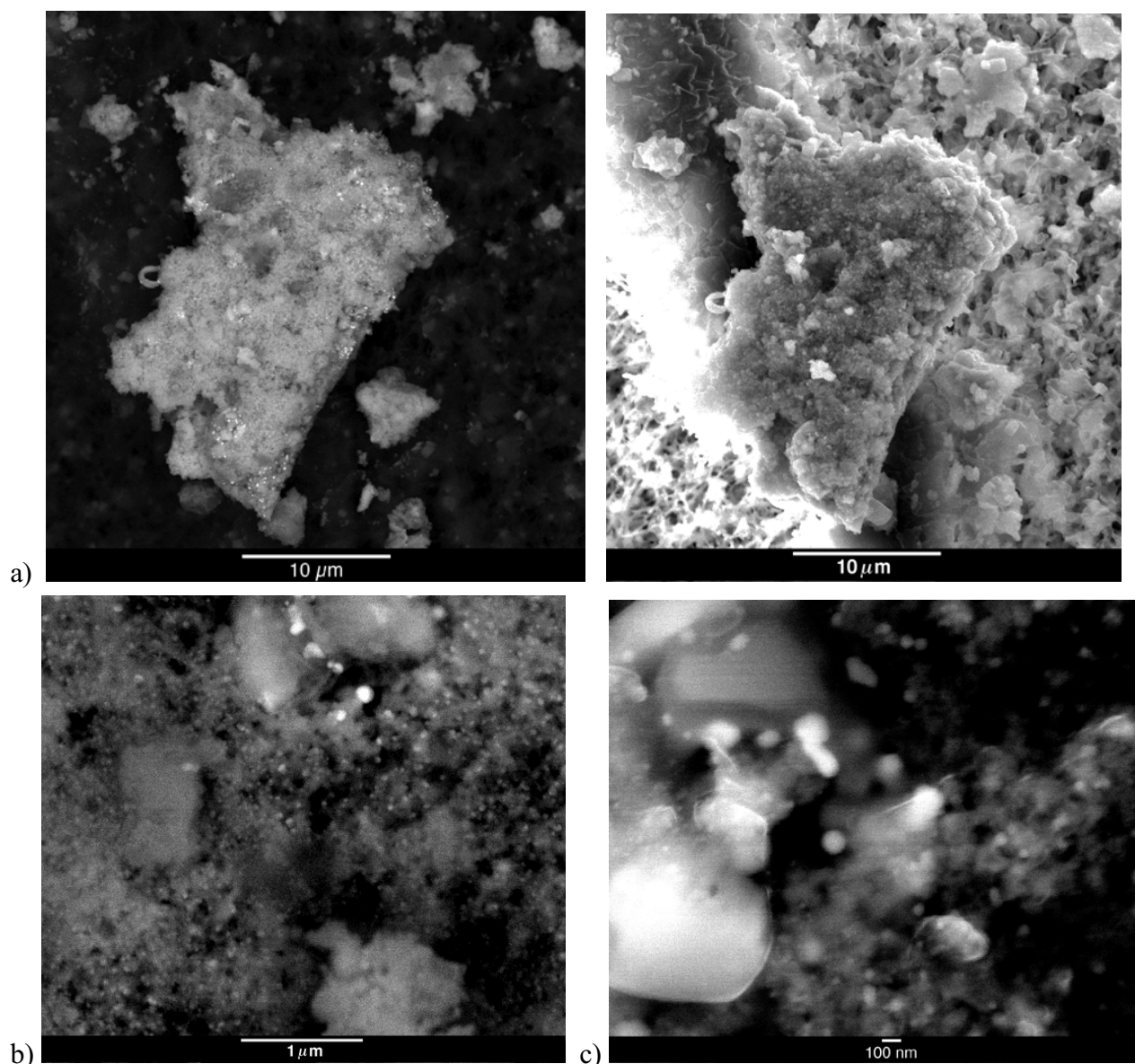


Figure 5. a) SEM micrographs of a tin-rich chondritic porous aggregate particle from sample G962-1 (fragment S2) seen in BSE mode (left) and SE mode (right). b) and c) show magnifications of two areas of this same particle which reveal the presence of a multiplicity of high-Z nanochondrules. Refer to EDS spectrum S2-3.

spherules. This nanochondrule photo presents the smoking gun evidence that the tin found in this sample is of cosmic origin. Further investigation should reveal if these inclusions are GEMs (Glass with Embedded Metal and Sulfides) similar to those found in chondritic interplanetary dust particles.

Figure 5c shows a 16 fold greater magnification in SE mode of a region near the bottom of the particle. These chondrules are likely responsible for the iron and nickel content of the particle seen in spectrum S2-3. The light fringe that shows up on the outer edges of a few bright particles in the lower left of figure 5c are indicative of hydrocarbon layer coatings. Such sticky hydrocarbon coatings are believed to surround such nanoparticles when they are dispersed in

space and assist their adhesion to form porous aggregate particles such as this.

Figure 6a shows a "chunky" aggregate particle in BSE mode (left) and SE mode (right) measuring 11 X 18 μm in size. Its main component is silicon which if in the form of quartz would comprise 41% of the particle weight. Alternatively it may be in the form of pyroxene due to the presence of Na, Mg, Al, and Ca; see EDS spectrum S2-4. The particle also has a small amount of Pb (2% if present as PbO) and relatively insignificant amount of SnO₂ (0.5%) which could be coming from smaller tin-rich particles lodged on its surface or incorporated into its particle aggregation. The SE mode view shows it to consist of an aggregation of flat platy particles ranging in size from less than a micron to 4 μm in breadth. Figure 6b shows in SE mode a 20 fold further magnification of the bright appendage that projects from the right end of the particle seen in 6a. It appears to be composed of a cluster of nanoparticles ranging from 100 to 200 nm in size. Figure 6c shows a four fold close up of the central portion of the particle in SE mode. Here it is seen that even the larger flakes in the aggregate appear to consist of a cemented aggregation of nanoparticles, some as small as 50 nm. Its morphology has the hallmarks of a chondritic porous aggregate particle. This interpretation is further supported by the EDS results which indicate that its relative abundance of iron and nickel (3.1%: 0.19%) matches the ratio found in C1 carbonaceous chondrites, implying that at least 17% of its composition may be of C1 chondrite origin. Since nickel is present at 24 times earth crust abundance, a terrestrial interpretation is rather unlikely. The presence of titanium at near terrestrial abundance (1%) might at first lead to the suspicion that the particle is of terrestrial origin. But titanium is occasionally found at significant levels also in cosmic dust.

Figure 7a shows a rather large triangular-shaped particle from sample S2 which measures 65 μm along its diagonal. Its coral-like morphology indicates that it is a porous aggregate extra-terrestrial dust particle. It consists predominantly of tin oxide (69%) and like the other aggregate shown in figure 5a contains a 12% abundance of lead oxide; see EDS spectrum S2-5. Hence it is likely of interstellar origin. It also is high in sodium, silicon, and aluminum, and its iron and nickel abundances suggest that approximately 4 to 6% of its dust may be of C1 chondrite derivation. Figure 7b shows a 20 fold magnification of the central lower portion of the particle.

Figure 8a shows in BSE mode (left) and SE mode (right) a particle measuring 18 X 33 μm in size, which appears to be buried under a mud pack layer of submicron particle filtrate. Like the other tin-bearing particles it is quite flat in morphology. It consists primarily of tin oxide (81%) and lead oxide (11%), this compositional measurement including also the overlying filtrate; see EDS spectrum S3-1. Figure 8b shows a particle measuring 7 X 34 μm whose main constituents again are tin oxide (86%) and lead oxide (5%) with traces of nickel and copper; see EDS spectrum S3-2. It has a generally flat, smooth morphology with parts being covered with submicron particle deposits. Figure 8c shows in SE mode a portion of the tin-rich particle field that composes the "mud cake" covering the filter membrane in sample G962-1 (fragment 2). This shows particles having a characteristic platy morphology that range in size from 50 nanometers to a few microns. It is interesting that of the seven particles examined in sample G962-1, all have a convincing extraterrestrial origin, including the one particle (S2-4) that did not show an elevated tin abundance.

Figures 9a shows micrographs in BSE mode (left) and SE mode (right) of two overlapping tin-rich particles found in the older ice core sample, G1038-1 (fragment S4). Both have a flat morphology and are crusted with an even finer particle texture which gives their surface a splotchy appearance. One particle is roughly oval in shape, measuring 24 X 32 μm , and the other rectangular, measuring 14 X 32 μm . They are overlain by a large number of chunky

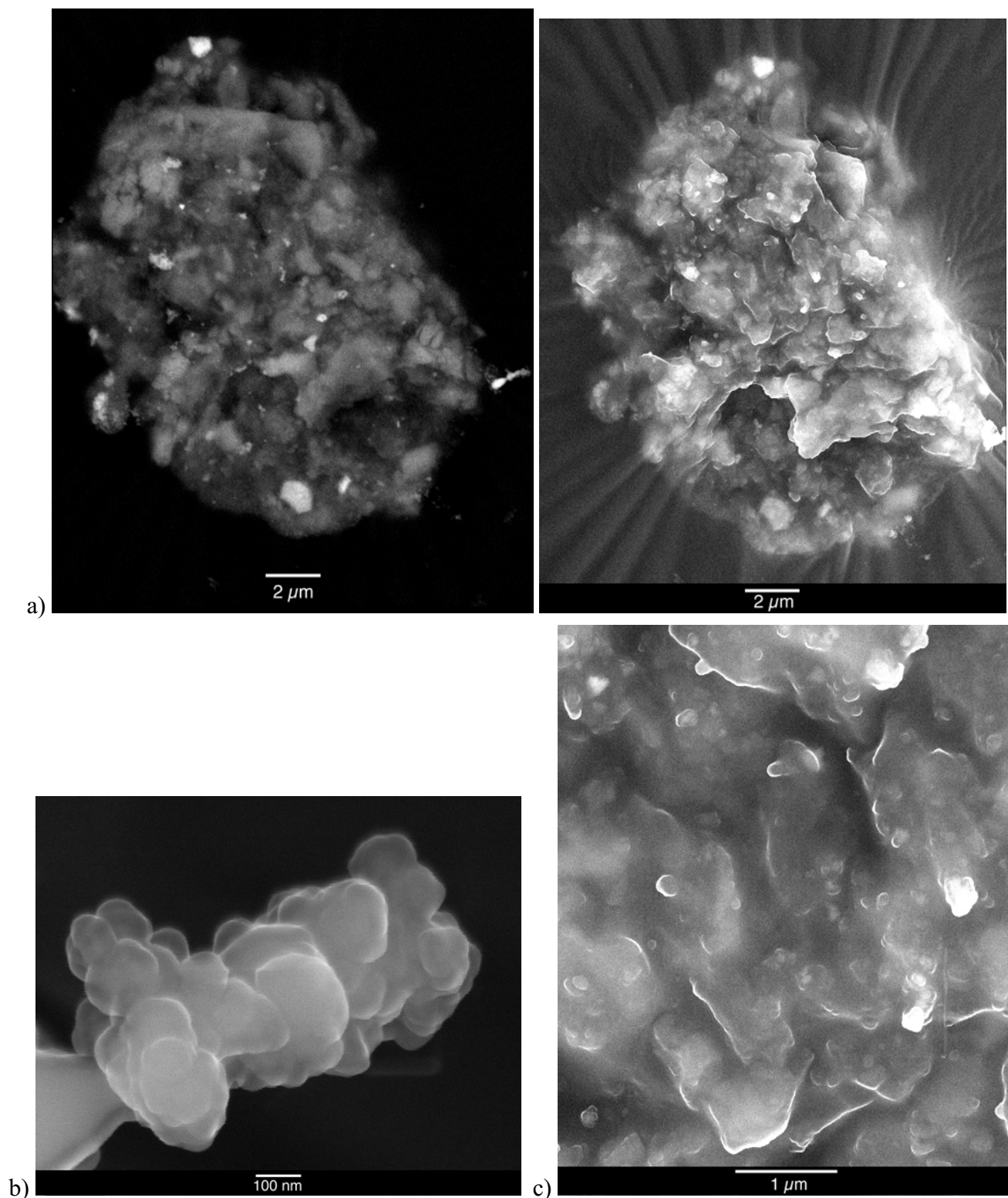


Figure 6. A chunky aggregate particle rich in silicon, iron, and nickel from sample S2 seen in BSE mode (a) and SE mode (b). b) A 20 fold greater magnification (SE mode) of the appendage seen protruding from the right side of the particle. c) A four fold magnification of upper central portion of the particle seen in SE mode. Refer to EDS spectrum S2-4.

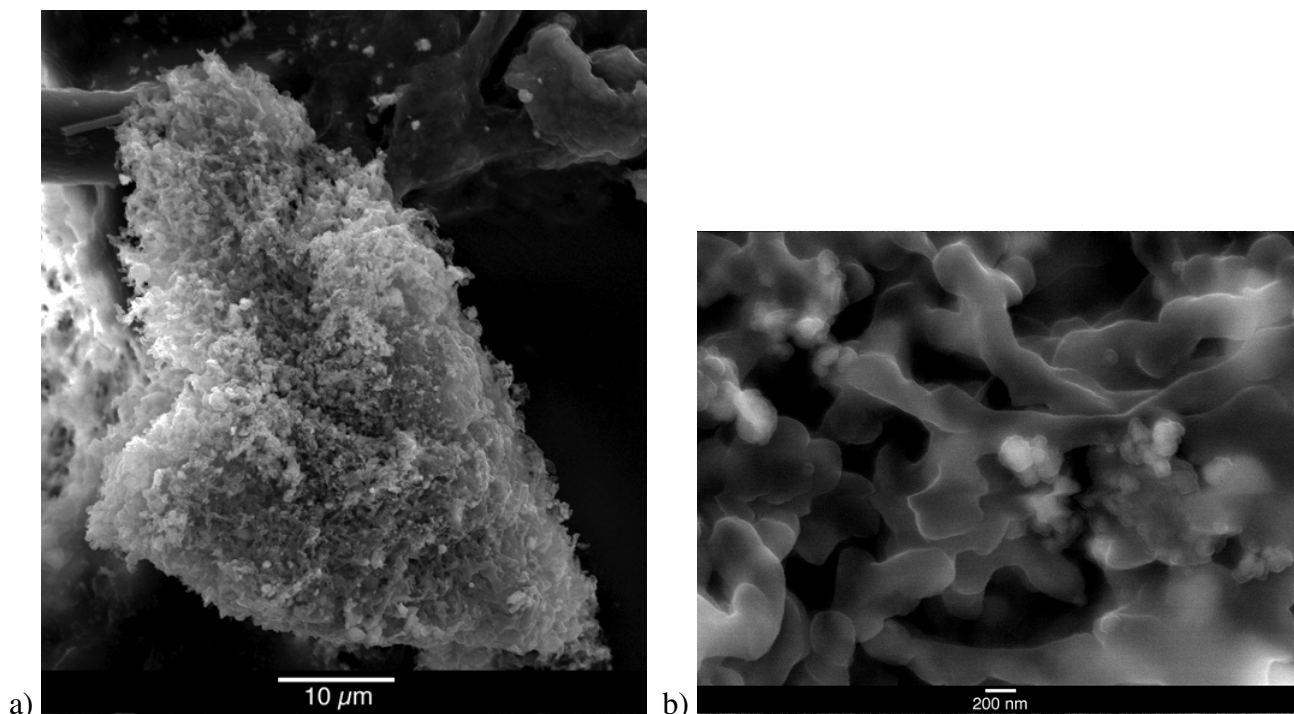


Figure 7. a) A porous aggregate dust particle from sample S2 of G962-1 measuring $65\ \mu\text{m}$ on diagonal. b) A 20 fold magnification of the lower portion of the particle shown in (a).

particles ranging from 1 to $7\ \mu\text{m}$ in size. Their composition shows them to consist of approximately 54% tin oxide and 7% lead oxide and to have a significant amount of sodium, aluminum and silicon and some magnesium which together may be present in the form of a pyroxene; see EDS spectrum S4-1. They also have traces of iron, nickel, and copper.

Figure 9b shows a micrograph in BSE mode of three quartz grains from the same dust sample. The particles are approximately 13 to 16 microns in size. The composition of the lower right grain is presented as EDS measurement S4-2 (Table 3). The small amount of tin present in the spectrum (1%) is likely scattered from background particles. Note that below and immediately adjacent to the lower right quartz grain lies a 1.9 micron diameter cosmic spherule. A magnification of this is shown in figure 9c in SE mode. In backscattered electron mode, the spherule is seen to have the same brightness as the large quartz grain above it, which suggests that it may be of silicate composition. The spherule may have been ablated from a meteor during its passage through the atmosphere. Since it was the only such cosmic microsphere found in the survey of sample G1038-1, one may conclude that most of the particles in this sample entered the atmosphere in dispersed form rather than as a result of a comet impact or meteorite shower. No cosmic microspheres were seen in sample G962-1, only the nanochondrules that were found incorporated within porous aggregate particle S2-3.

2.4. Tin Mass Spectrometry Measurements

To check the relative abundances of the Sn isotopes in the tin-rich dust sample No. 5 (G962-1), $304\ \mu\text{g}$ of filter paper from a split of Camp Century ice core dust sample G962-1 were dissolved in HCl and tin and silver were extracted by ion exchange chemistry to yield about $4.4 \pm 0.4\ \mu\text{g}$ of tin and $\sim 14\ \text{ng}$ of silver. The isotopic ratios of both were measured using a modified AE1 MS 12 thermal ionization mass spectrometer at the Curtin University mass spectrometry laboratory

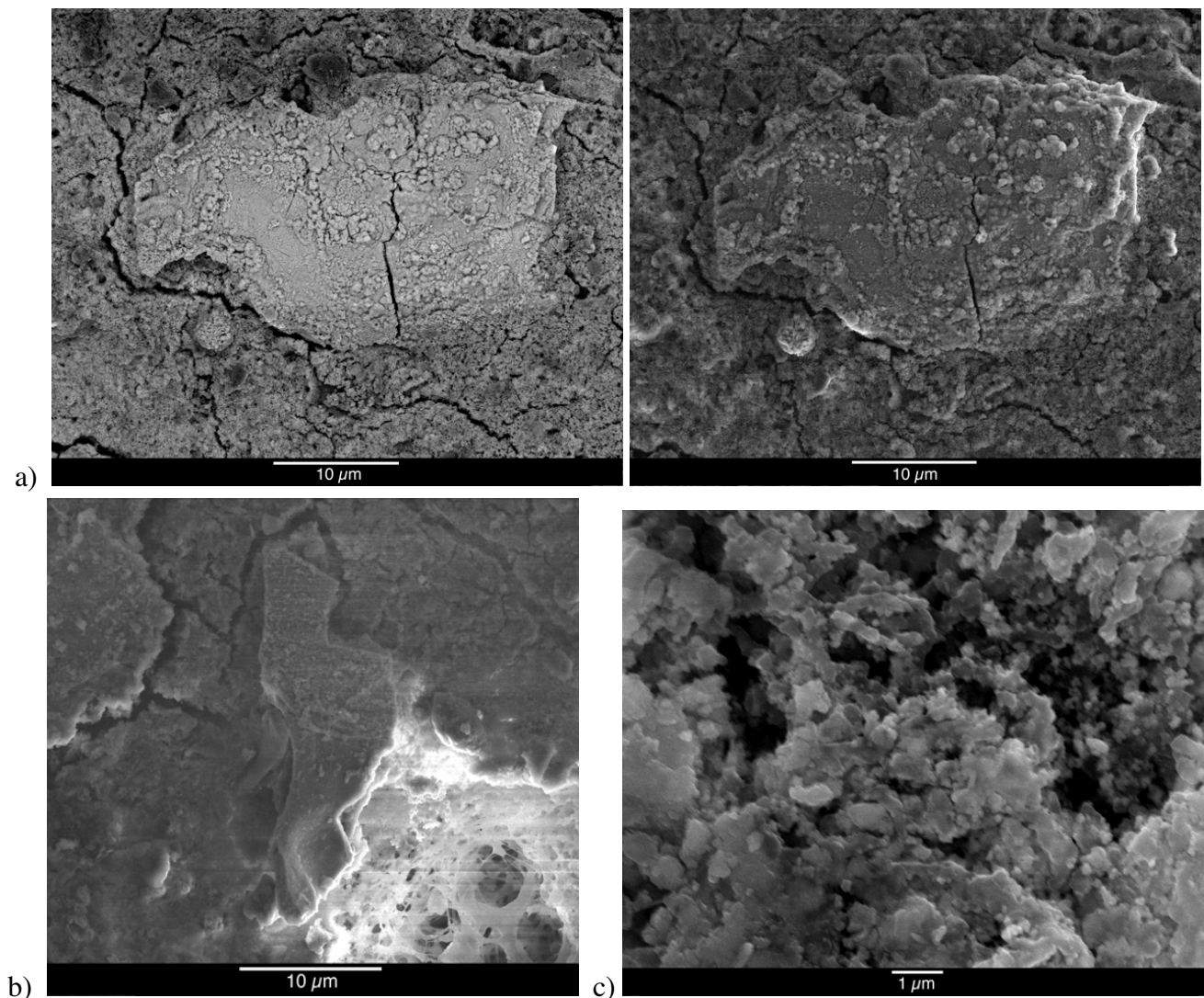


Figure 8. a) micrographs in SE mode and BSE mode of a tin-rich particle found in sample G962-1 (fragment S3). b) Another tin-rich particle from fragment S3 (SE mode). c) A close up of the filtrate in sample G962-1 showing submicron particles of varying sizes having a platy morphology.

(samples processed courtesy J. de Laeter). A silica gel/boric acid activator was used to enhance the tin ion beam and discriminate against interference by In, Cd, and Te, a method developed by Rosman, et al. (1984). A single spectrometer run was made on the sample which yielded an ion current of $\sim 10^{-14}$ amp. Also four 10 μg laboratory standards (Johnson Matthey "Specpure" tin metal, JM 540 laboratory S2807) were run. The tin isotopic ratios found for the tin-rich dust sample and for the mean of the four Sn standards are presented in Table 4. The data have been adjusted to a $^{116}\text{Sn}/^{120}\text{Sn}$ ratio of 0.4460 so as to remove variable isotopic fractionation. The stated errors give 95% confidence limits (2σ values). The sample was found to have excesses in two of the minor isotopes: $+17 \pm 12 \text{ ‰}$ (3σ) for ^{114}Sn and $+33 \pm 8 \text{ ‰}$ (8σ) for ^{115}Sn , as well as a possible depletion of $-5 \pm 3 \text{ ‰}$ (3σ) in the major isotope ^{117}Sn .

Interference from Cd (112, 114, and 116) should have been minimal since Cd was about 1200 times less abundant than Sn in sample No. 5. Interference from ^{115}In to the ^{115}Sn peak is also a matter of concern even though the flux technique developed by deLaeter, et al. preferentially

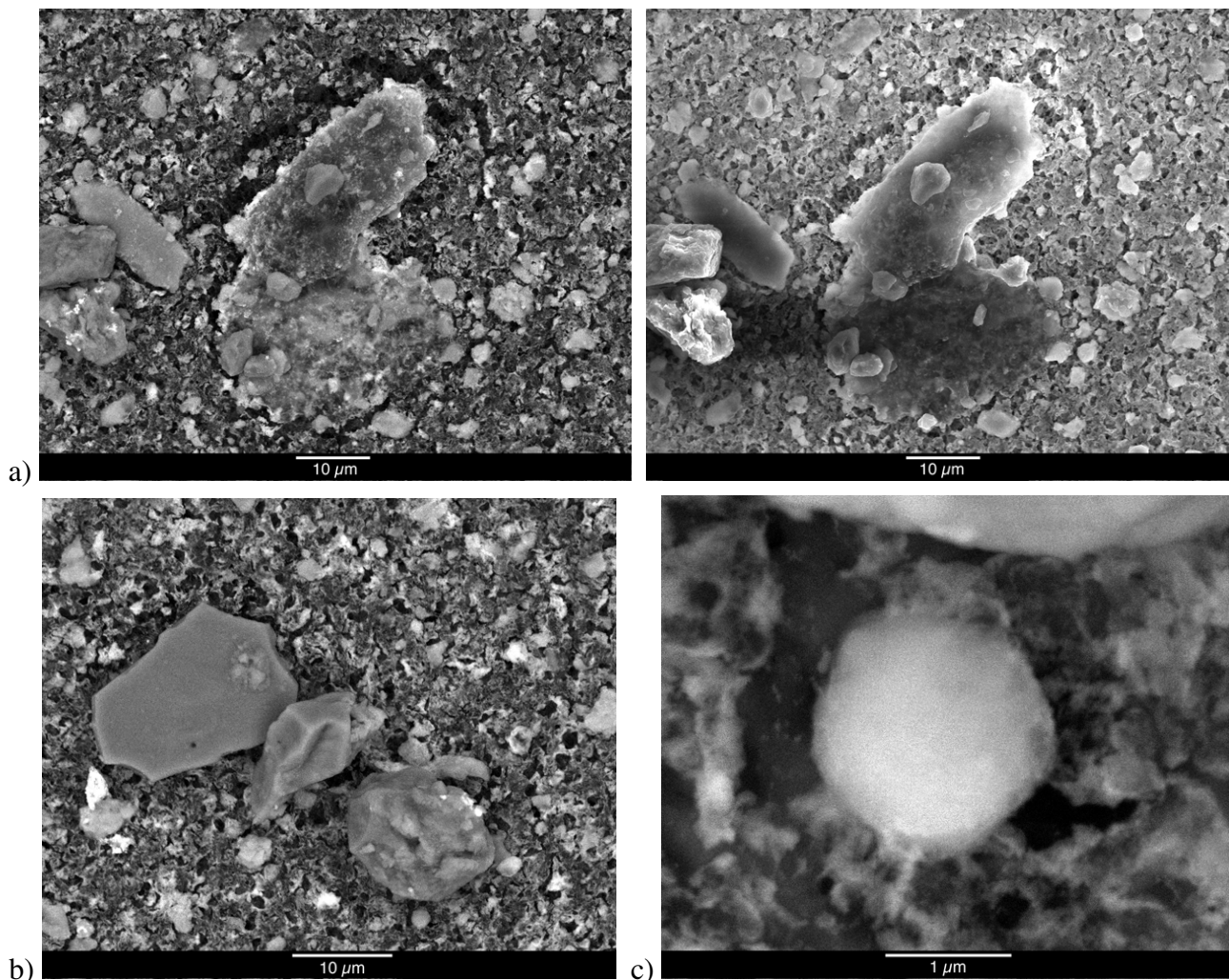


Figure 9. SEM micrographs of particles found in sample G1038-1 (fragment S4): a) Overlapping tin-rich particles shown in BSE mode (left) and SE mode (right), b) quartz grains shown in BSE mode, and c) a 12.5 fold magnification (BSE mode) of the cosmic spherule seen in (c) below the lower right quartz grain.

vaporizes tin rather than indium in the mass spectrometry analysis. But no indium was detected in G962-1 in the EDS analysis and also no ^{113}In peak was detected in the mass spectrometry analysis performed on this sample. However, since only one run was performed in this preliminary analysis, additional mass spectrometry measurements are needed to better quantify these discovered isotopic anomalies. No anomaly was found for the ^{109}Ag isotope.

3. DISCUSSION

3.1. Overview of the Neutron Activation Analysis Data

An examination of figure 2-a and 2-b shows that certain elements show a dramatic increase and others a decrease in the anomalous tin-rich sample (No. 5). Within the space of 1 meter of ice core depth, spanned by samples 6 and 5, Sn increased by >33,000 fold, Ag by >290 fold, Ir by >108 fold, Au by >27 fold and Ni by >21 fold. The full magnitude of the abrupt increase in the concentrations of metals Sn, Ni, Ag, Ir, and Au could not be determined because the levels of these

elements in sample No. 6 were either below the threshold of detection or below the filter background levels. Cobalt exhibits only a 30% increase over this interval. Also quite interesting is the observation that at the time of this heavy metal enhancement there was a significant decrease in the concentrations of Ba, Sc, Fe, Cs, La, Ce, and Tb.

Comparing figures 1 and 3, it is seen that elements whose ice meltwater concentrations increase to high values in sample No. 5 (1230.5 m depth) are those elements that have abundances significantly higher than crustal abundances, while those that decrease in concentration have abundances significantly lower than crustal abundances. Of the 15 elements measured in this sample, tin is found to be the most abundant, with SnO_2 making up $62\% \pm 2\%$ of the dust weight, with elemental Sn comprising $49 \pm 2\%$ of the dust fraction. Enhancement factors for these elements referenced to the aluminum abundance (Table 1-b, EF-2) are 1.45×10^6 for Sn, 2.4×10^4 for gold, 2.5×10^4 for silver, 1.16×10^4 for iridium, 5060 for antimony, and 50 for nickel.

Two NAA determinations were made of sample G962-1. The main portion of this sample, No. 5, was analyzed in a first nuclear irradiation and a sample split, fragment No. 5', which is estimated to comprise ~3% of the weight of No. 5, was analyzed in the second sample irradiation. Comparing the results for the two given in Table 1b, it is seen that the concentrations of Sn, Ir, Au, and Fe in sample No. 5' are within 5% of the values in No. 5 and the values of Ag and Sc in No. 5' are within 20% of those in No. 5. But, Co and Ni show significant depletions in No. 5' and Cs and the rare earths La, Ce, and Tb show dramatic enhancements. These larger discrepancies are likely due to the inhomogeneous distribution of some components on the filter medium and to the fact that sample No. 5' was 30 times smaller than No. 5 and not as representative of the whole sample. Figures 1 and 3 plot the concentration and abundance values for sample No. 5, the larger of the two.

The average value for iron observed on sample fragments S1, S2, and S3 in the EDS study was over two fold lower than the value reported in the neutron activation results. Since iron is not a main constituent of the tin-rich dust component dominating the sample, variations in the distribution of iron-rich particles on the filter membrane could lead to the observed discrepancy.

The concentrations of the extraterrestrial material indicators Ir, Ni and Au are found to increase in sample No. 5, which supports the proposal that the other enhanced elements, Sn, Sb, and Ag are also likely of extraterrestrial origin. A similar correlated increase of Ir and Ni with Ag and Sn is also seen in samples No. 1 and No. 8 at depths of 1212 m and 1275 m. It may be worth mentioning that sample No. 1, which dates to 40.2 kyrs BP, falls close to the time of the Laschamp geomagnetic reversal which is associated with a very large long-term rise in ^{10}Be deposition rate an indicator of increased galactic cosmic ray intensity.

As seen in figure 10, the five samples for which it was possible to get definite values for both iridium and nickel have Ir:Ni ratios that conform to that of C1 chondrites. Figure 11 shows how the enhanced elemental abundances found in sample No. 5 compare with those in C1 carbonaceous chondrites listed in row C1 of Table 2. The weight concentrations are shown here normalized relative to concentrations found in C1 chondrite material. The values for the siderophile elements, Ir, Fe, Co, and Ni, make a reasonably good fit to a C1 chondrite abundance pattern, suggesting that C1 chondritic dust comprises about 9 percent of the sample. The low melting point elements, on the other hand, are highly enhanced relative to abundances normally present in C1 chondrites, tin being greater by more than five orders of magnitude, and antimony, gold, and silver by two to three orders of magnitude. This same circumstance is seen in sample Nos. 1 and 8, where Sn and Ag are found to be more than 4 orders of magnitude overabundant relative to the C1 chondrite abundances for those samples as estimated on the basis of their Ir and Ni abundances.

Ice core contamination or bedrock scrapings are unlikely sources for the Sn and other trace elements found to be enhanced in sample No. 5 since such sources would have caused rare earth

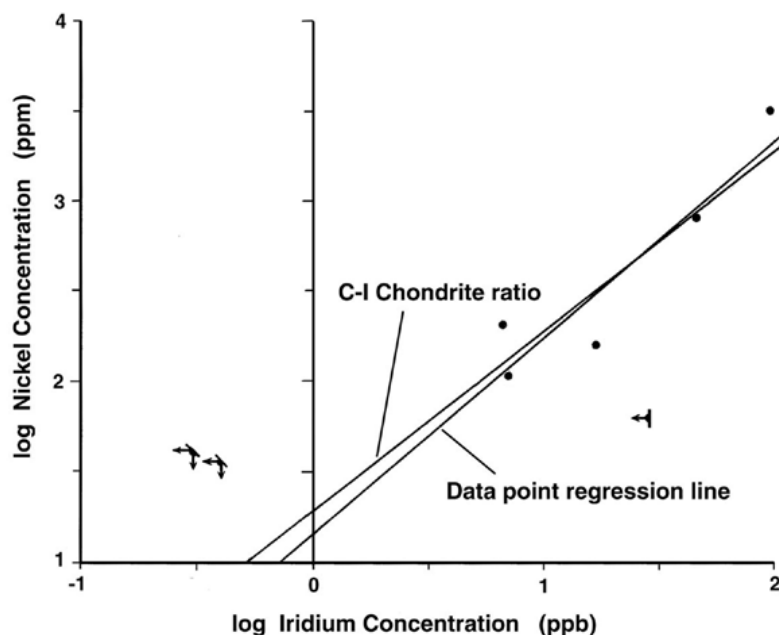


Figure 10. Log-log plot of Ir/Ni ratios found in dust from Camp Century, Greenland ice over the period 40.2 - 74.9 kyrs BP. The slope of the regression line of the five Camp Century data points matches that for a C-1 chondrite ratio.

meltwater concentrations to similarly increase in this sample, not to decrease as is observed. Compared to their average values in sample Nos. 4 and 6, rare earths in sample No. 5 exhibit about a 4 to 7 fold decrease in concentration per liter of ice meltwater; see Table 1b. For example, scandium is 4 fold lower, cerium is 7.1 fold lower, terbium is 6.6 fold lower, and lanthanum is more than 5 fold lower. Among the non rare earth elements, cesium experienced a 4.4 fold decrease, and barium which had the most prominent decline exhibited a 33 ± 10 fold decrease.*

This same decline is seen in the elemental abundances. As compared with adjacent ice core samples, the rare earths in sample No. 5 are from one third to one fifth as abundant relative to the total dust fraction; see table 2 and figure 3. Barium, which experienced the most extreme meltwater concentration decrease of any element in sample No. 5, dropped to an abundance of 3.8% (-0.8%, +1.7%) in this sample. The C1 chondrite-to-earth-crust-abundance ratio for Ba is also the lowest of any these elements, being only 0.006. For the rare earths this ratio is 0.007 for La, 0.008 for Ce, and 0.23 for Sc. Hence these elements, and particularly barium, should serve as good indicators for the presence of the windblown continental dust component in the ice core samples.

Taking barium as a proxy for continental dust influx, and assuming 390 ppm for the barium abundance of the terrestrial dust component and 2.34 ppm for the barium abundance for the extraterrestrial dust component, similar to that found in C1 chondrites, then the observed 14.8 ± 3 ppm Ba abundance in sample No. 5 is consistent with 96.8% of the sample dust coming from extraterrestrial sources and 3.2% coming from terrestrial sources. This corroborates the finding

* Note that in the author's dissertation (LaViolette, 1983a), there had been a three decimal place error in recording the per liter concentration for barium due to a confusion between μg and ng units in recording the data. The Ba abundance value given here is the correct value.

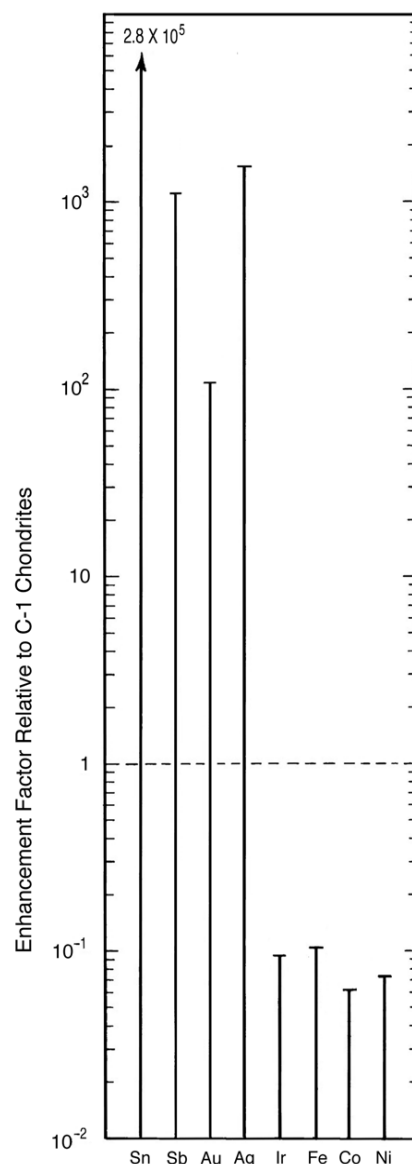


Figure 11. Elemental abundances relative to C1 chondrites for the tin-bearing dust sample.

that in dust sample No. 5 the barium meltwater concentration was about 3% of the concentration found in adjacent samples which showed predominantly terrestrial compositions.

The abundance of the lithophile element hafnium in sample No. 5 experienced only a slight decline to 63% of the values in adjacent ice core sections, which is surprising since hafnium is 25 times less abundant in carbonaceous chondrites as compared with the earth's crustal abundance. Also it is noted that the rare earths did not decline as much as barium. So, on the assumption that the heavy-metal-rich dust component in this sample is of extraterrestrial origin, perhaps its source is somewhat enriched in Hf and rare earths as compared with typical chondritic material.

This dramatic depletion in continental dust concentration at the time that the tin-bearing particles were deposited implies that either the ice accumulation rate had dramatically increased or that there was a real decrease in the deposition rate of terrestrially derived airborne dust, e.g., as a result of reduced wind speeds or lessened continental aridity. Given that the majority of the dust in sample No. 5 is of extraterrestrial origin, it is reasonable that stratospheric congestion associated with the

influx of such a large amount of dust would have significantly attenuated insolation and extremely perturbed the Earth's climate. Temperature differentials between the warmer oceans and the cooling continental regions could have significantly accelerated the rate of snow precipitation and ice accumulation. Consequently, if the observed barium concentration decrease is attributed to a 33 ± 10 fold increase in ice accumulation rate, the 6 cm ice core section represented by sample No. 5 would then span only about 1.2 years, rather than the 40 year duration that would be expected if snow had accumulated at the rate most typical for that part of the Camp Century ice core record.

3.2. Significance of the EDS and SEM results

Lead is an element that is not easily detected using NAA since it does not activate well. So the EDS findings on sample No. 5 complement the earlier NAA findings in that they show that in addition to tin, lead also is a major constituent of this tin-rich dust, both elements of which have low melting points. The average Sn and Pb weight abundances from the three moving beam measurements on filter fragments S1, S2, and S3 of G962-1, described in Section 2.2, yields a Sn:Pb weight abundance ratio of 0.17 ± 0.03 . The meltwater concentration for Pb in sample No. 5 (G962-1) may then be estimated to be 156 ng/g which is 10^4 to 10^5 times higher than values previously reported for ice age polar ice. For example, Boutron and Patterson (1986) report lead concentrations ranging from 1.3 to 29 pg/g in 14,000 to 27,000 year old Dome C, Antarctic ice. In their study, they caution about the necessity of carefully removing the outer layers of ice from stored ice core samples to avoid contamination by modern manmade lead particles circulating in the environment due to the era of leaded gasoline use. They report that lead levels were as high as 340 to 2300 pg/g on the outer uncleaned layer of one of their ice age ice core samples and attribute this to modern lead pollution. Moreover, Ng and Patterson (1981) have shown that the same ice core cleaning technique used by Thompson is able to dramatically reduce Pb surface contamination. For example, by removing 2 mm of the outer surface of the ice sample, Thompson should have reduced surface lead contamination by one hundred fold to < 0.02 ng/g. By comparison, the Pb concentration found throughout the entirety of ice sample No. 5 averages 160 ± 27 ng/g which is four orders of magnitude higher than this lead contamination estimate. So one may conjecture that given Thompson's stated core cleaning technique, a negligible amount of lead contamination would have entered this tin-rich sample, i.e., several orders of magnitude below the stated measurement error for lead.

The silicon abundance of ~6% for ice core sample G962-1, based on the average SiO_2 abundance determined for fragments S1, S2, and S3 given in Table 3, is low compared to its abundance both in C1 chondrites (10.4%) and the Earth's crust (27.7%), but closer to the former. So this provides additional evidence that terrestrial material comprises a small fraction in this sample. The silicon abundance found in sample G1038-1 (fragment S4), ~8.6% also is closer to the C1 chondrite value than to the Earth crustal value and hence supports that terrestrial dust was also significantly reduced in this sample as well.

The SEM and EDS survey of particles reported here confirms Thompson's report of tin-rich particles in both samples G962-1 and 1038-1. The presence of nanochondrules in one porous aggregate as well as elevated nickel concentrations in a number of dust particles establishes that the dust in both of these polar ice core samples has an extraterrestrial origin.

Some may wonder whether the exterior of Thompson's ice samples may possibly have been contaminated by metal particles abraded from the high speed band saws used during the sample cutting process. Such band saws are made of high-carbon steel containing major percentages of tungsten and/or molybdenum as well as chromium, vanadium and sometimes cobalt. During

tempering the alloying elements combine with carbon to form very strongly bonded carbides that could be several microns in size. For example, variable-sized particles of FeMo_3C will be present in a saw alloyed with Mo. To further improve tool performance physical/chemical vapor deposition started to be used to coat the steel with several micrometer thin coatings of TiC, TiN or $\text{TiN}/\text{Al}_2\text{O}_3$ possibly in the early to mid 1970s. One might envision that small grains of titanium could become embedded in the outer layers of ice core during sawing and ultimately have entered his samples.

The author believes that such contamination is unlikely for the following reasons. Iron had a particularly low abundance in sample No. 5 (G 962-1) and molybdenum was not detected. As mentioned earlier, Thompson's report of Mo in his electron microprobe results was a misidentification of a lead peak. While cobalt was found to be about twice as abundant in G 962-1 as the other samples tested, its concentration (27 ppm) was still comparatively low and had a proportion relative to the other siderophile elements which was consistent with a cosmic dust origin. In the case of titanium, traces of Ti were found in only two out of seven particles in sample G 962-1 (0.75% and 1.0%) and two of the three moving beam measurements conducted on this sample indicated titanium to be present at only 0.15 - 0.24%. The particle with the highest titanium abundance (S2-4) had a particularly low abundance of Sn and Pb. So, the high levels of tin and lead found in G 962-1 are not easily attributed to band saw abrasion. Nevertheless, it must be acknowledged that robust procedures for removing an adequate outer ice layer from the sample to minimize contamination from the band saw were not normative at the time that these samples were prepared.

3.3. Significance of the Mass Spectrometric Data

The finding that the tin in sample No. 5 has significant isotopic anomalies in two minor isotopes and possibly in one major isotope provides additional evidence suggesting an extraterrestrial origin for the Sn, although further work is needed to refine the precision of these values. This analysis constitutes the first time that an isotopic anomaly has been found for tin in interplanetary dust particles. Several authors (Woosley and Howard, 1978; Ward and Beer, 1981; de Laeter et al., 1984) have pointed out a number of nucleosynthetic mechanisms for producing such tin isotopic anomalies: p-process taking place within stars, r-process within supernovae, and s-process taking place in the gas envelopes of red giant stars. In particular, an excess in ^{114}Sn would be a p-process anomaly, whereas an excess in ^{115}Sn could arise from all three processes.

Loss, et al. (1990) subsequently measured the isotopic abundances for tin in a 100 ng sample of acid-resistant Sn residue extracted from the Allende meteorite and found small excesses in the minor isotopes of tin, namely, $+30 \pm 10\%$ for ^{112}Sn , $+22 \pm 10\%$ for ^{114}Sn , and $58 \pm 15\%$ for ^{115}Sn . Their stated errors give 95% confidence limits. The excesses they found in ^{114}Sn was about the same magnitude as the corresponding anomaly reported here and their ^{115}Sn excess was about two fold greater. The polar ice sample did contain a slight excess of ^{112}Sn , 10%, but it was not as significant as the other excesses. These differences suggest that the tin-rich polar dust came from a different source than the tin in the Allende meteorite, one that was possibly interstellar.

The ion current that Loss, et al. (1990) obtained in their mass spectrometric determination of the Allende meteorite tin residue, 5×10^{-13} A, was about 50 fold higher than the ion current obtained in the analysis they had performed some years earlier on the tin-rich polar dust sample whose sample weight was 40 fold greater. This points to the improvement of their technique in the intervening period and to the feasibility of doing future mass spectrometry analysis on what remains of the archived tin-rich dust sample.

Loss, et al. mention that they detected a 113-mass peak in their mass spectrometry Allende

meteorite analysis but that the presence of 113-mass hydrocarbons made it difficult for them to monitor the intensity of ^{113}In in this peak and to correct their ^{115}Sn peak for possible ^{115}In interference. Although the spectrometric determination reported here for the tin-rich polar dust sample utilized a much lower ion current than they used in their Allende meteorite study, a 113 mass peak was not detected. So most likely, ^{115}In interference made a minimal contribution to the ^{115}Sn anomaly reported here.

3.4 Ice Core Sample Contamination Considerations.

At various places in the manuscript the issue was discussed as to whether ice core contamination could explain the high levels of tin and lead found in sample No. 5. Because such high dust sample abundances of tin and lead have not previously been reported for polar ice, it is helpful to summarize reasons why, in the author's opinion, contamination does not reasonably account for these findings.

- 1) The tin-rich dust sample (No. 5) was filtered in a class 100 clean room facility with particular attention being paid to the elimination of particle contamination.
- 2) The finding that the elevated tin and lead concentrations in this sample are associated with high enhancements in iridium, nickel, and gold which are rare in terrestrial dust, but commonly found in extraterrestrial dust favors an extraterrestrial source over a terrestrial contamination source.
- 3) The finding that the elevated Sn and Pb concentrations are associated with significant depletions in barium, cesium, several rare earths, and aluminum, all of which are commonly found in terrestrial dust and less commonly found in cosmic dust also favors an extraterrestrial interpretation for the heavy metal enhancements.
- 4) Thompson's finding that the microparticle concentrations of particles in this sample (greater than $0.65\ \mu\text{m}$ in size) are half the value of microparticle concentrations found 20 meters higher in the same core and one third as high as late Wisconsin stage microparticle concentrations found 50 meters higher argues against the entry of terrestrial contaminants into the sample.
- 5) The indication of a dramatic change of climate at the time this dust was deposited, as evidenced by the many fold rise in ice accumulation rate, argues in favor of a cosmic dust fall out event that could have impacted the Earth's climate.
- 6) The finding that the average tin-lead abundance ratio matches that found in interstellar space and does not match that found in terrestrial dust or typical solder sources argues against contamination.
- 7) The existence of a $120\ \mu\text{m}$ monomineralic tin oxide grain in sample No. 5 argues against tin solder alloy as being the origin of at least this unique tin-rich particle.
- 8) The finding that the tin-silicon abundance ratio in the tin-rich dust sample does not match that of Sorensonite ores found in southern Greenland and that the indium-tin abundance ratio in this dust sample is over 200 fold lower than that typical of terrestrial tin sources argues against contamination.
- 9) The finding that some of the porous aggregate tin-rich dust particles show evidence of nanometer-sized high Z spherules which are not normally found in terrestrial dust but are found in extraterrestrial dust argues against contamination as a cause.
- 10) The finding that there is evidence of isotopic anomalies in several of the tin isotopes indicates that this material did not originate from earth and hence argues against terrestrial contamination.
- 11) The finding that one other research group has discovered large numbers of tin-rich particles having a similar tin abundance in a different ice core (1500 year old GISP2 ice), using a different

method of ice sample preparation, and have concluded that the presence of ET indicators suggests that the particles have an extraterrestrial origin (see section 3.7), again this calls into question a contamination cause. Also given that other groups have occasionally found tin-rich particles embedded in interplanetary dust particles currently entering the Earth's atmosphere, contamination appears a less likely interpretation over and extraterrestrial dust interpretation.

- 12) The finding that one research group has reported the presence of two dust layers in Antarctic ice with extraterrestrial dust mass loadings similar to the tin-rich sample (see Section 3.7) indicates that extreme extraterrestrial dusting events do occasionally occur and leave their mark in the polar ice record,. This also makes less likely any argument that contamination may be a cause of the unusual dust findings.

3.5. Origin of the Ice Age Tin-rich Dust

Golenetskii et al. (1981) point out that in progressing from C3 to C1 type carbonaceous chondrites, it is found that the abundance of water, gases, and volatile elements steadily increases, while the abundance of the more refractory elements decreases. They argue that cometary bodies lie at the extreme end of this progression, containing even more volatiles than C1 chondrites. This would explain why dust residues deposited at the site of the 1908 Tunguska cometary body explosion are found to be enriched in Sn and other low melting point elements, tin being reported at 20 ppm or 12 times C1 chondrite abundance (Golenetskii et al., 1977, 1978). Consequently, the finding that the relatively volatile elements Sn, Sb, Au, and Ag have a high abundance relative to Ir and Ni in sample No. 5 (G962-1) would make a cometary origin for these heavy metals more likely than a meteorite or asteroid origin.

These Sn-rich particles, however, are unlikely to be debris resulting from a comet impact event for a number of reasons. First, a comet impact should have dispersed large quantities of microspheres into the atmosphere, and no cosmic microspheres were found in SEM investigations of dust from ice core sample G962-1. Also only one microsphere was found in an investigation of particles in the older tin-rich ice core sample, G1038-1. Second, if such an impact had been on land, a large amount of crustal material would have become mixed in with the extraterrestrial material, diluting the cosmic dust fraction by a factor of ten or more (Alvarez et al., 1980; O'Keefe and Ahrens, 1982). But this scenario is contradicted by the observation that sample No. 5 contains a relatively low abundance of barium and rare earths, indicative of a small continental dust contribution. Third, a planetesimal impact would have produced a very large spike-like concentration peak in the ice record of no more than a year duration. But no significant spike is apparent in the microparticle concentration profile spanning this interval. For example, as seen in figure 12, taken from the microparticle concentration data of Thompson (1977a), the dust forming sample No. 5 was being deposited onto the ice sheet at a relatively continuous but variable rate over the period represented by 35 cm of ice core depth, which spans at least 6 years (or longer if a lesser portion of the Ba decline is attributable to an increased rate of snow accumulation). The peak at 2 to 4 cm, which has an approximately 5 month span and rises just 3 fold above the average concentration present in the rest of the graph, is not high enough to be interpreted as a nearby impact event.

Clube and Napier (1984) have suggested that the tin-bearing dust in sample No. 5 may have come from the break up of a giant comet that after entering the solar system transferred to a stable Apollo-Amor orbit. They predict a velocity relative to the Earth of ~30 km/s for dust from such a break up. At such velocities, typical silicate-rich particles of size greater than 50 μm would have melted or ablated upon entering the Earth's atmosphere generating cosmic microspheres. But, as

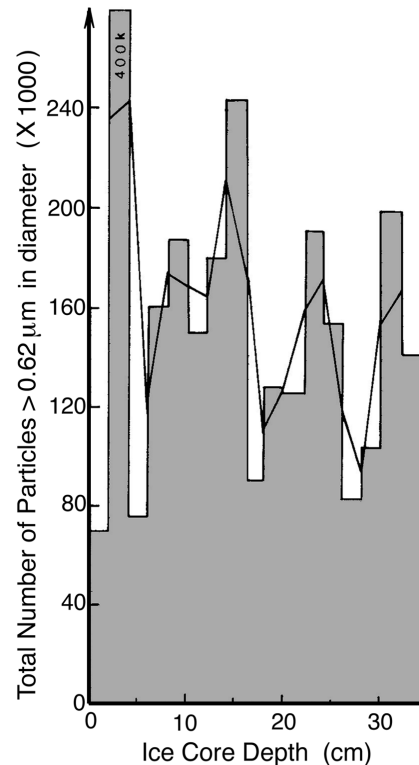


Figure 12. Microparticle concentration profile spanning 35 cm of the Camp Century ice core record at a depth of 1230.48 - 1230.78 meters (Thompson, 1977a, fig. 76, p. 128). The dust sample analyzed in the present study constituted the filtrate from three of this series of meltwater measurements.

already mentioned, thus far, no evidence of cosmic microspheres has been found in this sample. Furthermore, the cosmic dust particles in sample No. 5 are composed for the most part of tin which, if it had been in its native metallic state in the reducing environment of space, would have had a rather low melting point of 232 C. The particle size threshold for melting or vaporization during high velocity entry into the atmosphere for such particles would be far smaller, perhaps less than 5 μm . For example, Flynn (1988) estimates that for 20 μm diameter particles having a density of 1 g/cm^3 entering the atmosphere even at the low velocity of 10 km/s, 98% would reach temperatures above tin's melting point. Yet, many of the tin-rich particles in this sample are far larger than this, some ranging up to 120 μm in size. So, based on observation, high-velocity entry of dust particles from a cometary break-up can be definitely ruled out. Furthermore to explain the 49 kyrs BP tin dust event, cosmic dust would need to be supplied to the Earth's orbital vicinity for at least six years and less than one hundred years, whereas in the scenario suggested by Clube and Napier (1984) the earth-orbit-intersecting dust torus from such a break up would have a residence time on the order of 10^4 years.

The elevated concentrations of extraterrestrial dust in polar ice samples G962-1 and G1038-1 are best explained if this material had entered the Earth's atmosphere at a relatively low velocity already in particulate form, suggesting that the inner solar system zodiacal cloud has been episodically flooded with tin-rich cometary dust particles. If this episodic flooding were due to the disintegration within ~ 2 AU of the Sun of a giant long-period comet of anomalous composition, these particles would have had to approximate the Earth's orbital velocity by the time they had reached Earth in order to pass through Earth's atmosphere at a sufficiently low velocity. Moreover

the progenitor object supplying this material would itself need to shortly afterward exit the solar system following its orbital trajectory. Another possibility is the scenario discussed by Hoyle and Wickramasinghe (1978) in which Earth may have had an encounter with dust from the nebular tail of a comet. But again, these cometary dust particles would need to have approximated the Earth's orbital velocity prior to entry through the Earth's atmosphere.

Another way in which large quantities of dust could enter the zodiacal cloud is through the action of galactic cosmic ray volleys. It has been suggested that galactic core outbursts periodically produce intense cosmic ray volleys, or "galactic superwaves" that penetrate through the galaxy and reach the solar vicinity at near relativistic speeds (LaViolette, 1983a, 1987a). It had been predicted that on numerous occasions during the last ice age such superwaves elevated the cosmic ray background radiation intensity in the Earth's vicinity and produced the numerous ^{10}Be concentration peaks observed in the polar ice record (LaViolette, 1987a, 1990). The Taylor Dome and Vostok ice core records do show the presence of a moderate ^{10}Be peak coinciding with the 49 kyrs BP dust event.

During its passage through the solar vicinity, an incident cosmic ray volley would have formed a bow shock around the heliopause sheath and induced hydromagnetic fronts to propagate through the interplanetary medium into the solar system (LaViolette, 1983a, 1987a). The elevated cosmic ray intensities in this region could have been sufficient to evaporate the outer surfaces of cometary bodies orbiting in the inner Oort cloud and envelop the solar system in a dust and gas nebula. Upon acquiring electrical charges, dust particles in this nebula would have been susceptible to being captured by propagating shock fronts and transported into the solar system.

However, the tin, lead and iron abundance ratios in this tin-rich dust suggest that this material is of interstellar origin rather than solar system origin. The presence of interstellar dust surrounding the solar system has been described by Aumann (1988), and this may have been contributed by the interstellar cloud that the solar system is currently passing through (Frisch, 1981; Frisch and York, 1983). Also an interstellar dust wind is currently observed to enter the solar system from the Galactic center direction (Grün, 1993), and the past passage of a Galactic superwave would likely have enhanced this dust inflow rate (LaViolette, 1993). There is evidence that in the Earth's vicinity interstellar dust particles commingle with particles of solar system origin as indicated by the findings of Floss, et al. (2004).

While the heavy metal abundances found in ice core samples Nos. 1 and 8 (Table 2) are not overly extreme, those in ice core samples G962-1 (sample No. 5) and G1038-1 are rather unusual, tin and lead in particular having abundances 10^5 times higher than typical cosmic abundances. So something out of the ordinary is implied. Not only would the invading dust have had to be composed mostly of tin and lead, but it also would have had to enter in great quantities. Since available knowledge does not indicate that comets would have such high tin or lead concentrations, one is left to consider that these particles had somehow become concentrated in interstellar space while in a dispersed state.

One possibility is that the tin-lead-rich dust particles were originally in a metallic state in interstellar space and cold enough to be superconducting. Propagating magnetic fronts could then have propelled these particles through Meissner effect repulsion resulting in their preferential selection and concentration. The Meissner effect occurs when a superconductor expels the lines of force of an external magnetic field. As a result, if this external field is moving, it will create a propulsive force on the superconductor, moving it in the direction of travel (Robertson, 1991). Non superconducting particles would experience no Meissner effect force and hence would not similarly be susceptible to concentration by propagating magnetic fronts.

Another possibility is that the tin particles could have acquired magnetic moments by virtue of their superconducting state, which would have aligned them and entrained them into the movement of propagating hydromagnetic fronts. Superconducting tin-lead particles would have been concentrated in much the same way that a magnet, when moved over soil that contains a dispersed mixture of ferromagnetic grains, attracts and concentrates those grains near its pole. Tchernyi (2013), for example, has suggested that Saturn's rings may be composed of superconducting particles which are organized into their observed morphology by Saturn's magnetic field. Although in the case of Saturn's rings, only a high temperature superconducting ceramic alloy such as $\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{11}$ ($T_c \sim 122$ K) could explain this behavior since particles in Saturn's rings are known to have temperatures as high as 110 K. The question that remains in the case of Saturn is whether such high temperature superconducting ceramics similar to this manmade alloy exist naturally in space in sufficient quantities.

Interstellar tin and lead are both believed to be produced mainly by s-process neutron capture in the helium burning shells of intermediate and low mass asymptotic giant branch (AGB) stars. Ultraviolet spectroscopy studies of diffuse interstellar clouds have shown that of the heavy elements, tin is the only element whose gas phase abundance relative to hydrogen is suprasolar, about 0.05 dex above the solar Sn/H ratio (Sofia, et al., 1999; Sofia, 2000). The actual abundance enhancement is believed to be much higher since much of the interstellar tin would have condensed into a dust phase. By comparison, the gas phases of other elements detected in interstellar clouds show depletions relative to solar abundance values. One such element is lead, whose atomic abundance relative to tin is depleted 6 to 7 fold as compared to the Pb:Sn ratio found in C1 chondrites (Welty, et al., 1995); see Section 2.2. This is surprising since usually it is elements with higher condensation temperatures that are found to have greater depletions relative to their solar system abundances. It is, then, a puzzle why Pb, which has a lower condensation temperature than Sn, is depleted in interstellar space. It may indicate that it is produced at a lower rate through neutron capture than has been previously supposed.

Metallic tin and lead particles become superconducting at temperatures below 3.7 K and 7.2 K respectively. Also tin and lead whose surface has been implanted with hydrogen or deuterium atoms has been observed to have its superconducting critical temperature raised to 5.7 K and 7.8 K respectively (Ochmann, et al. 1981). The latter would likely occur for individual tin particles exposed to the interstellar hydrogen wind. Also the critical temperature (T_c) for tin-lead alloys is found to range up to 7.8 K. For example, T_c is 7.2 for a 40%-60% Sn-Pb alloy K, and 7.8 K for a 60%-40% Sn-Pb alloy. Moreover the critical magnetic flux (B_c) for such alloys can be more than twice that for lead or tin alone; e.g. for native lead $B_c = 0.08$ Tesla, whereas for a 60%-40% Sn-Pb alloy $B_c = 0.2$ Tesla. Hence tin-lead alloys have an advantage that they not only have a higher critical temperature, but also are able to maintain their superconductive state in the vicinity of higher magnetic field intensities.

Temperatures below this critical temperature threshold of 7.2 to 7.8 K would have existed beyond 1400 to 1500 AU (0.025 light years) from the Sun, or six times further out than the position of the solar system's bow shock front. So this superconductive segregation mechanism could have occurred quite close to the solar system, for example within the inner Oort cloud. Alternatively, such particle segregation and concentration could also proceed within the cores of molecular clouds where the temperature of dust grains may get as low as 5 K (Field, 1969, Greenberg, et al., 1999). This segregation process could have caused the accumulation of tin-rich dust clouds, and even the formation of planetesimals of anomalous composition enriched with such superconducting particles.

If present in a dispersed state, these superconducting dust particles could have easily been

transported into the solar system by cosmic-ray-wind-driven shock fronts, causing the inner solar system at times to be flooded for a few years with particles rich in tin and lead as this shock front passed through the solar system. These metallic interstellar dust particles would have acquired electrical charges as they entered the solar system forming what is termed a "dusty plasma". Charged grains passing within the influence of the Earth's magnetic field would have become magnetically bound to the Earth's field lines and become part of the circumterrestrial dust sheath traveling with the Earth as it orbits the Sun. The greatest numbers of particles would likely be trapped in the outer Van Allen belts where they would have been subject to additional charging under the action of cosmic rays circulating in this belt. Since this outer belt occupies the region between 13,000 to 60,000 km from the earth's surface (3 to 10 Earth radii), it would have presented a large cross section for capturing passing dust particles, 50 to 100 fold greater than the Earth itself. If these particles drifted downward towards the Earth's surface, at a speed of 10 cm/s it would have taken them about 5 to 20 years to make this journey. They would have slowed upon reaching the stratosphere. The terminal settling velocity in the stratosphere for particles 100 μm in size is of the order of 1 cm/s with correspondingly lower settling velocities for smaller dust particles, e.g., less than a tenth of a millimeter per second for 2 μm particles. So the proposed mechanism allows the possibility for a low relative velocity influx of cosmic dust particles over a period of decades. We do not know the true extent of the 49 kyrs BP dusting event since ice core sample G962-1 appears to be sampling midway through the course of the event. But one might guess that this dust influx had lasted anywhere from six years to a several decades.

Of course, through this same geomagnetic field trapping mechanism, the Earth could have acquired dust from the tail of a passing tin-rich comet. This would presume either that the comet had originally accreted these particles from a dust cloud rich in tin and lead while in interstellar space, or had picked them up in its coma during its orbital journey and swept them along as it entered the solar system.

Vanadium, which is superconducting below a critical temperature of 5.4 K and has a meteoritic abundance about 100 times greater than that of tin or lead, was not found in sample No. 5. However, due to its high reactivity with oxygen, nitrogen, and carbon, it would have been less susceptible to having formed metallic particles in space. For example, vanadium is more reactive than zinc which in turn is more reactive than iron, which in turn is more reactive than tin or lead. Other elements which could be superconducting in interstellar space, but which were not detected in sample No. 5, and which if present are at concentrations below 0.1%, include niobium ($T_c = 9.2$ K), mercury ($T_c = 4$ K), and indium ($T_c = 3.4$ K). But niobium has a cosmic meteoritic abundance seven times lower than tin, and like vanadium, is less susceptible to condensing as a native metal, being more reactive than zinc, and far more reactive than tin or lead. Mercury and indium have cosmic abundances respectively seven and 20 fold lower than tin. Also in a vacuum of 10^{-8} torr, mercury sublimates at temperatures above -72 C. Hence it would not have been in the form of distinct dust particles once it had passed the asteroid belt. So of all the elements, tin, lead and tin-lead alloys appear to be the most likely to form metallic superconducting particles in interstellar space in the greatest abundances and survive the journey to Earth, and these are exactly the elements found in unusually high abundances in these compositionally anomalous ice age dust samples.

3.6. Implications for Cosmic Dust Accumulation Rates During the Last Ice Age

If only 3% of sample No. 5 is of terrestrial origin and the remaining 97% is of extraterrestrial origin, this would indicate that the meltwater for this sample contained cosmic dust at a concentration of about 1820 ± 270 $\mu\text{g/l}$. Snow at Camp Century, Greenland is believed to have

accumulated at the average rate of 16 g/cm²/yr water equivalent during the last ice age, or about 50% of the current snow accumulation rate at this site. If snow had accumulated at 33 times this average rate during the deposition of sample No. 5, as implied by the observed decline in barium concentration, this would imply an episodic cosmic dust deposition rate of $\sim 10^{-3}$ g cm⁻² yr⁻¹, which would be among the highest cosmic dust influx rates that has been discovered in polar ice up to the present time.

This influx rate is about 1.7×10^4 times higher than the current cosmic dust deposition rate onto the Antarctic ice sheet of 60 ng/cm²/yr inferred from the nickel concentration measurements of Hanappe et al (1968), or about 4.5×10^5 times higher if referenced to the value of 2.2 ng/cm²/yr, determined by Takahashi (1978) from iridium measurements made on ice from Dome C. The elevated Ir and Ni deposition rates found in five of the other Camp Century ice core samples exhibited lesser enhancements amounting to a one to two orders of magnitude increase relative to current extraterrestrial dust deposition rates (LaViolette, 1985).

If the dust influx in sample No. 5 is instead reported in terms of $\mu\text{g}/\text{cm}^2$, the total influx in the sample would amount to $11 \pm 2 \mu\text{g}/\text{cm}^2$. The true dust influx for the event would be greater if it is being sampled midway through. By comparison, Narcisi, et al. (2007) have discovered two layers in the EPICA Dome C Antarctic ice core dating 434 and 481 kyrs BP which each contain a cosmic dust loading of $\sim 30 \mu\text{g}/\text{cm}^2$ based on Coulter counter measurements of the 0.7 to 13 μm dust fraction in their samples. These layers were found to contain angular grains ranging in size up to 100 μm as well as numerous cosmic microspheres with sizes ranging up to 25 μm in size indicating that high velocity entry of the material was involved. As a result, they interpreted that these were produced by meteorite impacts.

Further research should establish whether the two tin-rich Camp Century ice core dust layers reported here were local deposition events or of global extent. Given that tin-rich particles are present as inclusions even in interplanetary dust particles falling on the Earth today, one is led to believe that these ice age dust incursion events occurred as a result of incursion of material entering the zodiacal cloud. Hence this dust would have accumulated over the entire surface of the Earth. The total mass influx over the 1.2 year interval spanned by sample No. 5, then, would come to $\sim 6 \times 10^{13}$ g. It would indicate that at certain times during the last ice age the mass concentration of the zodiacal dust cloud was much greater than at present, and had attained concentrations sufficient to substantially effect the Earth's climate (LaViolette, 1983a, 1985, 1987a). Since this dusting event was transient, it would be difficult to estimate precisely the rise in the zodiacal cloud dust concentration at the time of the event. But an increase of a few orders of magnitude over the present day concentration seems reasonable. Since these tin-rich dust particles would have efficiently scattered and absorbed sunlight, their presence in the solar system and in the Earth's stratosphere would have had significant climatic effects and would explain the dramatic increase in ice accumulation during the event. The Camp Century oxygen isotope profile shows a stadial beginning at the time of this event, Dansgaard/Oeschger stadial number 13. Climatic coolings also followed the other two tin dust anomalies found at depths 1162 m and 1342.2 m; see arrows in figure 2.

If large concentrations of tin-enriched material had entered the solar system, evidence should be found also in the Antarctic ice record. Thompson (1977a) had analyzed randomly selected particles from 15 Byrd Station ice core samples and reported finding tin in 1 out of 8 particles examined in Holocene ice from a depth of 700 meters (7400 yrs BP). None of the other depths he had studied were contemporaneous with the tin-rich deposition events found in Camp Century ice, and no other studies have analyzed for tin in Antarctic ice. Assuming that it was global, the 49 kyrs BP tin dusting event should be found in the Antarctic Taylor Dome ice record between depths of 443 and

448 meters and in the West Antarctic Ice Sheet ice record between depths of 3225 and 3250 meters.

3.7. Other Reports of Tin in Cosmic Dust

Darrah et al. (2007) conducted SEM analysis of magnetic separates taken from the 12.9 kyrs BP Younger Dryas boundary at several C-14 dated Clovis sites across the U.S. and found that certain of the retrieved particles contained ET indicators such as Ni and Pt in association with volatile metals such as tin and copper. Volatile metal combinations found included Fe-Sn-Ni containing 25% to 28% Sn, and Cu-Ni containing 12% to 90% Cu. The grains were found to be in a metallic state and relatively unoxidized. Rather than being debris from a comet impact event, as these authors suggest, this material may have entered the stratosphere already in particulate form. LaViolette (2011) has suggested that extreme solar activity that occurred around 12,887 years BP would have been sufficient to temporarily collapse the earth's geomagnetic field and jettison into the stratosphere cosmic dust particles trapped in the Earth's circumterrestrial dust sheath. Alternatively, the magnetically bound plasma of a sufficiently large coronal mass ejection could have injected cosmic dust into the Earth's stratosphere that was orbiting in the Earth's immediate vicinity.

The discovery of tin grains in cosmic dust particles presently being captured from the stratosphere suggests that a small fraction of this tin-enriched material is still present in the solar system even today. Carbonaceous porous aggregate (CPA) particles collected from the stratosphere are believed to be of cometary origin, and certain studies have found that some contain elevated tin abundances in some cases 10^3 - 10^4 times higher than chondritic (Millman, 1972; Dohnanyi, 1976; Fraundorf et al., 1982). For example, Fraundorf (1981) reports that about 3% of the monomineralic grains he examined in CPA 13-08-16 are composed of tin.

Also Rietmeijer (1989) finds that the CPA dust particle W7029*A, 44% of which consists of carbonaceous material, also contains a substantial number of platy monomineralic tin grains measuring a few tenths of a micron in size. His energy dispersive spectrometer measurements indicate that the tin abundance is 6 times higher than typically found in C1 chondrites. Interestingly, a similar plate-like morphology is characteristic of the Sn rich particles found in Camp Century ice. Five percent of the grains in this porous aggregate have also been found to be composed of bismuth, another element that has a low melting point (MacKinnon and Rietmeijer, 1984).

In a stratospheric particle collection made by the DUSTER experiment (Dust in the Upper Stratosphere Tracking Experiment and Retrieval), Ciucci, et al. (2010) found a 2 μ m compact aggregate comprised of nanometer scale tin oxide grains. The energy dispersive X-ray spectrum of one of these tin-rich grains showed that Cr, Fe, Ni, and Au were also present. This element association pattern is similar to that found in the Camp Century sample No. 5 discussed here.

A perusal through NASA's cosmic dust catalog (volume 18), which contains spectra of 983 particles collected from the stratosphere indicates that just one shows a definite content of Sn and Pb (Warren, et al., 2011). If this sampling is representative of what is falling on Earth today, it indicates that roughly 0.1% of the particles entering the Earth's stratosphere today are rich in tin and lead. This particular particle, measuring 8 X 5 μ m and designated as L2071 D2, is shown in Figure 13. It has a much higher percentage of iron and lead than the tin-rich particles found in the Camp Century polar ice samples, its weight percentages being approximately 45% Sn, 35% Fe, and 20% Pb from analysis of the published spectrum. Its Pb-to-Sn ratio is about twice the ratio seen in interstellar space, but still is about one third of the abundance ratio found in C1 chondrites. Although the catalog classifies it as TCA (Artificial Terrestrial Contamination), the findings of the present study suggest that it be reclassified as a special class of cosmic dust particle, a tin-and-lead-

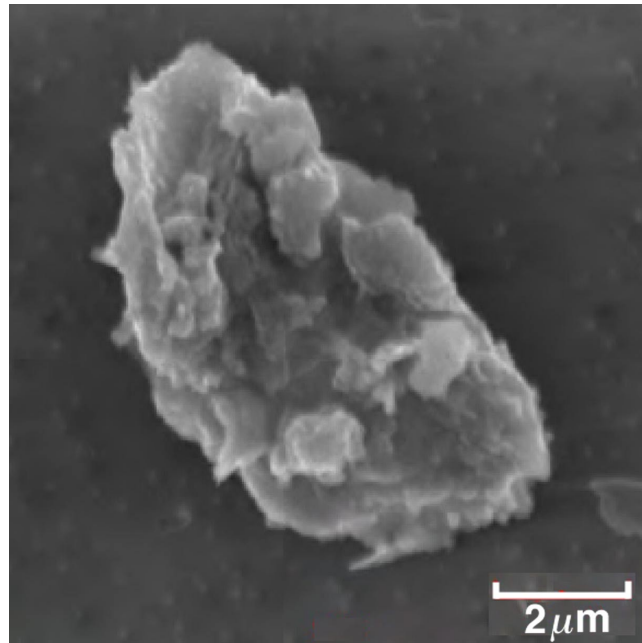


Figure 13. Particle L2071 D2 collected from the stratosphere found to be rich in tin, iron, and lead.

rich particle of possible interstellar origin. Further analysis should reveal whether extraterrestrial indicators such as nickel or iridium are also present.

More recently, Abbott, et al. (2014a, 2014b) found large numbers of carbonaceous tin-rich particles in a section of the GISP2 Greenland ice dating between 533 and 540 AD. Like the ice age particles described here, these have a platy morphology, with Sn being their primary component accompanied by traces of nickel, zinc, and copper. But their particle sizes only ranged up to $2\text{ }\mu\text{m}$ with many of their tin-rich particles being only small inclusions in larger aggregated particles. The tin-rich particles in Camp Century ice core sample G962-1 were found to range to much larger sizes, many particles being in the 20 to $50\text{ }\mu\text{m}$ size range and one as large as $120\text{ }\mu\text{m}$. Recently reviewing their samples, they find Pb also to be present in one of their particles, but not in association with Sn (D. Abbott, personal communication).

A second particulate population they found in this sixth century cosmic debris layer are carbonaceous particles rich in nickel but deficient in tin and which range up to $45\text{ }\mu\text{m}$ in size. One such particle is shown to have an angular morphology while another presents an amorphous shape containing many embedded ribbon-like nanofibers. Both the tin-rich and nickel-rich particles show no signs of any extensive melting, but rather give the impression that they had floated to the Earth's surface unablated. They also report finding a number of silicon rich and iron rich cosmic spherules having sizes ranging from 0.5 to $10\text{ }\mu\text{m}$. This indicates that some larger sized debris also entered during this cosmic dust event and suffered melting and ablation during its atmospheric passage.

Abbott, et al. also report the occurrence of two southern hemisphere comet impact events having found low latitude diatoms and silicoflagellates at two depths in their Greenland GISP2 ice core samples which dated at around 535.4 AD and 536.1 AD. They associate the nickel-rich particles and cosmic spherules with fragmentation of such a body as it entered the atmosphere and suggest that the tin-rich particles also entered as a result of, or in association with, these impacts. They suggest a cometary origin and note that at the time of this dusting event Halley's comet had made a close passage to the Sun with a pericenter of $\sim 1\text{ AU}$, making it likely that it had a close encounter

also with the Earth. The high prevalence of Sn in extraterrestrial dust entering at that time would then suggest that either Halley's comet may have been somehow involved. We have no direct measurements indicating that Halley's comet is enriched in heavy metals such as tin, but it is possible that on previous orbital passes Halley's comet may have acquired tin-rich interstellar particles during its passage below the ecliptic and brought these along with it as it entered the solar system.

Abbott, et al. also report that the 536 AD dust influx event correlated with a modest climatic cooling and solar obscuration, although impact ejecta may have played a significant role in producing these effects. This establishes an important link between stratospheric dusting events and climate and calls to mind the observation that the incursion of tin-rich particles around 49 kyrs BP occurred in connection with a period of cold climate and excess snow accumulation in Greenland.

Averaging the weight abundances for four tin-rich particles for which Abbott, et al. (2014b) report compositions in their Table 4, yields a Sn elemental abundance of $48 \pm 14\%$ by weight. This comes quite close to the Sn elemental abundance of $49 \pm 2\%$ found for the average of sample G962-1; see Table 3, S1, S2, and S3 moving beam measurements. These same four tin-rich particles in their study had an average carbon weight abundance of $13 \pm 13\%$. Carbon was not measured in the present study of Camp Century dust because the samples are retained on a hydrocarbon filter membrane substrate and have been carbon coated to make them conductive for SEM studies. However, if this dust contains a similar native average carbon abundance, the Sn abundance reported earlier for G962-1 would need to be adjusted downward to around 43%.

The four tin-rich particles Abbott, et al. report on have an average silicon abundance of $4 \pm 2\%$, which is close to the average for the moving beam EDS measurements on Camp Century ice core sample G962-1 ($6.3 \pm 1.2\%$). The 6th century AD particles also have more copper and zinc than those in G962-1. Analysis of the isotopic ratios of tin and lead found in particles both from the sixth century layer in the GISP2 ice core and from the pre-Holocene tin-rich layers in the Camp Century ice core should be done to check what appears to be a close link between these various deposition events. Because of their unique composition, it is quite likely that the tin-rich particle inclusions currently entering the stratosphere in IDP porous aggregates and those that entered in large amounts during the sixth century AD could be remnants of the tin dusting events of the last ice age and previous interglacial (e.g., G962-1 and G1038-1).

4. CONCLUSION

The results reported here indicate the presence of unusually high heavy metal concentrations in several dust samples filtered from the Wisconsin section of the Camp Century ice core. Particularly high elemental weight abundances of tin (49%) and lead (8.4%), accompanied by high levels of Sb, Ag, Au, Ir, and Ni, are found in one compositionally anomalous dust sample from a depth of 1230.5 meters dated at ~49 kyrs BP. The low concentrations of rare earth elements, such as La, Ce and Tb, and particularly of Ba, suggest that windblown continental dust makes up only 3 percent of the dust in this sample.

The relative abundances of Ir, Fe, Co, and Ni conform to a C1 chondrite pattern of around 9 percent carbonaceous chondrite material. Although the Sn, Sb, Au and Ag components of the enhanced group exceed chondrite abundances by several orders of magnitude, their association with these chondritic pattern elements suggests that all are of extraterrestrial origin. It is estimated that as much as 97 percent of the dust in this sample is of extraterrestrial origin, with tin oxide (62%) and lead oxide (9%) making up the majority. Both of these components likely have an interstellar origin since their Pb:Sn ratio matches that observed for gaseous interstellar Pb and Sn. The observation of isotopic anomalies in several isotopes of tin in this sample also suggests an

extraterrestrial origin. Additional measurements are needed to further verify the precise magnitude of these isotopic anomalies.

Similarly high levels of Sn and Pb are found in a dust sample from an ice core depth of 1342.2 meters dated at ~130 kyrs BP and the Pb:Sn ratio in that sample also closely matches the interstellar Pb:Sn ratio. Since Sn and Pb are superconducting at temperatures prevailing in interstellar space, propagating magnetic fields could have served as a mechanism segregating these elements and concentrating them to such high levels

The cosmic dust deposition rate discovered for the 49 kyrs BP tin-rich dust event is one of the highest so far discovered for the ice age period. Both of these dust events represent the first time that evidence has been found for the entry into the solar system of a large quantities of interstellar dust and in particular particles having superconducting properties in their native metal state. Recurrent cosmic dust invasions may be the missing link that could account for many of the abrupt climatic changes that took place during the ice age. Tin and lead should take their place next to nickel, iridium, gold, platinum, and nanodiamonds as valid extraterrestrial dust indicators when present at high abundances.

If the Sn-rich dust events are evidence of global deposition, then similar metal-rich layers should be found in other ice cores as well. Any such discoveries would eliminate any lingering doubts that the high tin and lead concentrations reported here for sample G962-1 and G1038-1 might be due to ice core contamination. If future research establishes the presence of corresponding tin and lead rich horizons in other terrestrial locations, these finding would be of paleontological interest in regard to a paleo health threat. The lead concentration levels found in the 49 kyrs BP ice (158 $\mu\text{g/l}$), for example, are 10.5 times the lead action level set by the U.S. EPA as the maximum allowable threshold for drinking water.

There is currently a lack of data on the distribution of heavy metals in polar ice. A thorough stratigraphic analysis of deep ice cores to search for the presence of such elements is needed. Meanwhile the 49 kyrs BP and 130 kyrs BP dust layers may contain the greatest repository of interstellar dust thus far discovered for the Pleistocene/Holocene period. They offer sites for collecting large numbers of cosmic dust particles in a pristine state free of twentieth century pollutants such as aluminum oxide rocket fuel spherules or adhesive oils such as those used in the aerial capture of stratospheric particles.

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Table 1a. Camp Century ice core sample characteristics and total dust concentration in the sample meltwater.

Sample No. ^a	Core Tube Number	Depth meters	Age yrs b2k	Length cm	Span yrs. ^b	Dust Weight μg	Water Vol. ml	Dust conc. $\mu\text{g/liter}$
1	949	1212.0	40,200	8.7	61	235 ± 50	72	3260 ± 700
2	955	1221.0	43,700	6.4	49	23.4 ± 4.7	44.5	526 ± 100
3	959	1226.2	46,300	4.3	17	541 ± 7	175	3090 ± 40
4	960	1227.7	47,400	6.6	29	449 ± 7	182.4	2470 ± 40
5	962-1	1230.5	49,150	6	1.2	98 ± 10	52	1880 ± 280
5'	962-1	1230.5	49,150	6	1.2	3.0 ± 0.6	1.58	
6	962-2	1231.5	49,850	4.5	36	466 ± 7	186	2510 ± 40
7	969	1241.0	54,000	2.6	8	6.7 ± 1.3	19.5	344 ± 70
8	992	1275.0	74,900	3.5	20	132 ± 26	40.5	3260 ± 700

^a Dust samples (Nos. 1, 2, 5, 7, and 8) were filtered by L. Thompson (1977a) and are designated in his study by core tube number as G-949, G-955, G-962-1, G-969, and G-992. Sample 5' is a split of sample 5.

^b Duration for sample No. 5 assumes that the ice accumulation rate in Greenland was 33 fold higher during this interval.

Table 1b. Ice meltwater concentrations of 15 trace elements in the eight ice core samples.

Sample No.	Core Tube Number	Elemental Concentrations ^a														
		Co	Ni	Ag	Sn	Sb	Ba	Ir	Au	Sc	Fe	Cs	La	Ce	Tb	Hf
1	949	57	0.53	146	2.3	< 13	6.0	54	<1.5	36	163	11.0	47	78	1.58	10.1
2	955	7.9	< 0.05	< 8	< 0.15	< 36	0.12	14.6	<1.8	5.6	26.3	1.75	<16	(20)	0.47	1.28
3	959	54	< 0.13	< 2	< 0.044	26	0.85	<0.9	<1.0	51	187	24.6	80	230	2.47	13.7
4	960	41	(0.26)	< 6	0.059	10	1.18	17.1	<2.0	27	111	11.0	42	120	1.35	6.6
5	962-1	51	1.50	610	920	310	0.028	85	29	6.8	38	2.7	< 8	(17)	0.19	3.3
5'	962-1	39	1.14	520	920	200	----	86	27.8	7.7	37	4.6	73	190	----	----
6	962-2	32	< 0.09	< 3	< 0.034	----	0.65	<1	<1.4	28	102	12.6	43	120	1.14	7.3
7	969	(5.6)	1.11	< 21	< 0.14	<120	<0.11	31	<4.3	4.1	16.9	2.3	< 21	<38	<0.24	1.33
8	992	66	0.64	1120	2.2	<110	2.9	20.5	<0.7	34	163	10.9	37	89	1.28	10.6

^a Concentrations are given in ng/lit, except for Ni, Sn, Ba, Fe and total dust ($\mu\text{g/lit}$) and Ir (pg/lit).

Table 2. Concentrations of 15 trace elements (relative to total dust) for 8 Camp Century ice core dust samples.^a

Sample	Co	Ni	Ag	Sn	Sb	Ba	Ir	Au	Sc	Fe	Cs	La	Ce	Tb	Hf
1	17.4	162	45	710	< 4.0	1830	16.6	< 0.47	11.1	5.0	3.4	14	24	0.49	3.1
2	15.0	< 64	< 14	< 280	< 68	226	28	< 3.4	10.7	5.0	3.3	< 30	(38)	0.88	2.4
3	17.6	< 41	< 0.6	< 14	8.3	275	< 0.3	< 0.33	16.6	5.8	7.9	26	74	0.80	4.4
4	16.7	(107)	< 7	24	3.9	479	6.9	< 0.82	10.9	4.3	4.5	17	49	0.55	2.7
5	27	800	327	49%	163	14.8	45	15.4	3.6	2.0	1.45	< 4	8.9	0.10	1.77
6	12.9	< 36	< 1.1	< 14	---	260	< 0.4	< 0.56	11.2	4.0	5.0	17	48	0.45	2.9
7	(16.4)	3220	< 61	< 420	< 340	< 310	96	< 13	11.8	5.0	6.7	< 60	< 110	< 0.70	3.9
8	20.2	195	340	690	< 3.3	900	6.3	< 0.20	10.5	5.0	3.3	11	27	0.39	3.3
C1 ^b	502	1.10%	0.199	1.72	0.142	2.34	481	0.140	5.82	19.0	0.187	0.24	0.50	0.036	0.10
EC ^c	29	99	0.08	2.1	0.2	390	0.024	0.004	25	6.2	2.6	34.6	66.4	1.18	2.8
EF-1 ^d	0.93	8.08	4090	2.33x10 ⁵	815	0.038	1875	3850	0.144	0.32	0.56	< 0.12	0.13	0.085	0.63
EF-2 ^e	5.74	50.2	2.53x10 ⁴	1.45x10 ⁶	5060	0.235	1.16x10 ⁴	2.38x10 ⁴	0.89	1.99	3.45	< 0.7	0.83	0.52	3.91

^a All concentrations in ppm except for Ir (ppb), Fe (%), and Sn (Sample No. 5: %).

^b Elemental concentrations in C1 carbonaceous chondrites (Anders and Grevesse, 1989).

^c Earth's average crustal abundances. All values are from Ronov and Yaroshevsky (1972), except for Ir which is from Shaw et al. (1976).

^d Elemental enhancement factors for sample No. 5 relative to the Earth's average crustal abundance.

Table 3. Qualitative microanalysis of randomly selected particles and fields from two compositionally anomalous tin-rich dust samples

Sample No.	Na Na ₂ O (wt %)	Mg MgO (wt %)	Al Al ₂ O ₃ (wt %)	Si SiO ₂ (wt %)	P P ₂ O ₅ (wt %)	S SO ₄ (wt %)	K K ₂ O (wt %)	Ca CaO (wt %)	Cr Cr ₂ O ₃ (wt %)	Ti TiO ₂ (wt %)	Fe FeO (wt %)	Ni NiO (wt %)	Cu CuO (wt %)	Sn SnO ₂ (wt %)	Pb PbO (wt %)
G 962-1															
S1 Moving Beam	7.4	1.4	4.4	11.6	0.4	---	---	---	---	0.24	1.13	---	---	62.5	10.8
S2-1*	---	---	---	0.3	---	0.16	0.67	---	0.01	---	0.2	0.25	---	98.2	0.2
S2-2**	0.1	0.1	0.1	0.5	---	4.0	1.0	---	0.04	---	0.07	---	0.24	90.6	2.0
S2-3	0.5	0.8	7.1	14.3	2.0	---	1.3	---	0.02	---	1.5	0.16	0.30	60.1	11.9
S2-4	3.0	1.1	7.1	40.8	3.2	19.0	0.7	17.0	0.2	1.0	4.0	0.24	---	0.45	2.2
S2-5	28.6	0.5	3.4	9.3	0.7	---	2.3	0.1	---	0.75	1.5	0.06	---	69.4	12.0
S2 Moving Beam	7.4	1.3	4.5	12.5	0.5	---	---	---	---	0.15	1.24	---	---	64.2	8.2
S3-1	2.9	0.6	0.7	2.7	0.5	---	0.2	---	0.03	---	---	---	---	81.3	11.1
S3-2	3.0	0.9	0.6	3.2	1.1	---	0.16	---	0.02	---	0.1	0.05	0.03	86.0	4.9
S3-3 (field)	17.3	0.5	0.6	2.3	0.4	---	0.16	---	0.03	---	---	---	---	69.3	9.4
S3-4 (field)	9.9	2.7	7.7	21.8	1.7	0.36	0.01	0.01	0.01	---	0.01	0.01	0.01	44.1	11.7
S3-5 (field)	7.1	1.8	7.2	18.4	1.06	0.35	0.2	0.01	0.01	---	---	---	---	54.1	9.9
S3 Moving Beam	5.4	1.4	6.3	16.5	1.0	0.26	0.7	---	0.01	---	0.7	---	---	59.7	8.1
G 1034-1															
S4-1	12.8	1.5	5.4	10.6	0.8	3.0	0.9	---	---	---	1.8	0.24	1.7	54.4	7.0
S4-2	1.2	0.4	1.6	94.6	0.08	---	0.12	---	0.03	---	0.8	---	---	1.0	0.3
S4 Moving Beam	10.3	1.2	6.1	18.3	0.35	1.5	1.1	---	0.07	---	3.0	---	0.24	49.7	8.1

* This particle also showed a 1.8% chloride signal which is omitted from the abundance estimate. Whether the reading came from the particle or from chloride in the filter background is not certain.

** This examined particle also contains 1.3% Zn.

Table 4. The isotopic composition of tin in tin-rich Camp Century ice core sample G962-1.

Isotope ratio:	124/120	122/120	119/120	118/120	117/120	116/120	115/120	114/120	112/120
Laboratory Standard	0.17766 ±0.00018	0.14202 ±0.00040	0.26332 ±0.00032	0.74309 ±0.00039	0.23533 ±0.00010	0.4460 —	0.01040 ±0.00001	0.02022 ±0.00002	0.02992 ±0.00005
Sample 962-1	0.17791 ±0.00086	0.14253 ±0.00074	0.26345 ±0.00100	0.74335 ±0.00296	0.23413 ±0.00075	0.4460 —	0.01075 ±0.00009	0.02056 ±0.00024	0.03021 ±0.00039
Deviation (‰)	1.4±4.9	3.5±5.9	0.5±4.0	0.4±4.0	-5.1±3.2	—	33±8.4	17±12	10±12
Significance:					↓ 3σ		↑ 8σ	↑ 3σ	↑ 1.6σ