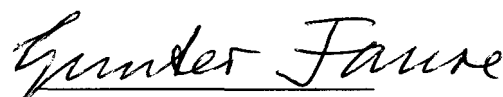


**Chemical Comparison of Spherules from the Ross Sea and Glacial  
Sediment of Antarctica; an SEM Study**

by  
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### **Abstract**

Four (about 100 $\mu$ m in diameter) clear spherules from seafloor sediments of the Ross Sea differ physically and chemically from three microscopic dark spherules of about the same size from glacial deposits in Antarctica and upper New York state.

The major-element concentrations (determined by SEM) show that the clear spherules differ in composition from the dark spherules. The clear spherules were found to be similar in composition to the continental crust, indicating a terrestrial origin. Based on their physical structure and chemical composition, they are likely a biogenically-produced form of opal.

The composition of each dark spherule was compared to the compositions of the continental crust and CI chondrites. The results are inconclusive. Therefore, they may be either terrestrial or extraterrestrial in origin. In addition, the dark spherules differ markedly in composition amongst themselves.

## **Introduction**

Microscopic spherules have been found in many environments including glacial deposits and seafloor sediments. The glacial deposits and ice of Antarctica contain spherules, because the cold, dry conditions allow them to be preserved.

Spherules from seafloor sediments have been described by Blanchard et al. (1980). They have been explained as micrometeorites or ablation debris of large meteorites, meaning that they are extraterrestrial in origin. The type of meteorites that were used for comparison are known as CI chondrites.

Hagen et al. (1989) later described spherules found in Antarctic glacial deposits. They concluded that these spherules are also extraterrestrial in origin.

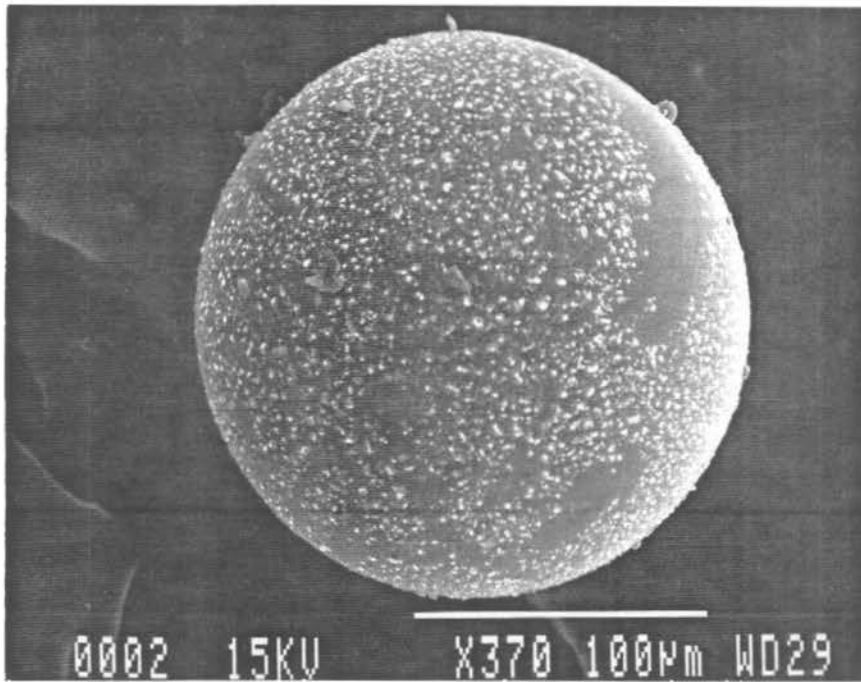
The present study examines seven spherules recovered from three locations around the Earth. Four of the spherules are from seafloor sediments of the Ross Sea; two were recovered from the Meteorite Moraine in Antarctica; and one spherule was found in glacial till near the Adirondacks in upper New York state.

### **Description of the Spherules**

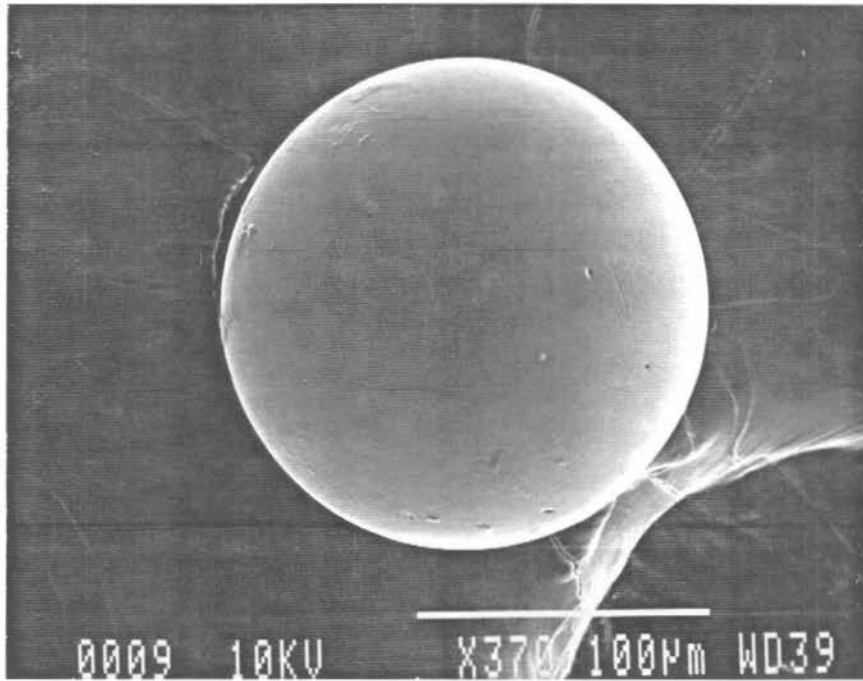
Scanning electron microscope (SEM) photographs of the spherules (Plates 1 - 9) show that the spherules fall into two distinct groups based on physical appearance.

The first group of spherules in Plates 1 - 6 were recovered from seafloor sediments in the Ross Sea near Antarctica by Dr. Enriqueta Barrera, and are designated as spherules RS-1,2,3, and 4 (RS = Ross Sea). They are all very smooth, highly spherical, and have particles scattered over their surfaces. The particles are mostly cubic in shape. Under a light microscope, these spherules are glassy and clear.

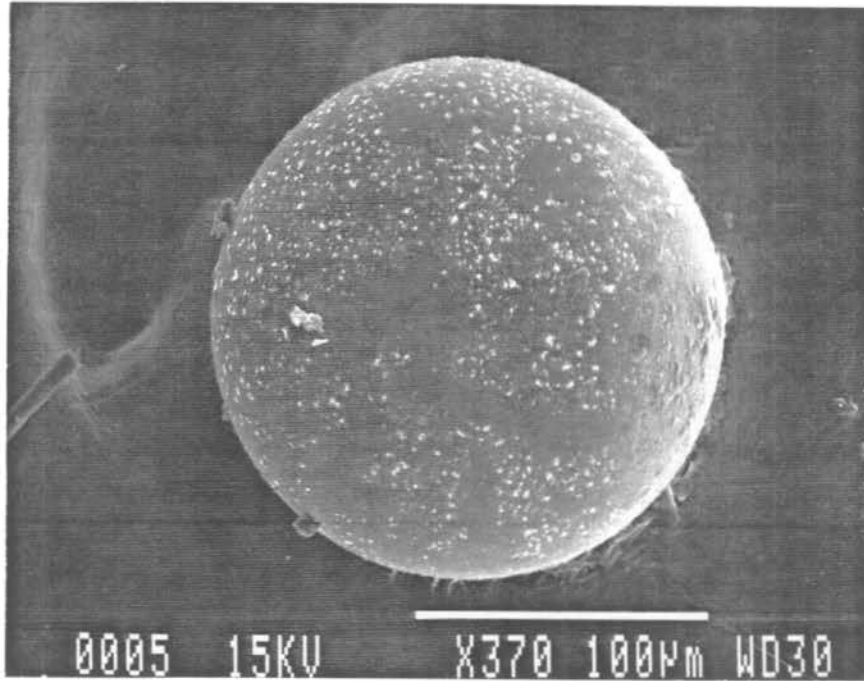
Two of the remaining spherules, designated as MM-1 and 2 (MM = Meteorite Moraine), were collected from the Meteorite Moraine in Antarctica by John Schutt. The other was recovered by Kent Whiting from till in the Hudson River valley south of Sanford Lake in the Adirondacks of upper New York state, and is designated AD-1 (AD = Adirondacks). All of these spherules are imperfectly spherical, do not appear to be smooth, and are black in color (Plates 7 - 9). Spherule MM-2 displays a "brickwork" structure that has also been described by Hagen et al (1989). The irregular shape of these spherules may be due to erosion.



**Plate 1.** Spherule RS-1 shows the high sphericity and covering of surface particles typical of the clear spherules. (magnification 370x, marker bar equals 100 micrometers)

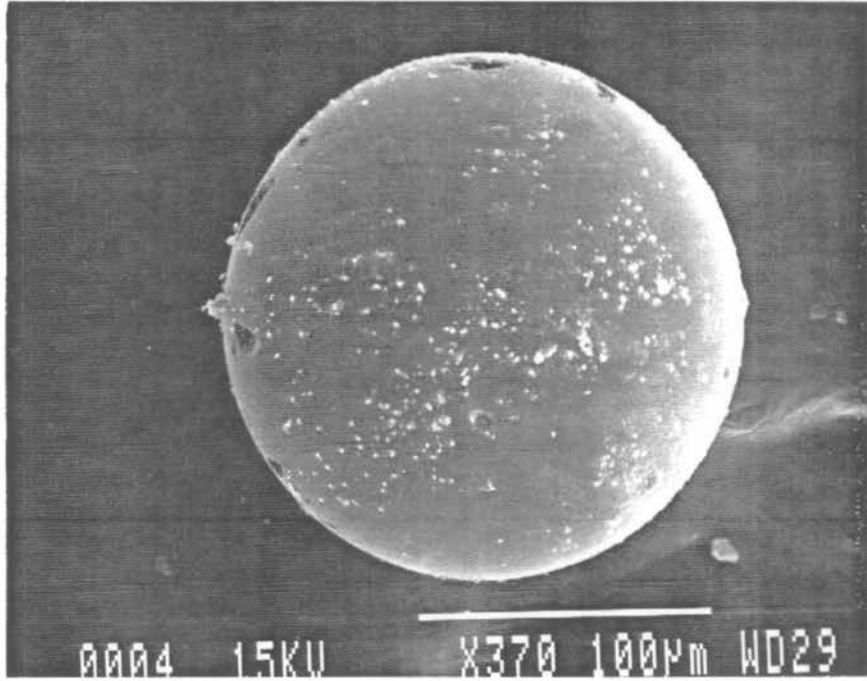


**Plate 2.** Spherule RS-2 after the surface particles have been removed. The spherule has a very smooth and glassy surface in addition to being highly spherical. (magnification 370x, marker bar equals 100 micrometers)

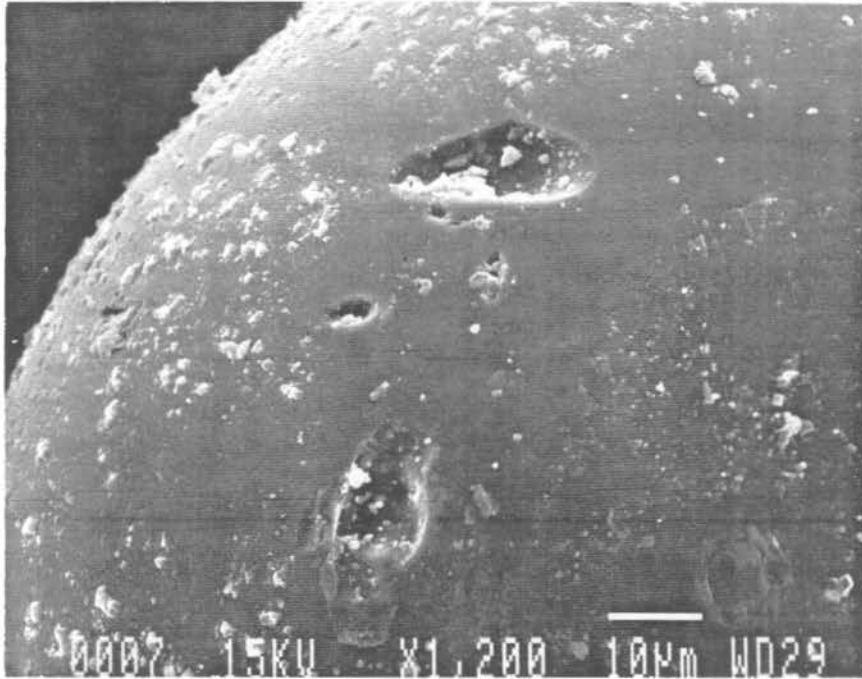


**Plate 3.** Spherule RS-3 displays an irregular surface on the right side. Several large surface particles are also on the sphere. (magnification 370x, marker bar equals 100 micrometers)

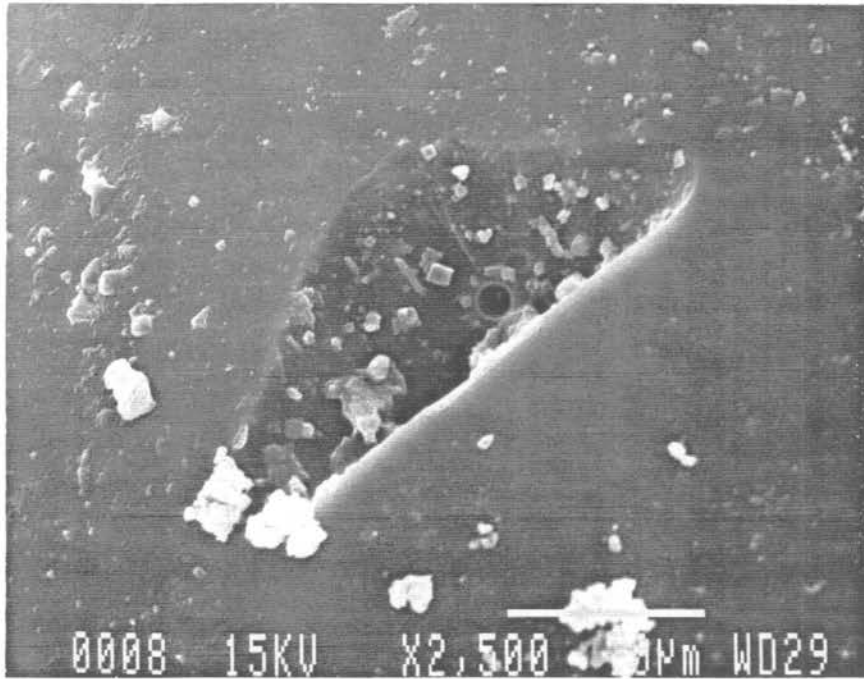




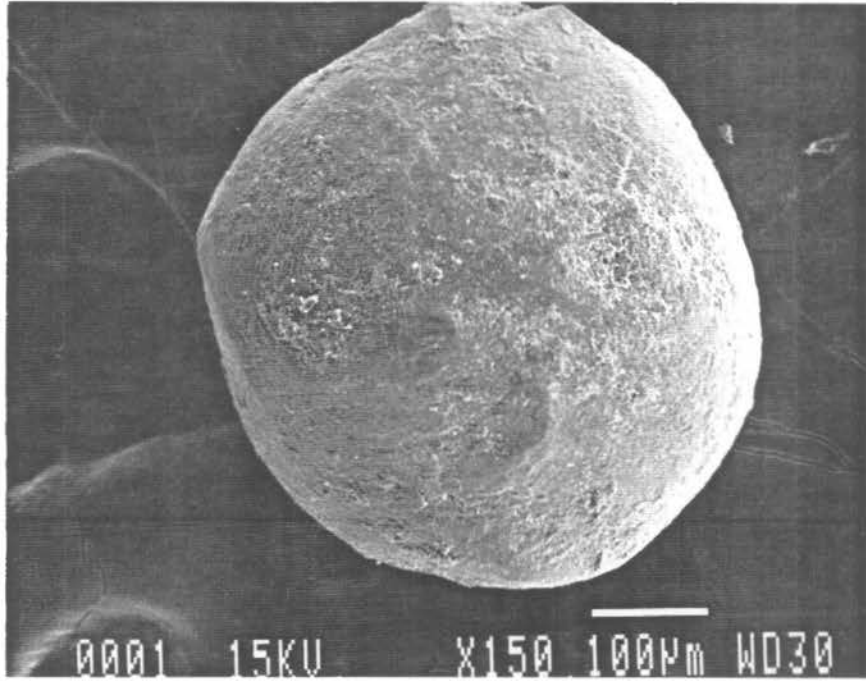
**Plate 4.** Spherule RS-4 has a pitted surface, and relatively few surface particles. (magnification 370x, marker bar equals 100 micrometers)



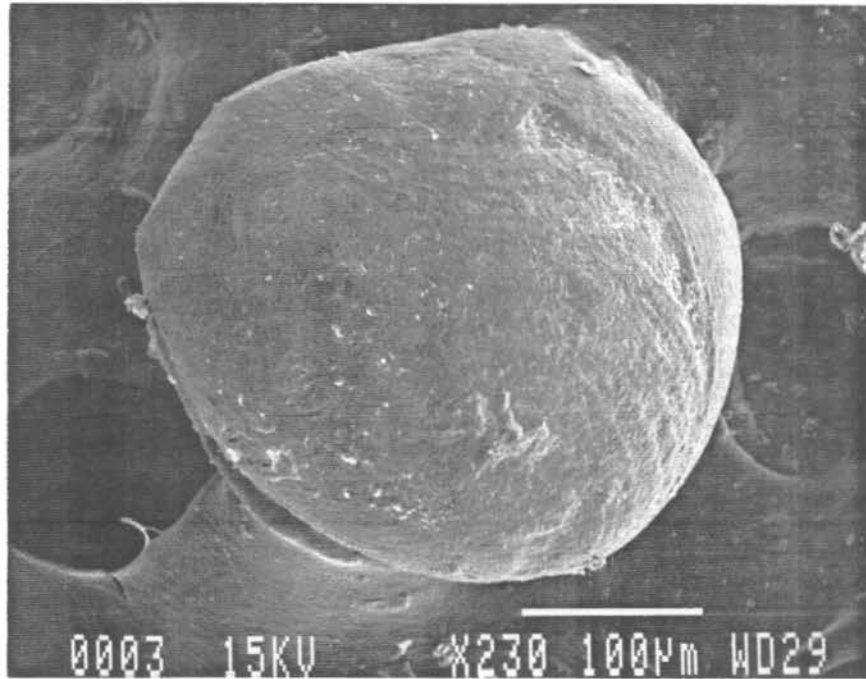
**Plate 5.** Close-up of the pitted surface of spherule RS-4. (magnification 1200x, marker bar equals 10 micrometers)



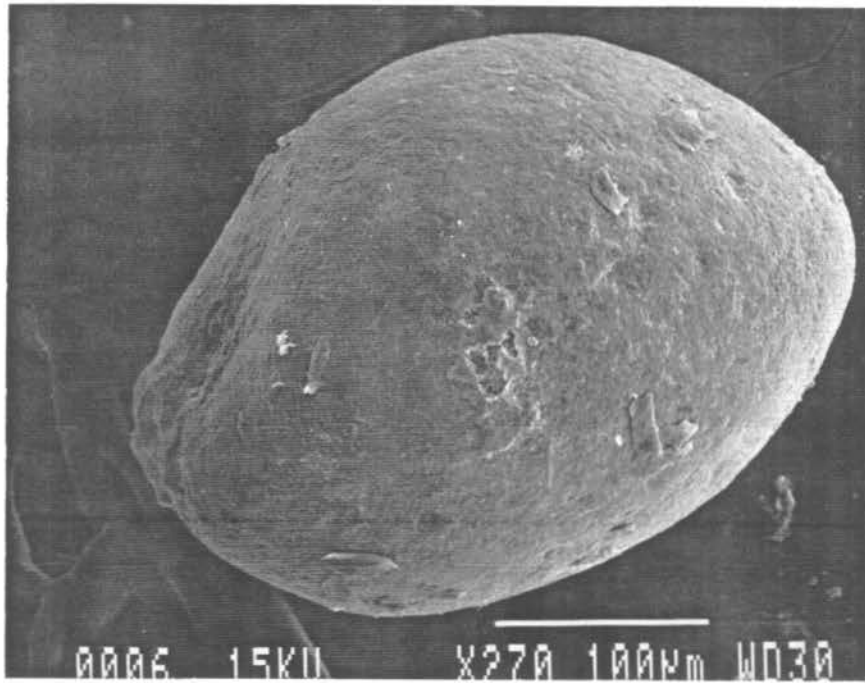
**Plate 6.** Close-up of a pit on the surface of spherule RS-4. The particles in and around the pit are cubic, which may indicate that they are halite or other marine salts. If they are marine salts, then the pitting occurred before the spherule was brought up from the bottom of the Ross Sea, because the particles are inside the pit. (magnification 2500x, marker bar equals 10 micrometers)



**Plate 7.** Spherule MM-1 is the largest of the seven spherules examined in this study. It has an irregular shape and does not appear to be smooth. (magnification 150x, marker bar equals 100 micrometers)



**Plate 8.** Spherule MM-2 displays “brickwork” structure as described by Hagen et al. (1989). (magnification 230x, marker bar equals 100 micrometers)



**Plate 9.** Spherule AD-1 is nearly elliptical rather than spherical. It appears to have the smoothest surface of the dark spherules. (magnification 270x, marker bar equals 100 micrometers)

## METHODS

### **Instrumentation - the Scanning Electron Microscope**

A JEOL JSM-820 scanning electron microscope equipped with a Link Analytical eXL energy dispersive x-ray analyzer (EDX) was used to perform the analyses of the spherules. The operating conditions included a 39mm working distance, an accelerating voltage of a 20,000 electron volts, and a vacuum of  $10^{-5}$  Torr in the sample chamber. A lithium-drifted silicon scintillation crystal, a probe current of 1.05 nA, and a collection time of 100 seconds were used to perform the analyses. The beryllium window that protects the detector was left open to allow the x-rays unhindered access to the detector. The analyzer software that calculates the elemental concentrations uses the ZAF-PB corrections. The Z correction takes into account that the intensity of the X-rays decreases with increasing atomic number of the elements being analyzed. The A correction compensates for absorption effects, which is when X-rays generated deep within an atom are absorbed by the electrons of the outer shell, or when X-rays from light elements are absorbed by heavier elements. The F correction adjusts for fluorescence, which is when X-rays from heavy elements generate X-rays from lighter elements. PB indicates that the software uses the peak area to background ratios of the elements analyzed and compares them to known ratios determined from pure element standards that are stored in the computer's memory.

### **Preparation of Standards and Samples**

The standards used were already mounted on a block that was borrowed from Dr. Micheal Barton of the Ohio State University Electron Microprobe Laboratory. The standard block was outgassed by placing it in a vacuum, and was then coated with a 60 to 100Å layer of carbon.

The spherules were mounted on double-sided carbon tape that covered the top of a carbon stub. The mounting was then outgassed and carbon-coated in the same manner as the standards. The spherule mount and standard block were both stored in a dessicator .

## Standards

Four standards were selected that provided a range of concentrations for the elements to be determined. The standards used were: chromium augite, hornblende, pyrope, and omphacite. Elements of interest were oxygen, sodium, magnesium, aluminum, silicon, potassium, calcium, titanium, manganese, and iron. These four standards make up part of a larger set of mineral standards known as the Harvard Block. The elemental concentrations of the Harvard Block standards have been determined using wet chemical methods. Table 1 lists the concentration of the oxides of the elements of interest in the four standards based on information published by Jarosevich et al. (1980).

**Table 1. Composition of the standards by weight percent of the elemental oxides as published by Jarosevich et al. (1980)**

Oxides	Cr-Augite <sup>1</sup>	Hornblende <sup>2</sup>	Pyrope <sup>3</sup>	Omphacite <sup>4</sup>
SiO <sub>2</sub>	50.35	40.37	41.34	55.40
Al <sub>2</sub> O <sub>3</sub>	8.01	14.90	23.66	8.89
Fe <sub>2</sub> O <sub>3</sub>	1.04	3.30	0.00	1.35
FeO	3.76	7.95	10.65	3.41
MgO	17.28	12.80	18.45	11.57
CaO	17.26	10.30	5.15	13.75
Na <sub>2</sub> O	0.84	2.60	0.00	5.00
K <sub>2</sub> O	0.00	2.05	0.00	0.15
TiO <sub>2</sub>	0.51	4.72	0.47	0.37
MnO	0.12	0.09	0.28	0.10
H <sub>2</sub> O	0.00	0.94	0.00	0.02
TOTAL	99.17	100.02	100.00	100.01

<sup>1</sup> Augite, Kakanui, New Zealand (USNM-122142)

<sup>2</sup> Hornblende, Kakanui, New Zealand (USNM-143965)

<sup>3</sup> Pyrope, Kakanui, New Zealand (USNM-143968)

<sup>4</sup> Omphacite, Roberts Victor Mine, South Africa (USNM-110607)



### Analysis of the Standards

Each of the four standards was analyzed using the SEM settings described earlier. Three analyses were performed for each standard by focusing the electron beam on three separate locations. The unprocessed data from the analyses of the standards are presented in Appendix A. A summary of the analyses is listed in Table 2.

### Calibration of the standards

The ZAF corrected elemental concentrations of the standards were normalized to 100% using the following formula:

$$\text{Normalized concentration} = [(\text{ZAF corrected concentration}) (100)] / \text{sum of the ZAF concentrations} \quad (1)$$

The differences between the known concentrations and measured concentrations were then calculated by subtracting the known concentrations from the normalized ZAF concentrations. In Table 2, this difference is expressed as a percent of the known concentrations, calculated in the following manner:

$$[(\text{Actual Wt } \%) - (\text{ZAF corrected } \%, \text{ normalized}) / (\text{Actual Wt } \%)] \times 100\% = \% \text{ difference} \quad (2)$$

The average percent differences of each element for the entire set of standards are listed in Table 3. The differences range from -96.10% to +50.58%. It was arbitrarily decided that an average difference of  $\pm 5\%$

**Table 3. Averages of the % differences of the standards**

Elements	1. Cr-Augite % difference	2. Hornblende % difference	3. Pyrope % difference	4. Omphacite % difference	Average % difference
O	-3.64	-2.72	1.71	-5.57	-2.56
Na	48.39	50.26	N/A	53.10	50.58
Mg	-8.64	-11.79	-15.54	-10.89	11.72
Al	3.77	-1.25	-1.68	-0.64	0.05
Si	-0.76	-2.07	-0.62	-0.97	-1.10
K	N/A	2.35	N/A	41.67	22.01
Ca	7.79	11.68	1.63	8.44	7.38
Ti	-35.48	-11.31	82.14	18.18	13.38
Mn	-200.00	42.86	-27.27	-200.00	-96.10
Fe	-0.85	12.01	12.68	23.40	16.88

Table 2. Summary of the analyses of the standards

Element	1. Cr-Augite				2. Hornblende			
	Actual Wt. %	P/B, avg.	ZAF corr. %, Normalized	Difference, %	Actual Wt. %	P/B, avg.	ZAF corr. %, Normalized	Difference, %
O	43.97	1.323	45.57	-3.64	43.06	1.210	44.23	-2.72
Na	0.62	0.064	0.32	48.39	1.93	0.182	0.96	50.26
Mg	10.42	1.140	11.32	-8.64	7.72	0.822	8.63	-11.79
Al	4.24	0.500	4.08	3.77	7.89	0.933	8.08	-1.25
Si	23.54	3.175	23.72	-0.76	18.87	2.439	19.26	-2.07
K	0.00	0.000	0.00	0.00	1.70	0.249	1.66	2.35
Ca	12.33	1.922	11.37	7.79	7.36	1.042	6.50	11.68
Ti	0.31	0.055	0.42	-35.48	2.83	0.393	3.15	-11.31
Mn	0.09	0.026	0.27	-200.00	0.07	0.004	0.04	42.86
Fe	3.65	0.302	2.94	-0.85	8.49	0.725	7.47	12.01
TOTAL	99.17		100.00		99.92		100.00	

Element	3. Pyrope				4. Omphacite			
	Actual Wt. %	P/B, avg.	ZAF corr. %, Normalized	Difference, %	Actual Wt. %	P/B, avg.	ZAF corr. %, Normalized	Difference, %
O	44.57	1.246	43.81	1.71	44.87	1.360	47.37	-5.57
Na	0.00	0.000	0.00	0.00	3.71	0.348	1.74	53.10
Mg	11.13	1.280	12.86	-15.54	6.98	0.774	7.74	-10.89
Al	12.52	1.540	12.73	-1.68	4.71	0.576	4.74	-0.64
Si	19.32	2.583	19.44	-0.62	25.90	3.470	26.15	-0.97
K	0.00	0.000	0.00	0.00	0.12	0.011	0.07	41.67
Ca	3.68	0.605	3.62	1.63	9.83	1.508	9.00	8.44
Ti	0.28	0.007	0.05	82.14	0.22	0.024	0.18	18.18
Mn	0.22	0.026	0.28	-27.27	0.08	0.023	0.24	-200.00
Fe	8.28	0.733	7.23	12.68	3.59	0.280	2.75	23.40
TOTAL	100.00		100.00		100.01		100.00	

was acceptable. The results show that the normalized ZAF corrected concentrations of oxygen, aluminum, and silicon agree within five percent of the known concentrations of these elements. The other elemental concentrations, however, differ by more than five percent and their concentrations were determined by plotting calibration curves based on the known concentrations of these elements in the standards and the measured peak-to-background ratios. The graphs were plotted using computer software (Tablecurve) that computed a best-fit straight line ( $y = mx + b$ ) to the data. The calibration graph for iron and equations for all elements are presented in Figure 1 and Table 4, respectively. Appendix B contains the entire set of calibration graphs. These graphs demonstrate that the calibrations form straight lines that run through the origin in all cases. With the exception of oxygen, aluminum, and silicon, the concentration of the other elements in the unknowns were calculated from the peak to background ratios using the calibration equations in Table 4.

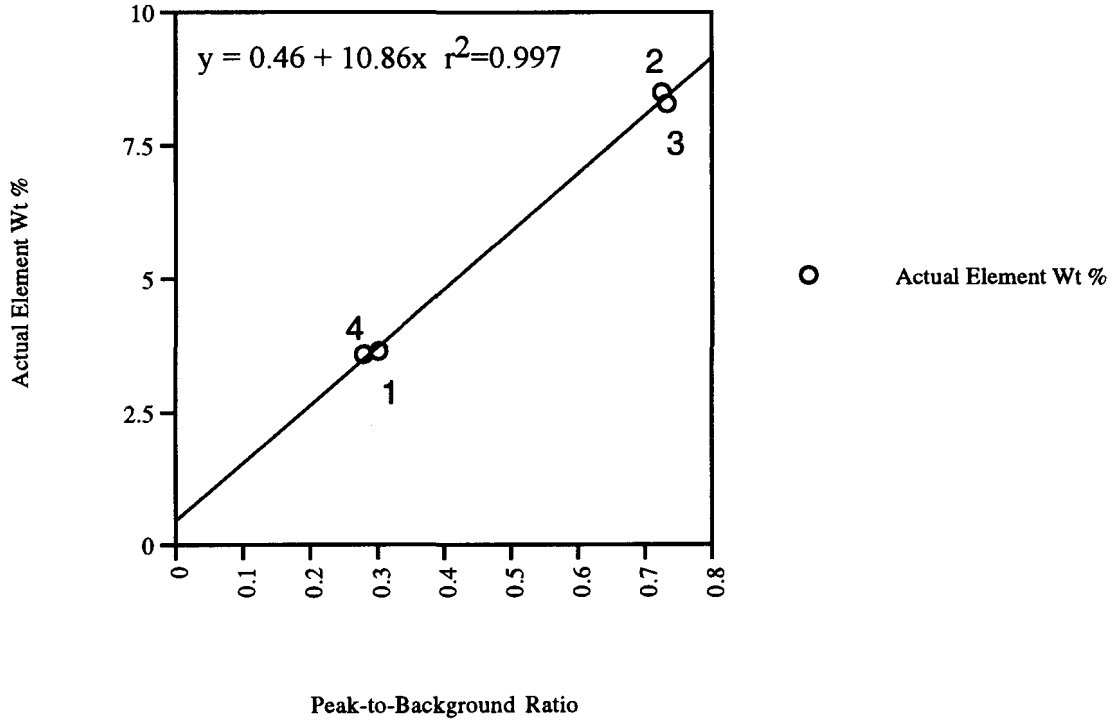
**Table 4. Calibration equations (see Appendix B for calibration graphs)**

Element	Calibration Equation
Na	$y = -0.06 + 10.87x$
Mg	$y = 0.84 + 8.18x$
K	$y = 0.05 + 6.64x$
Ca	$y = 0.13 + 6.43x$
Ti	$y = 0.08 + 6.95x$
Mn	$y = 0.05 + 3.25x$
Fe	$y = 0.46 + 10.86x$

#### **Analysis of the spherules**

The seven spherules were analyzed quantitatively by the same procedure used to analyze the standards. Three separate analyses were performed on each sphere. The locations on the spherules were chosen to avoid surface particles. A summary of the analyses is listed in Table 5. The ZAF-PB corrected concentrations were used for oxygen, aluminum, and silicon. The other elemental concentrations were determined by substituting the average peak to background ratio for the  $x$  value in the calibration equations in Table 4. For undetermined reasons, the oxygen concentration of spherules RS-1,2,3,4 and MM-1 was

Iron Calibration Graph



**Figure 1.** The calibration graph for iron. Each dot represents the average peak-to-background ratio determined by SEM analysis versus the actual element weight percent of each standard as determined by Jarosevich et al. (1980). 1 = Cr-Augite  
2 = Hornblende  
3 = Pyrope  
4 = Omphacite

present in elemental oxides, and by comparing that number to the moles of oxygen from the ZAF-PB analyses. The differences ranged from 8.45% to 11.79%. Therefore, the oxygen concentrations were replaced by the calculated values derived from the oxides for these 5 spherules. A sample calculation is presented in Figure 2, and the corrected oxygen values were used to determine the normalized values listed in Table 5. Appendix C presents the unprocessed analyses of the spherules.

Spherule RS-1	Avg. Calibration	Anion moles	oxygen moles	Wt % of oxygen
SiO <sub>2</sub>	39.03	1.390	2.779	
Al <sub>2</sub> O <sub>3</sub>	0.30	0.006	0.017	
FeO	1.25	0.022	0.022	
MgO	3.20	0.132	0.132	
CaO	6.76	0.169	0.169	
Na <sub>2</sub> O	2.64	0.057	0.057	
K <sub>2</sub> O	0.13	0.002	0.002	
TiO <sub>2</sub>	0.12	0.002	0.005	
MnO	0.00	0.000	0.000	
		<b>Total oxygen:</b>	<b>3.183</b>	<b>50.92*</b>
		<b>Analysis:</b>	<b>3.478</b>	<b>55.64</b>
		<b>% difference:</b>	<b>8.48</b>	

**Figure 2.** Sample calculation of the total moles of oxygen that should be present in the elemental oxides of the elements that were analyzed for spherule RS-1. The anion moles were calculated by the average calibration by the anion atomic weight. The oxygen moles were determined from the oxygen to anion ratio which is given by the chemical formulas of the oxides. The calculated weight percent value of oxygen (\*) was then used as the average calibrated value for oxygen. The analyses of the spherules could then be normalized to 100%.

**Table 5. Summary of the analyses of the spherules. The analyses have been calibrated, averaged, been removed of excess oxygen, and normalized to 100%.**

Element	RS-1 % concentration, normalized	RS-2 % concentration, normalized	RS-3 % concentration, normalized	RS-4 % concentration, normalized	MM-1 % concentration, normalized	MM-2 % concentration, normalized	AD-1 % concentration, normalized
O	48.80	48.84	48.91	48.80	42.93	43.54	48.13
Na	2.53	2.46	2.18	2.72	0.32	0.46	0.97
Mg	3.07	2.99	2.94	3.11	13.97	12.57	4.59
Al	0.29	0.18	0.17	0.41	4.95	7.31	22.06
Si	37.40	37.54	37.68	37.30	21.43	22.49	20.05
K	0.12	0.08	0.08	0.07	1.02	2.24	0.30
Ca	6.48	6.83	6.94	6.66	0.89	0.83	0.67
Ti	0.11	0.15	0.14	0.16	0.23	0.22	0.44
Mn	0.00	0.06	0.06	0.11	0.07	0.05	0.16
Fe	1.20	0.89	0.89	0.66	14.17	10.29	2.63
TOTAL	100.00	100.00	100.00	100.00	100.00	100.00	100.00

## Results

The results presented in Table 5 show that not only are the clear spherules (RS-1,2,3, and 4) physically different from the dark spherules (MM-1 and 2, and AD-1), but they are also chemically different. The clear spherules contain high concentrations of oxygen and silicon, as well as a significant calcium content. On the other hand, the dark spherules are composed mostly of oxygen, magnesium, aluminum, silicon, and iron. Based on the physical and compositional differences, the clear and dark spherules will be considered separately.

### The Clear Spherules

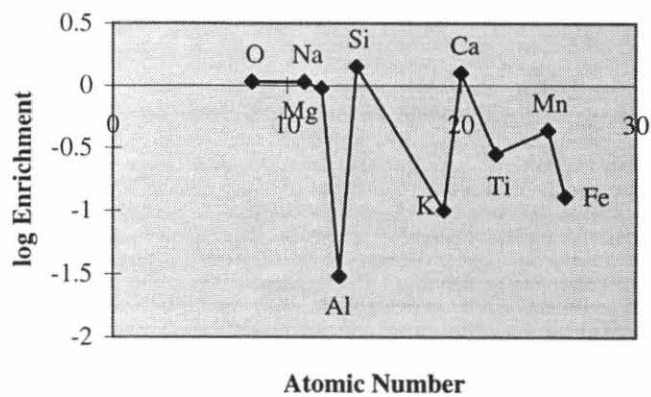
The clear spherules are so similar chemically that they can be considered by their average composition. Since these spherules were recovered from seafloor sediments, the ratios of the elemental concentrations of the spherules were compared to the elemental ratios of bulk seawater. The only ratio found to be of any significant interest was that of potassium (K) to sodium (Na). The K:Na ratio of bulk seawater is 0.0369, and that of the average clear spherule is 0.0356. These ratios are indistinguishable and thereby demonstrate that the K:Na ratio of the spherules is nearly identical to that of seawater. This is likely a result of K and Na salts that were deposited in the pores and on the surface of the clear spherules as seawater evaporated from them when they were brought out of the ocean. Because no other elemental ratios can be matched, it is unlikely that the spherules consist of marine salts.

Next, the spherules were compared to the elemental concentrations of the bulk continental crust (Faure, 1991) and CI chondrites (Taylor and McClennan, 1985). The comparison was made by dividing the individual elemental concentrations of the spherules by the individual elemental concentrations of the bulk continental crust or of CI chondrites. A ratio of 1.0 means that the spherule has the same elemental concentration as the bulk continental crust or CI chondrites. If the elemental ratio is greater than 1.0, then the spherule is enriched in that element with respect to the bulk continental crust or CI chondrites; if it is less than 1.0, then the spherule is depleted in that element. This ratio is called the enrichment factor.

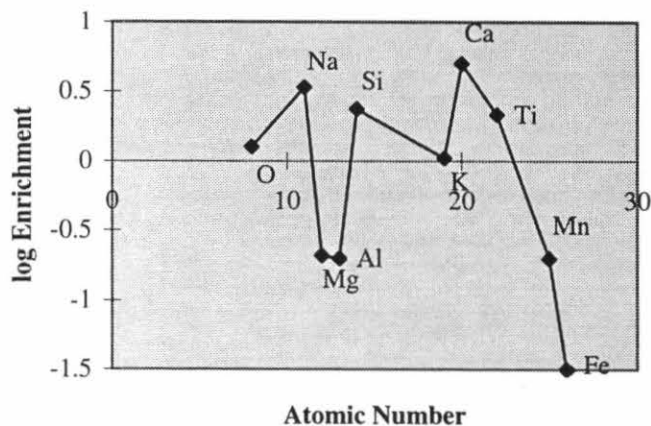
Figure 3 presents graphs of the log of the enrichment factors of the clear spherules versus the atomic number of each element in comparison to both the bulk continental crust and CI chondrites. Also included in the figure is a list of the enrichment factors, with the average and standard deviation. If the

Element	Sph/BCC	Sph/CIC
O	1.07	1.27
Na	1.07	3.41
Mg	0.95	0.21
AL	0.03	0.20
Si	1.40	2.34
K	0.1	1.06
Ca	1.27	4.98
Ti	0.28	2.14
Mn	0.43	0.20
Fe	0.13	0.03
<b>Average</b>	<b>0.67</b>	<b>1.58</b>
<b>Std. Dev.</b>	<b>0.53</b>	<b>1.64</b>

**Clear Spherules/Bulk Continental Crust Composition**



**Clear Spherule/CI Chondrite Composition**



**Figure 3.** Comparisons of the average composition of the clear spherules to the compositions of the bulk continental crust and CI chondrites.



average of the enrichment factors relative to the bulk continental crust is closer to 1.0 than the average enrichment factors relative to CI chondrites, then the clear spherules are more similar to the composition of the bulk continental crust, and vice-versa. The data and graphs presented in Figure 3 demonstrate that the clear spherules most closely resemble the composition of the bulk continental crust.

### **Origin of the Clear Spherules**

Since the clear spherules are most similar to the composition of the bulk continental crust, the probability of them being extraterrestrial is low, so they were most likely formed on the Earth. I would like to put forward the hypothesis that they are opaline and were produced biochemically. This hypothesis is based on four factors: 1) the high concentrations of oxygen and silicon;

2) the presence of excess oxygen;

3) the uniformity amongst the spherules; and

4) the high sphericity of the spherules.

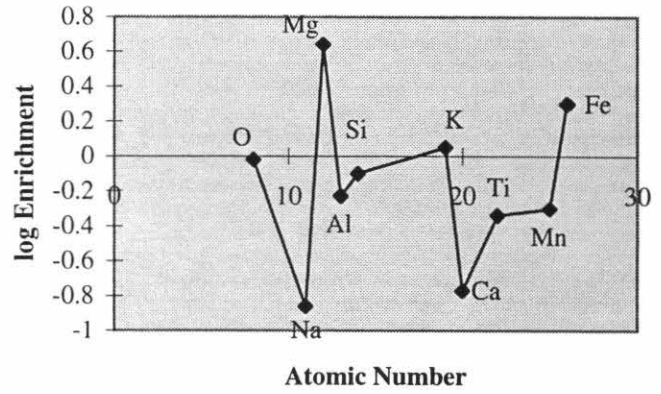
A high concentration of  $\text{SiO}_2$  would be consistent with the chemistry of opal ( $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), and the excess oxygen may possibly indicate the presence of  $\text{OH}^-$  radicals that are found in the opal structure. It should be noted that the scanning electron microscope cannot detect the presence of hydrogen. The uniformity amongst the spherules indicates that they formed by a common process. The sphericity suggests that they are biochemically precipitated, because inorganic opal is amorphous, so they had to have been shaped. Unfortunately, the analyses give no insight as to what sort of organism might have produced these spherules, except that they are probably marine organisms. A cross-section and internal analysis of the clear spherules might provide further clues as to their origin.

### **The Dark Spherules**

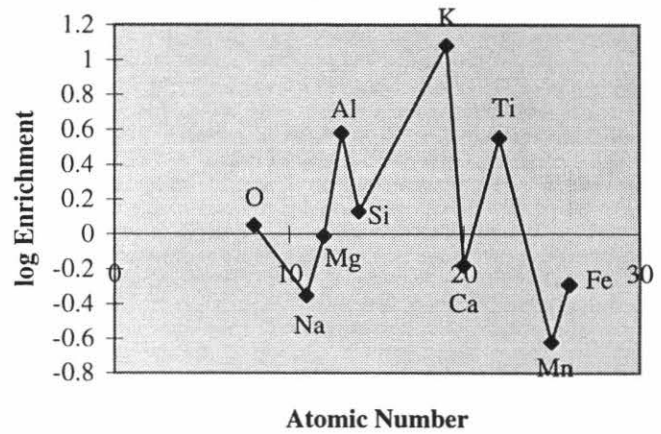
The three dark spherules are all compositionally distinct, so they cannot be considered by an average composition. These spherules were compared to the bulk continental crust and CI chondrites in the same manner as the clear spherules. The graphs and enrichment factors for each spherule are presented in Figures 4, 5, and 6. The results are inconclusive. At first glance, all three spherules more closely resemble the bulk continental crust than CI chondrites. In the cases of MM-1 and MM-2, however, if the enrichment factors for aluminum and potassium are removed from the averages, they much more closely

Element	Sph/BCC	Sph/CIC
O	0.94	1.12
Na	0.14	0.44
Mg	4.36	0.98
AL	0.59	3.84
Si	0.80	1.34
K	1.13	12.07
Ca	0.17	0.66
Ti	0.46	3.52
Mn	0.50	0.24
Fe	2.01	0.51
<b>Average</b>	<b>1.11</b>	<b>2.47</b>
<b>Std. Dev.</b>	<b>1.20</b>	<b>3.42</b>

#### MM-1/Bulk Continental Crust Composition



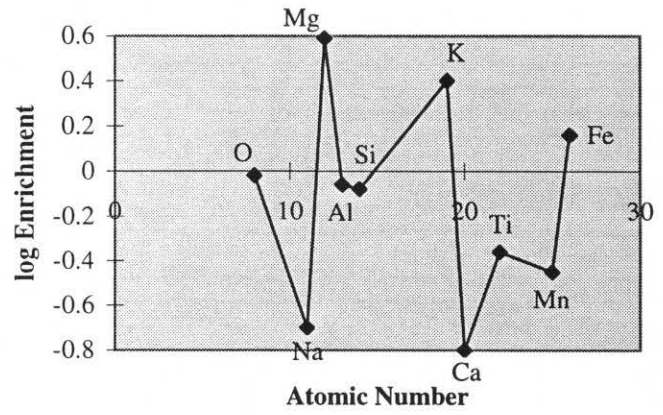
#### MM-1/CI Chondrite Composition



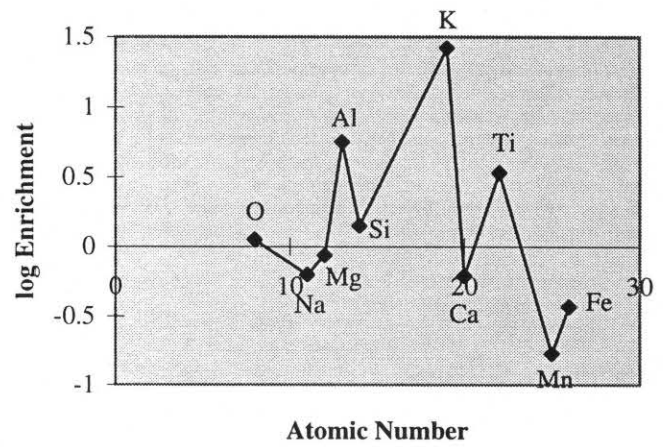
**Figure 4.** Comparisons of spherule MM-1 to the compositions of the bulk continental crust and CI chondrites.

Element	Sph/BCC	Sph/CIC
O	0.96	1.13
Na	0.20	0.63
Mg	3.93	0.88
Al	0.87	5.67
Si	0.84	1.40
K	2.49	26.23
Ca	0.16	0.61
Ti	0.44	3.36
Mn	0.36	0.17
Fe	1.46	0.36
<b>Average</b>	<b>1.17</b>	<b>4.04</b>
<b>Std. Dev.</b>	<b>1.19</b>	<b>7.98</b>

### MM-2/Bulk Continental Crust Composition



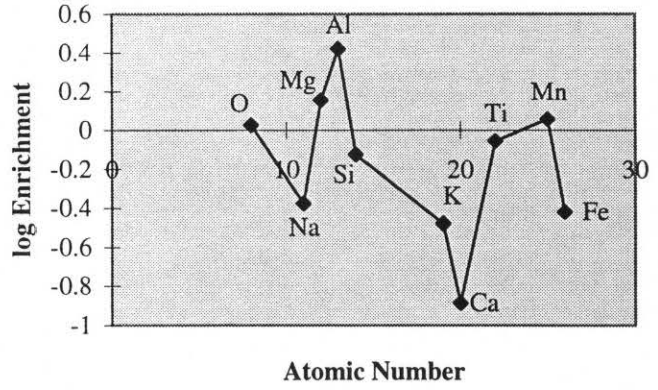
### MM-2/CI Chondrite Composition



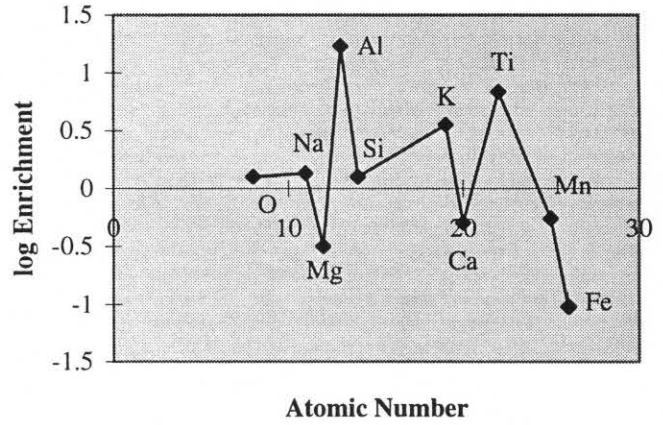
**Figure 5.** Comparisons of spherule MM-2 to the compositions of the bulk continental crust and CI chondrites.

Element	Sph/BCC	Sph/CIC
O	1.06	1.25
Na	0.42	1.34
Mg	1.43	0.32
AL	2.63	17.10
Si	0.75	1.25
K	0.33	3.51
Ca	0.13	0.50
Ti	0.88	6.73
Mn	1.14	0.54
Fe	0.37	0.09
<b>Average</b>	<b>0.91</b>	<b>3.26</b>
<b>Std. Dev.</b>	<b>0.73</b>	<b>5.26</b>

### AD-1/Bulk Continental Crust Composition



### AD-1/CI Chondrite Composition



**Figure 6.** Comparisons of spherule AD-1 to the compositions of the bulk continental crust and CI chondrites.

resemble the composition of CI chondrites. Therefore, these two spherules may be extraterrestrial in origin and happen to be enriched in these two elements. The spherule from the Adirondacks resembles the bulk continental crust even when the high enrichment factors are removed from the average of the CI chondrite comparison. Therefore, there is a strong possibility that this spherule is terrestrial in origin.

### **Origin of the Dark Spherules**

One factor common to all three of these spherules is that they were found in glacial sediments. This would suggest that the spherules were at one time embedded in ice sheets, with MM-1 and 2 in the Antarctic ice sheet and AD-1 in the continental Laurentide ice sheet that covered New York during the Pleistocene Epoch. The spherules presumably traveled with the ice and were released in the zone of ablation of the glacier to be deposited with the glacial sediments in which they were later found. Alternatively, spherules MM-1 and 2 from Antarctica may have been transported to the Meteorite Moraine by wind, whereas AD-1 could have been deposited by either wind or running water.

If any of the spherules are extraterrestrial in origin, they were likely formed in the ablation trails of meteorites moving through the Earth's atmosphere at high speeds. They would have then fallen onto the ice in which they became embedded. If any of the black spherules are terrestrial in origin, they provide no clues as to what process may have formed them. For example, they may have been ejected by volcanic activity into the atmosphere before falling onto the ice. Additional analyses of a cross-section would be useful. In addition the rare earth element concentrations may also provide insight into the origin of these dark spherules.

### **Summary**

The four clear spherules described were determined to be of terrestrial origin based on the fact that they most closely resemble the composition of the bulk continental crust. They were most likely formed biochemically by marine organisms based on their composition and structure. The results of the analyses of the dark spherules are inconclusive, and they may be either terrestrial or extraterrestrial in origin. This study also demonstrates that a scanning electron microscope equipped with EDX can be used to provide a reliable quantitative chemical analysis of these spherules when calibration factors are used.

### **Acknowledgments**

Thanks to Dr. Gunter Faure for providing me with an excellent research project, project funding, and a great deal of his time whenever I needed his help or advice. I would also like to thank John Mitchell for running the SEM analyses, and for always going the extra mile by using much of his personal time to do this. Thank you to Dr. Micheal Barton of the Ohio State University Microprobe Laboratory for providing the standard block used for the SEM calibrations. Finally, I would like to thank my mother, Lynn R. Everett, for providing assistance with computer applications, and for her general support. This research was funded by NSF grant DPP-9118485.

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## **APPENDIX A**

### **Unprocessed Data from the Analyses of the Standards**

**Table 6. Unprocessed Data from Analysis of Standard 1.**

1. Cr-Augite	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.363	53.01	1.283	50.23	1.322	51.19
Na	0.066	0.37	0.069	0.39	0.057	0.32
Mg	1.149	12.86	1.133	12.79	1.137	12.69
Al	0.498	4.58	0.492	4.56	0.510	4.68
Si	3.163	26.64	3.157	26.79	3.206	26.91
K	0.000	0.00	0.019	0.13	0.017	0.12
Ca	1.864	12.43	1.964	13.20	1.937	12.88
Ti	0.074	.63	0.058	0.50	0.034	0.29
Mn	0.024	.28	0.054	0.64	0.000	0.00
Fe	0.353	3.88	0.266	2.95	0.286	3.13

**Table 7. Unprocessed Data from Analysis of Standard 2.**

2. Hornblende	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.220	49.01	1.167	47.08	1.242	50.71
Na	0.178	1.03	0.184	1.07	0.185	1.08
Mg	0.842	9.71	0.825	9.56	0.798	9.35
Al	0.973	9.25	0.910	8.69	0.917	8.86
Si	2.495	21.64	2.359	20.55	2.464	21.72
K	0.240	1.76	0.257	1.89	0.249	1.86
Ca	1.067	7.32	1.005	6.92	1.053	7.34
Ti	0.382	3.36	0.401	3.55	0.397	3.55
Mn	0.012	0.14	0.000	0.00	0.000	0.00
Fe	0.648	7.35	0.671	7.65	0.856	9.86

**Table 8. Unprocessed Data from Analysis of Standard 3.**

3. Pyrope	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.287	50.22	1.240	47.65	1.211	47.68
Na	0.018	0.10	0.019	0.11	0.011	0.06
Mg	1.259	14.03	1.316	14.45	1.265	14.22
Al	1.504	13.78	1.566	14.15	1.551	14.34
Si	2.585	21.58	2.597	21.37	2.566	21.61
K	0.006	0.04	0.000	0.00	0.000	0.00
Ca	0.648	4.30	0.608	3.97	0.560	3.75
Ti	0.020	0.17	0.000	0.00	0.000	0.00
Mn	0.000	0.00	0.000	0.00	0.078	0.92
Fe	0.789	8.64	0.636	6.86	0.773	8.54

**Table 9. Unprocessed Data from Analysis of Standard 4.**

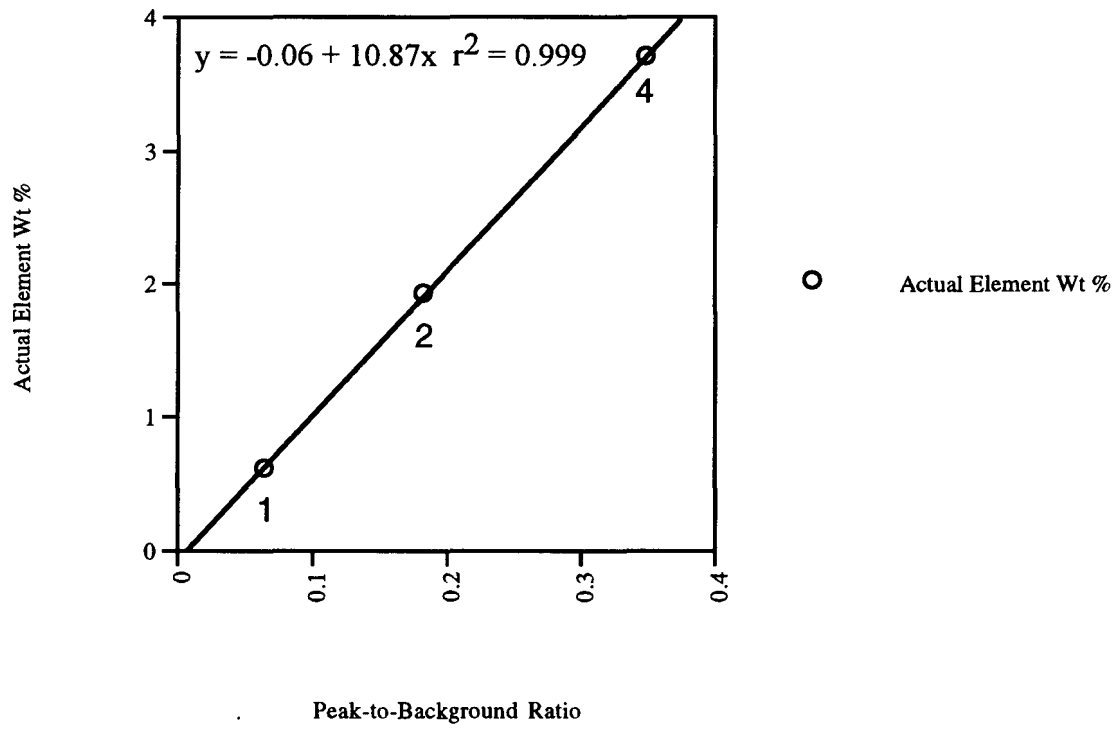
4. Omphacite	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.382	52.08	1.359	52.20	1.339	51.14
Na	0.351	1.90	0.344	1.90	0.350	1.92
Mg	0.750	8.12	0.816	9.00	0.757	8.30
Al	0.577	5.14	0.596	5.41	0.555	5.01
Si	3.501	28.55	3.532	29.35	3.378	27.92
K	0.000	0.00	0.017	0.12	0.016	0.11
Ca	1.464	9.46	1.518	9.98	1.541	10.08
Ti	0.007	0.06	0.015	0.12	0.050	0.42
Mn	0.000	0.00	0.055	0.64	0.014	0.16
Fe	0.279	2.97	0.300	3.25	0.262	2.82

## **APPENDIX B**

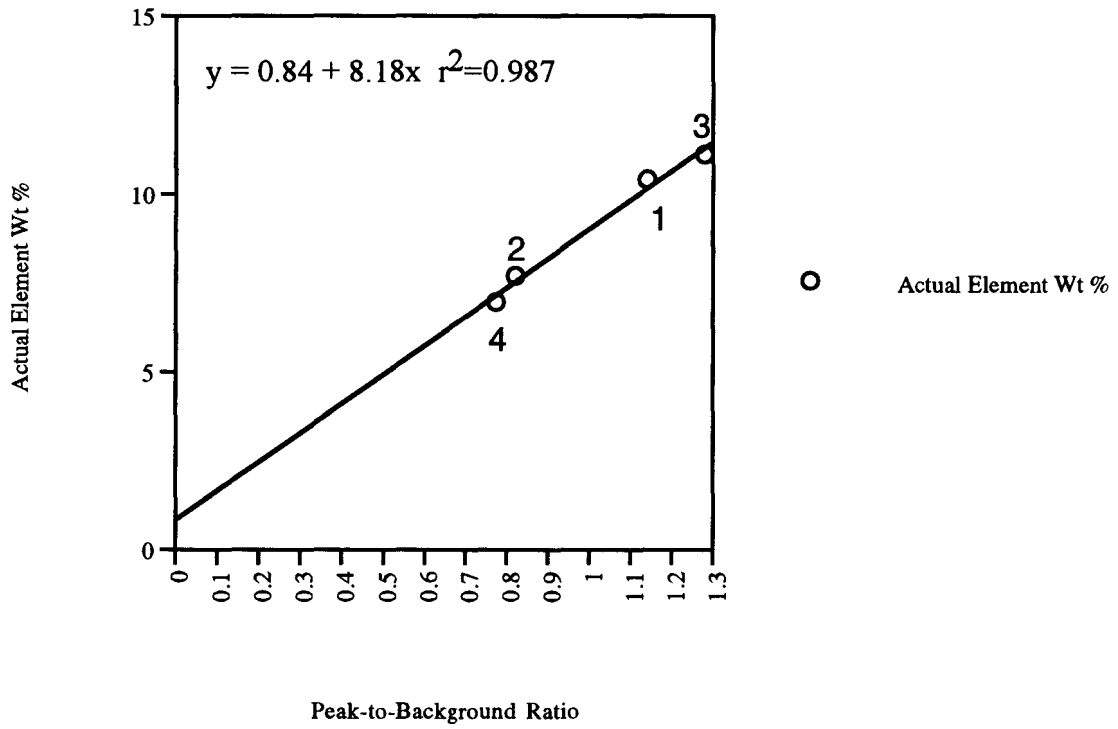
### **Calibration Graphs Determined from the Analyses of the Standards**

- 1 = Cr-Augite**
- 2 = Hornblende**
- 3 = Pyrope**
- 4 = Omphacite**

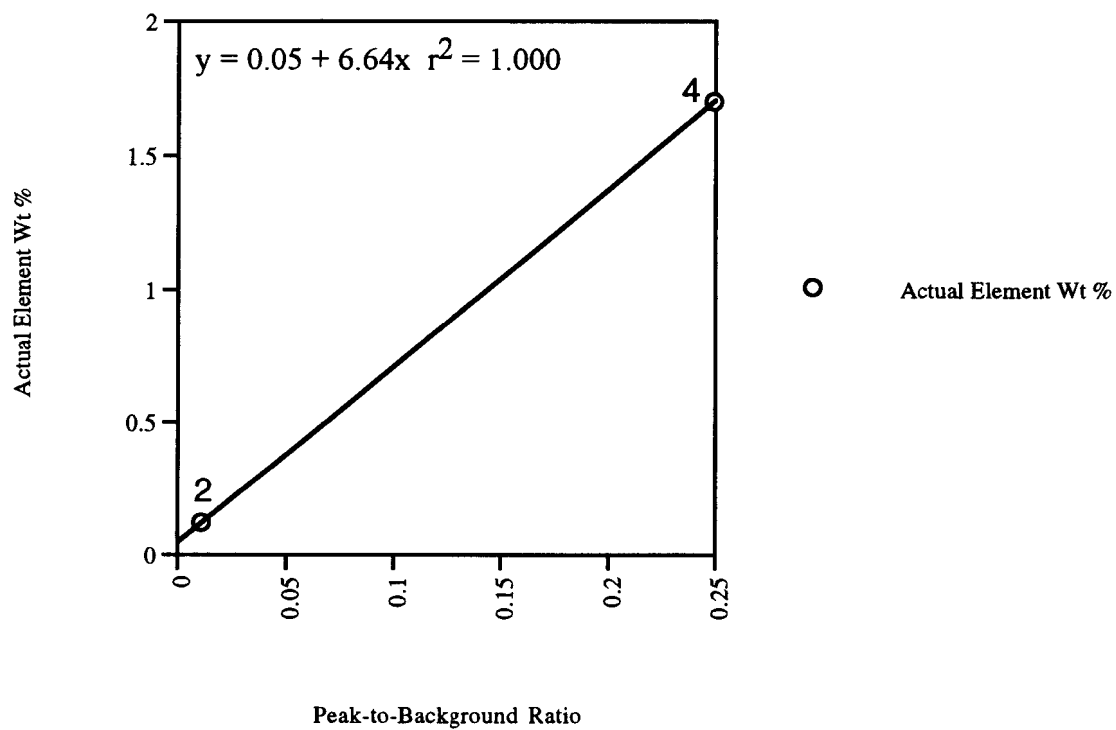
Sodium Calibration Graph



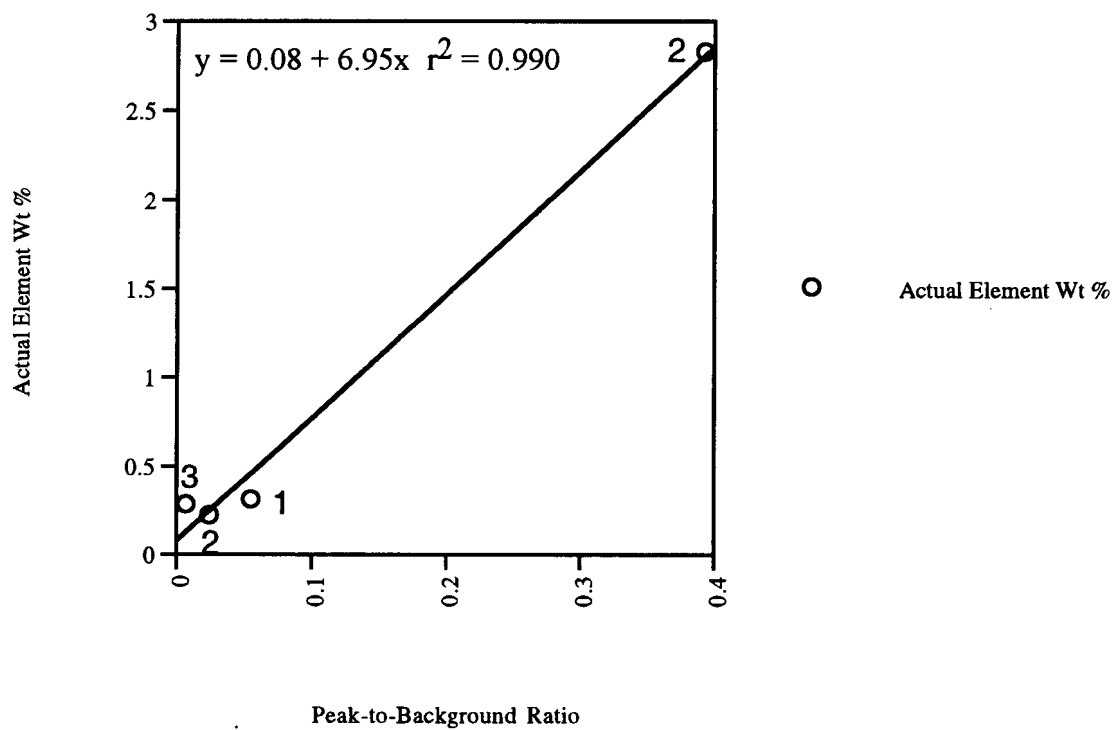
Magnesium Calibration Graph



Potassium Calibration Graph

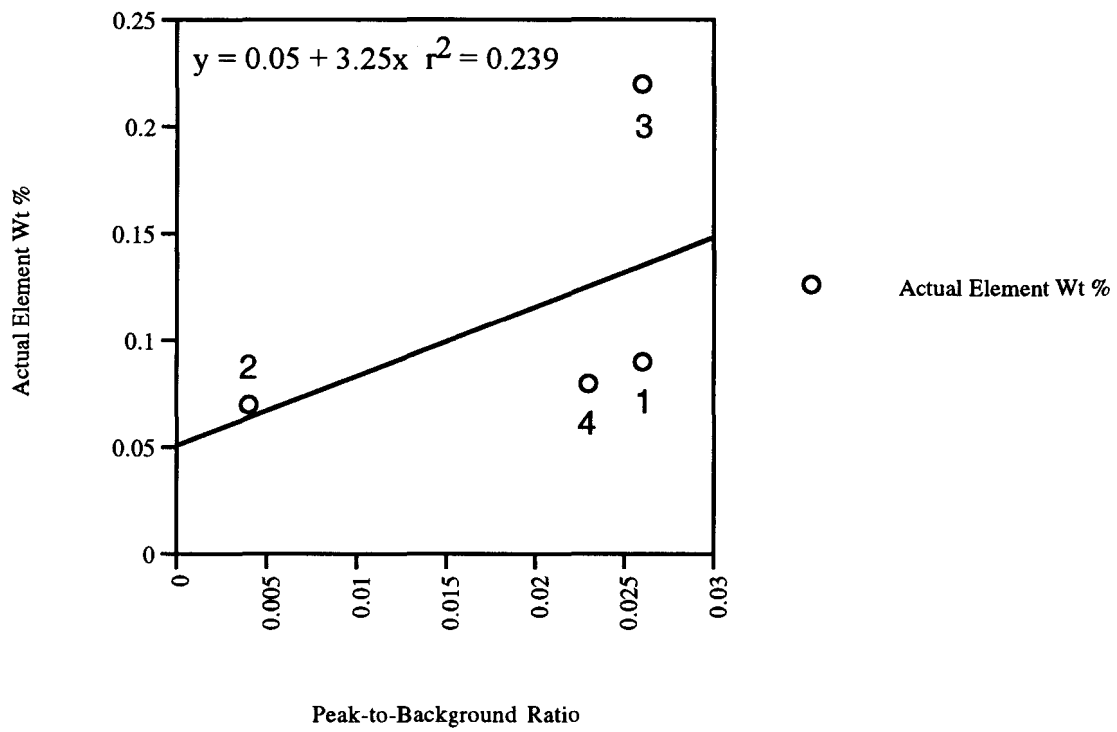


Titanium Calibration Graph

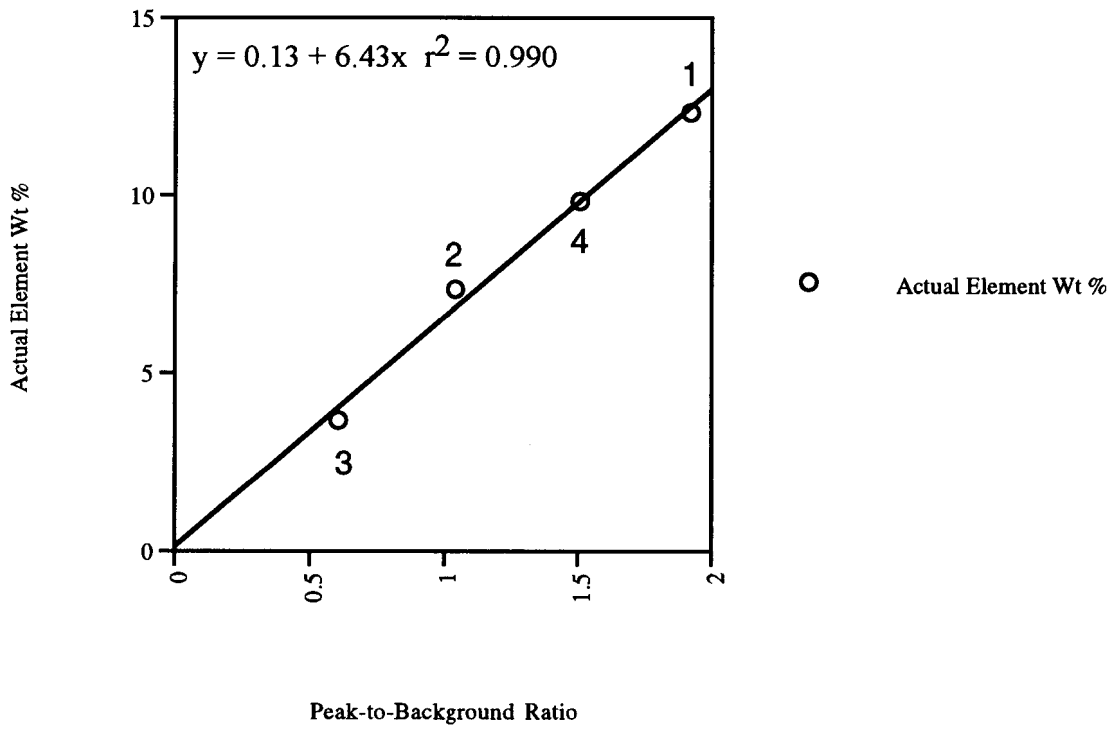




Manganese Calibration Graph



Calcium Calibration Graph



## **APPENDIX C**

### **Unprocessed Data from the Analyses of the Spherules**

**Table 10. Unprocessed Data from Analysis of Spherule RS-1.**

RS-1	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.461	53.70	1.526	55.87	1.585	57.35
Na	0.329	1.74	0.206	1.09	0.209	1.09
Mg	0.279	2.94	0.301	3.16	0.286	2.97
Al	0.027	0.23	0.040	0.34	0.040	0.34
Si	4.632	36.93	5.101	40.55	5.047	39.62
K	0.005	0.03	0.004	0.03	0.027	0.18
Ca	1.010	6.35	1.103	6.91	0.978	6.05
Ti	0.000	0.00	0.023	0.19	0.005	0.04
Mn	0.000	0.00	0.000	0.00	0.000	0.00
Fe	0.136	1.41	0.038	0.39	0.043	0.44

**Table 11. Unprocessed Data from Analysis of Spherule RS-2.**

RS-2	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.559	57.02	1.717	61.92	1.528	55.70
Na	0.230	1.21	0.200	1.03	0.302	1.58
Mg	0.275	2.88	0.285	2.94	0.286	2.99
Al	0.019	0.16	0.022	0.19	0.024	0.21
Si	5.121	40.65	5.022	39.24	4.914	38.90
K	0.002	0.01	0.000	0.00	0.013	0.09
Ca	1.082	6.76	1.106	6.82	1.110	6.92
Ti	0.001	0.01	0.000	0.00	0.032	0.25
Mn	0.008	0.09	0.000	0.00	0.005	0.05
Fe	0.052	0.54	0.075	0.76	0.006	0.06

**Table 12. Unprocessed Data from Analysis of Spherule RS-3.**

RS-3	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.663	60.43	1.630	59.32	1.638	59.46
Na	0.218	1.14	0.192	1.00	0.254	1.33
Mg	0.292	3.04	0.276	2.87	0.288	3.00
Al	0.027	0.23	0.018	0.15	0.017	0.15
Si	5.157	40.69	5.148	40.66	5.131	40.39
K	0.009	0.06	0.000	0.00	0.008	0.05
Ca	1.207	7.51	1.157	7.20	1.059	6.57
Ti	0.013	0.10	0.008	0.07	0.010	0.08
Mn	0.000	0.00	0.000	0.00	0.021	0.23
Fe	0.052	0.54	0.054	0.56	0.033	0.34

**Table 13. Unprocessed Data from Analysis of Spherule RS-4.**

RS-4	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.474	53.62	1.507	53.97	1.594	58.23
Na	0.336	1.76	0.244	1.26	0.195	1.02
Mg	0.285	2.97	0.280	2.88	0.279	2.92
Al	0.053	0.45	0.050	0.42	0.041	0.35
Si	4.682	36.95	4.677	36.33	5.009	39.67
K	0.008	0.05	0.002	0.02	0.000	0.00
Ca	1.020	6.35	0.969	5.94	1.087	6.79
Ti	0.026	0.21	0.007	0.05	0.002	0.01
Mn	0.018	0.20	0.000	0.00	0.039	0.43
Fe	0.006	0.06	0.000	0.00	0.051	0.52

**Table 14. Unprocessed Data from Analysis of Spherule MM-1.**

MM-1	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	0.933	38.89	1.025	42.42	1.031	40.30
Na	0.022	0.13	0.032	0.19	0.039	0.22
Mg	1.622	19.20	1.543	18.12	0.944	10.52
Al	0.217	2.11	0.288	2.78	0.864	7.92
Si	1.929	17.13	2.097	18.48	2.365	19.80
K	0.062	0.47	0.078	0.58	0.233	1.66
Ca	0.075	0.53	0.077	0.54	0.145	0.97
Ti	0.041	0.37	0.005	0.05	0.006	0.05
Mn	0.021	0.27	0.007	0.08	0.000	0.00
Fe	1.226	14.29	1.290	14.90	0.729	8.01

**Table 15. Unprocessed Data from Analysis of Spherule MM-2.**

MM-2	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.103	43.59	1.057	42.76	1.065	42.43
Na	0.054	0.31	0.037	0.21	0.050	0.29
Mg	1.205	13.60	1.658	19.12	1.376	15.65
Al	0.927	8.60	0.625	5.90	0.764	7.13
Si	2.521	21.35	2.589	22.38	2.674	22.81
K	0.423	3.05	0.252	1.85	0.299	2.17
Ca	0.135	0.91	0.077	0.53	0.111	0.75
Ti	0.032	0.27	0.000	0.00	0.037	0.32
Mn	0.000	0.00	0.030	0.37	0.000	0.00
Fe	0.798	8.85	1.016	11.51	0.861	9.62

**Table 16. Unprocessed Data from Analysis of Spherule AD-1.**

AD-1	Analysis 1		Analysis 2		Analysis 3	
Element	P/B	ZAF %	P/B	ZAF%	P/B	ZAF%
O	1.206	43.23	1.160	42.59	1.173	41.11
Na	0.078	0.40	0.083	0.43	0.089	0.44
Mg	0.404	4.13	0.406	4.25	0.351	3.50
Al	2.402	20.32	2.252	19.49	2.173	17.92
Si	2.319	17.77	2.289	17.95	2.239	16.73
K	0.000	0.00	0.058	0.39	0.045	0.29
Ca	0.131	0.80	0.103	0.64	0.000	0.00
Ti	0.111	0.87	0.030	0.24	0.000	0.00
Mn	0.037	0.40	0.017	0.18	0.028	0.29
Fe	0.116	1.16	0.319	3.28	0.072	0.70