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Trace Element Analyses of Spheres from the Melt Zone of the Greenland Ice Cap Using Synchrotron X Ray Fluorescence

P. CHEVALLIER¹, C. JEHANNO², M. MAURETTE³, S. R. SUTTON⁴ AND J. WANG¹

Synchrotron X ray fluorescence spectra of unpolished iron and chondritic spheres extracted from sediments collected on the melt zone of the Greenland ice cap allow the analysis of Ni, Cu, Zn, Ga, Ge, Pb, and Se with minimum detection limits on the order of several parts per million. All detected elements are depleted relative to chondritic abundance with the exception of Pb, which shows enrichments up to a factor of 500. An apparent anticorrelation between the Ni-content and trace element concentration was observed in both types of spherules. The fractionation patterns of the iron and chondritic spheres are not complementary and consequently the two iron spheres examined in this study are unlikely to result from the ejection of globules of Fe/Ni from parent chondritic micrometeoroids.

INTRODUCTION

Elemental compositions are important in understanding the source(s) of extraterrestrial particles and their alteration by atmospheric ablation and terrestrial weathering. Previous electron microprobe measurements on deep sea particles, as well as a few INAA analyses [Ganapathy and Brownlee, 1978], have shown that siderophile and volatile elements are depleted relative to chondritic abundances. In this paper we report our first attempt to use X ray fluorescence excited by synchrotron radiation (SXRF) to determine the trace element content of spheres extracted from sediments collected on the bottom of small lakes formed during the short Arctic summer on the melt zone of the Greenland ice cap [Maurette *et al.*, 1986]. SXRF analysis of these particles is attractive for several reasons. First, the high sensitivity permits the measurement of trace elements with different geochemical character and volatilities. Second, the analyses are nondestructive, leaving the particles available for further study by other techniques. Nickel, Zn, Cu, Ga, Ge, Pb, and Se have been detected in the spherules using this technique with minimum detection limits of the order of several ppm. A secondary objective of this research is to correlate the fractionation trends observed for the trace elements to high contrast textural observations of polished sections of the spheres with a JEOL-JSM-840 scanning electron microscope [Bonte *et al.*, 1986].

SAMPLES

Particles were extracted mechanically from the melt lake sediment by scrubbing over a 100 micrometer wire mesh to remove algae, exposing the material to water only. Spheres were then handpicked under an optical microscope. SEM characterization of polished specimens have revealed the following: (1) The Greenland chondritic spheres are much less corroded than deep sea spheres. The depth of the etch canals observed in most deep sea particles is about 100 micrometers (Figure 1, top) compared to the less than 10 micrometers observed in most Greenland spheres (Figure 1, bottom). The Greenland spheres are therefore more suitable than the deep sea spheres for analysis by SXRF before polishing. (2) Neither reaction products filling the etch canals nor secondary particles were observed adhering to the surface of the Greenland chondritic spheres. (3) Magnetite rims observed around the deep sea iron spheres are thicker than in the Greenland iron spheres (Figure 2). This last observation lends support to the hypothesis (J. Arnold, private communication, 1986) that secondary oxidation of the iron spheres occurs while they reside in their host sediments.

For SXRF analyses, the whole particles were simply attached to adhesive tape previously demonstrated to be of satisfactory purity. This technique minimized any contamination associated with usual polishing procedures and permitted the recuperation of the grains for other types of investigations.

EXPERIMENTAL

The majority of the analyses reported in this paper were performed using the SXRF facility of L.U.R.E. at Orsay. The primary synchrotron beam was monochromatized at 14 keV and focused with a curved highly oriented mosaic pyrolytic graphite crystal. The beam size was of the order of 1 mm, larger than the diameter of the spherules (about 300 micrometers). The fluorescence spectra were obtained with a wavelength dispersive spectrometer consisting of a flat mosaic graphite crystal viewed by a position sensitive proportional counter. The wavelength window of this detector is varied by changing the angle of the analyzing crystal and the resolution is inversely proportional to the crystal to detector distance. In the present work, the instrument was set to collect secondary X rays between 8 and 12 keV (Ni to Se (K lines) and Ta to Bi (L lines)). A second set of experiments was undertaken at the National Synchrotron Light Source at Brookhaven National Laboratory (beamline X26C) using a microbeam (typically 50 micrometers) of continuum synchrotron radiation and a Si(Li) energy dispersive spectrometer. Analysis of these data are still in progress and only preliminary observations are presented here. Spectra obtained for an infinitely-thick (i.e., much thicker than the characteristic absorption depth defined as the inverse of density times mass absorption coefficient) slab of Orgeuil

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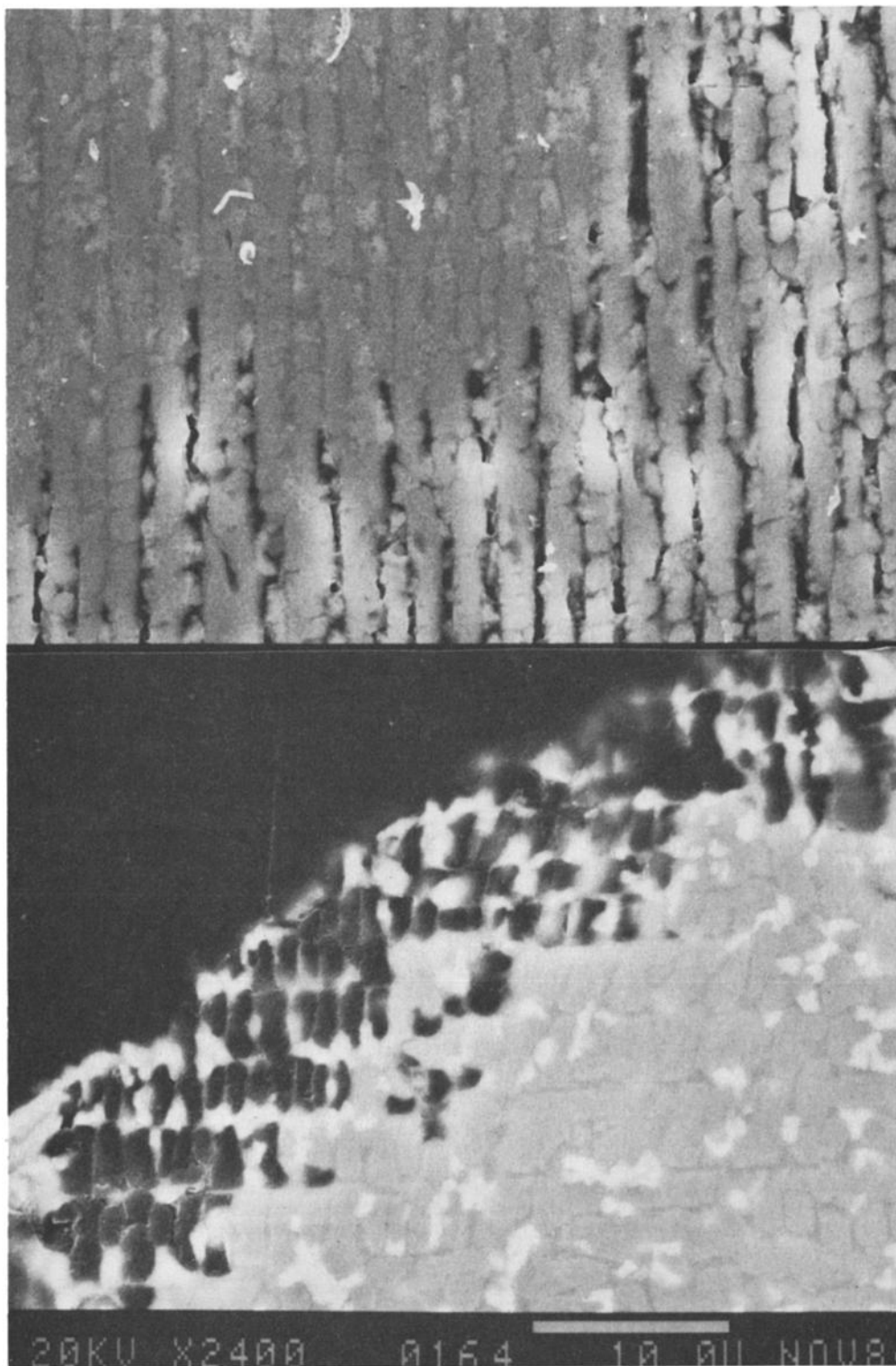


Fig. 1. SEM micrographs (courtesy of M. Wheelock) of chondritic spheres with a barred texture illustrating the much deeper etch canals observed in the deep sea sphere (top micrograph) than in the Greenland sphere (bottom micrograph).

with each of the two instruments are shown in Figure 3 for comparison. An easily discernible peak due to the 10 ppm of gallium is detectable in both spectra.

Elemental concentrations were calculated from the area of each spectral peak after correcting for attenuation of the incident beam through the depth of a uniform sphere and for

self-absorption of the outgoing fluorescence X rays. The incident flux was monitored during the SXRF measurements by routinely measuring the Ni fluorescence intensity from particles with known Ni content, i.e., those with sufficiently high Ni content to be measured with the electron probe.

For a homogeneous sphere of matrix m , density ρ , and ra-

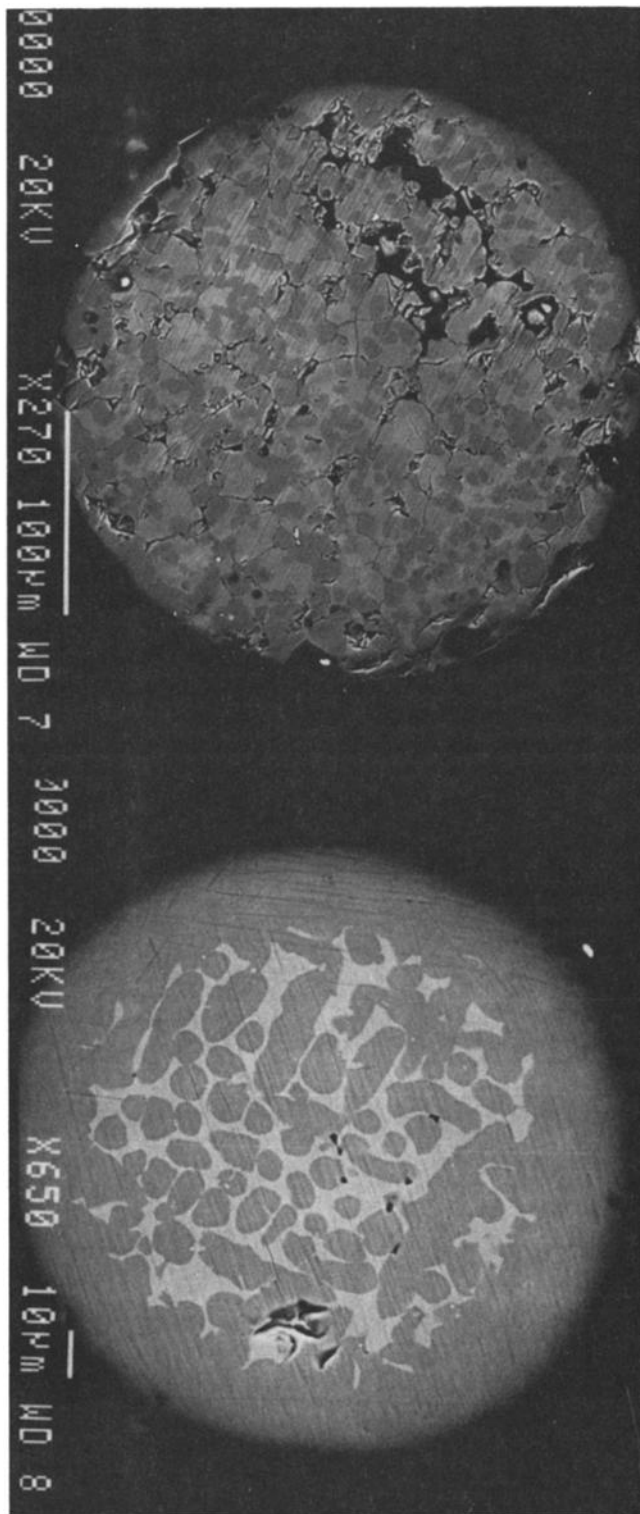


Fig. 2. SEM micrographs of iron spheres from Greenland (top) and from deep sea sediments (bottom) illustrating the thinner rim of magnetite generally observed on Greenland spheres.

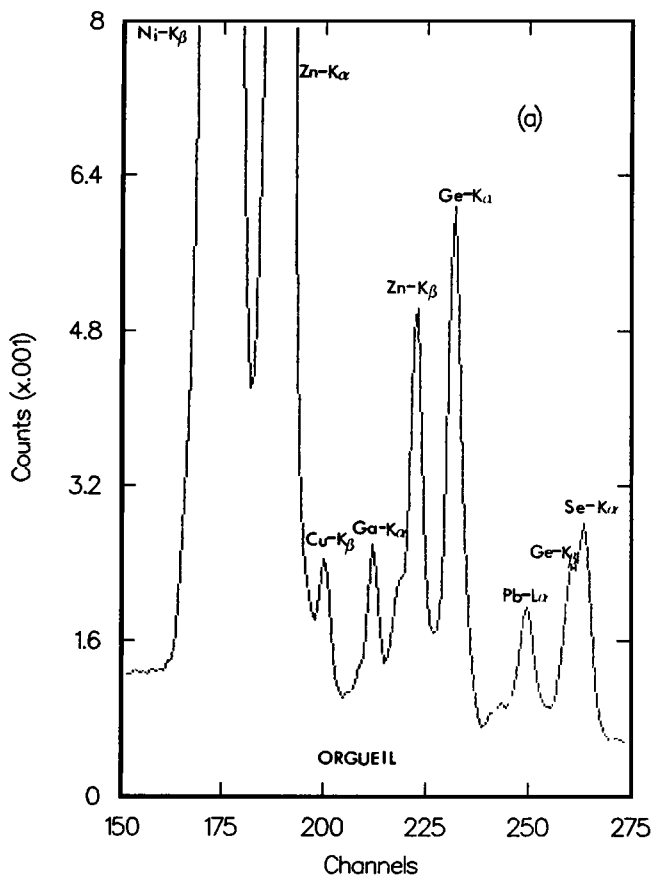
radius R_0 excited by nearly monochromatic radiation of energy E_0 , the concentration of element z in the sample C_z is related to the measured peak area I_z by

$$C_z = \frac{I_z}{\Phi} \quad (1)$$

The sensitivity factor Φ depends on the incident energy spectrum, the absorption characteristics of the sample and the detector efficiency ϵ and is given by

$$\Phi = \epsilon \rho P_z \int_E I_0(E) \mu_{m,z}(E) F(E) dE \quad (2)$$

The fluorescence parameter P_z is



SXRF Spectrum for the Orgueil Chondrite

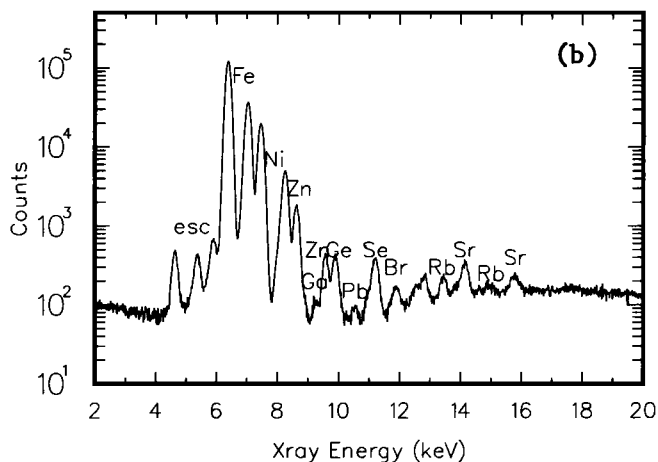


Fig. 3. Synchrotron X ray fluorescence spectra for Orgueil obtained with (a) the Orsay (monochromatic/wavelength dispersive) apparatus and (b) the Brookhaven (continuum/energy dispersive) apparatus.

TABLE 1. SXRF Results for Standards

Specimen	Ni (%)	Cu (ppm)	Zn (ppm)	Ga (ppm)	Ge (ppm)	Pb (ppm)	Se (ppm)
Orgueil (C1)	(1.1)	300	108	11.7	34	40	57
		(308)	(112)	(10)	(32)	(2.4)	(18)
Toluca (I)	(8.14)	2140	942	112	221	5200	< 10
		(33)	(140)	(70)	(246)	(na)	(na)
Sarepta (I)	(6.82)	176	79	73	142	86	< 10
		(na)	(200)	(100)	(457)	(na)	(na)
Negrillos (IIA)	(5.38)	652	115	104	166	272	< 10
		(na)	(113)	(59)	(179)	(na)	(na)
Gibeon (IVA)	(7.96)	326	165	10	< 10	308	< 10
		(1)	(170)	(2)	(0.1)	(na)	(na)

Literature values for bulk meteorite in parentheses [Buchwald, 1975].
na = not available.

$$P_x = \frac{J_K - 1}{J_K} \omega_K p_\alpha \quad (3)$$

(J_K , absorption edge jump ratio, ω_K , fluorescence yield; p_α , K_α to K_β ratio), the incident energy distribution is

$$I_o(E) = A \exp[-B E] \exp\left[\frac{-(E - E_o)^2}{2\sigma^2}\right] \quad (4)$$

(A and B are constants depending on the electron storage ring conditions, E_o is the energy corresponding to the Bragg take-off angle of the monochromator, and σ is its mosaic angular spread), and the absorption correction factor $F(E)$, for incident beam along the x axis and detection along the y axis, is given by

$$F(E) = \int_{-R_o}^{+R_o} \int_{-r}^{+r} \exp\left[-\left((R^2 - x^2)^{0.5} + y\right) \rho \mu_m(E)\right] + \left[\left((R^2 - y^2)^{0.5} + x\right) \rho \mu_m(\alpha)\right] dx dy d\zeta \quad (5)$$

[$r = (R_o^2 - \zeta^2)^{0.5}$; $\mu_{m,z}(E)$, mass attenuation coefficient for element z at energy E; $\mu_m(E)$, mass attenuation coefficient for the matrix at energy E; $\mu_m(\alpha)$, mass attenuation coefficient for the matrix at energy of the $K\alpha$ line of element z].

Mass attenuation coefficients were calculated from major element compositions determined using the JEOL-JSM-840 scanning electron microscope of the Centre des Faibles Radioactivites at Gif-sur-Yvette. Other constants were obtained from tabulated data [Veigele, 1971; Krause, 1979; Nelson et al., 1970]. Standards and Ni concentrations previously measured allow the determination of the constants ϵ, ρ, A , and B.

A complication in SXRF analyses is that effective depth analyzed depends on fluorescence X ray energy and matrix composition, typically tens of micrometers for iron spheres

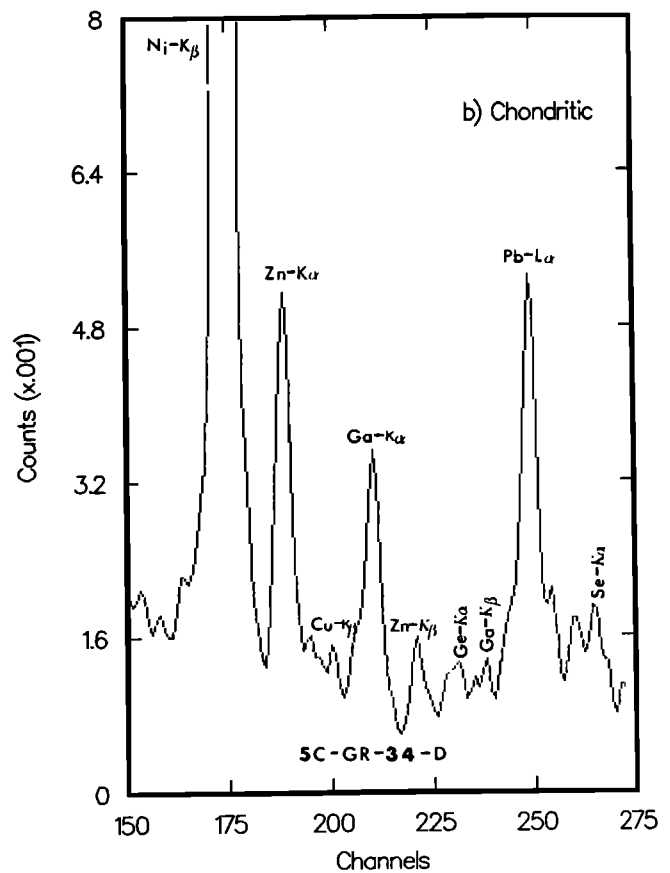
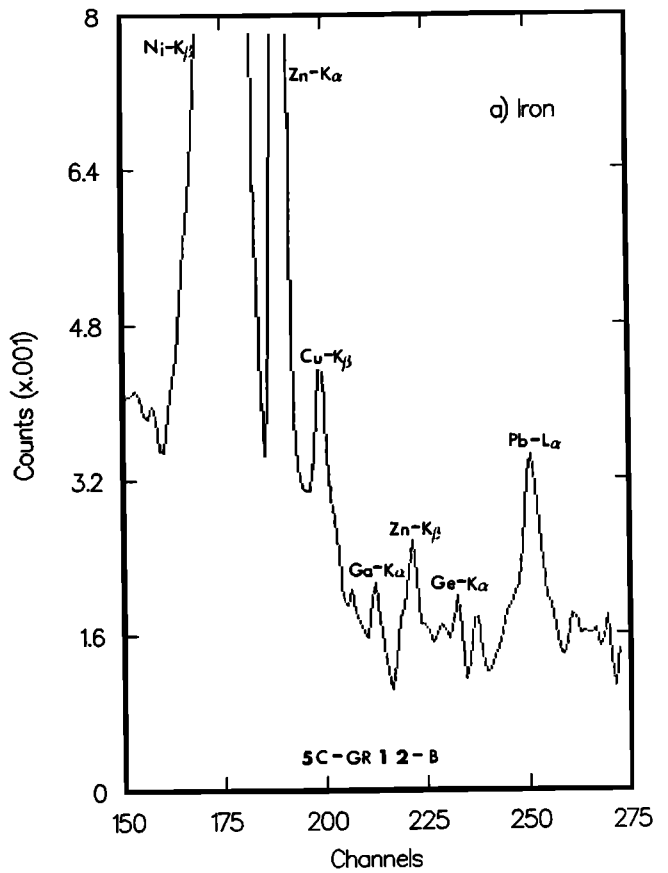


Fig. 4. Synchrotron X ray fluorescence spectra of (a) an iron and (b) a chondritic sphere obtained on the Orsay instrument.

TABLE 2. SXRF Results for Particles

Specimen	Ni (%)	Cu (ppm)	Zn (ppm)	Ga (ppm)	Ge (ppm)	Pb (ppm)	Se (ppm)
Chondritic							
A) 5ac	0.041	23	32	7.7	< 1	302	1.24
B) 5c(3.4)a	0.1124	< 10	84	17.6	3	1200	< 1
C) 5c(3.4)c	0.69	50	47	6.7	3	46	< 1
D) 5c(3.4)d	0.122	< 10	13.4	6.7	1.4	67	14.4
E) 5bb	0.0031	6.6	8.4	5.0	1.4	17	< 1
F) 5ba	0.98	86	83	2.5	1.3	24.5	< 1
Iron							
G) 5c(1.2)b	3.38	407	192	11	3.5	245	< 1
H) DS-A	7.11	< 10	158	< 1	< 1	68	< 1

and hundreds of micrometers for chondritic spheres. Thus concentrations are close to bulk values for the latter and external analyses for the former. The assumption of homogeneity should be valid for stony Greenland particles as the observed corrosion structures that extend to very shallow depths (in general, less than 10 micrometers) are quite small compared to the penetration depth. It should also be accurate for the iron spheres, which show very smooth edges with no noticeable mark of corrosion. On the other hand, this assumption is probably invalid for the more heavily corroded deep sea spheres.

RESULTS

Standards

The validity of the spectral deconvolution and abundance computation routines was tested by analyzing specimens of well-characterized meteorites, a carbonaceous chondrite (Orgueil) and four iron meteorites (Toluca, Sarepta, Negril-

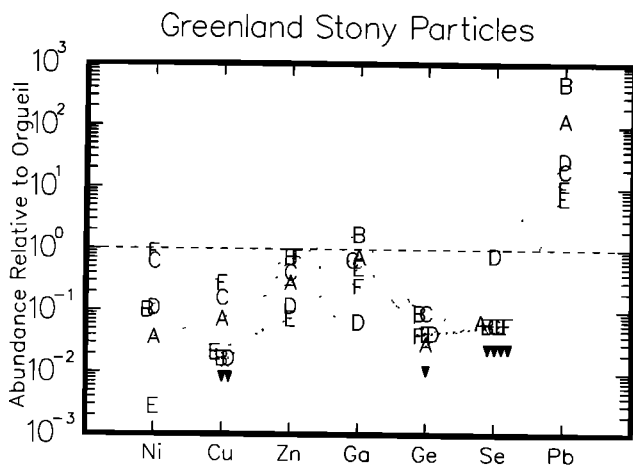


Fig. 5. Elemental abundances relative to Orgueil for six chondritic Greenland particles showing the marked enrichments in Pb and depletions in the other detected elements. See Table 2 for symbol legend.

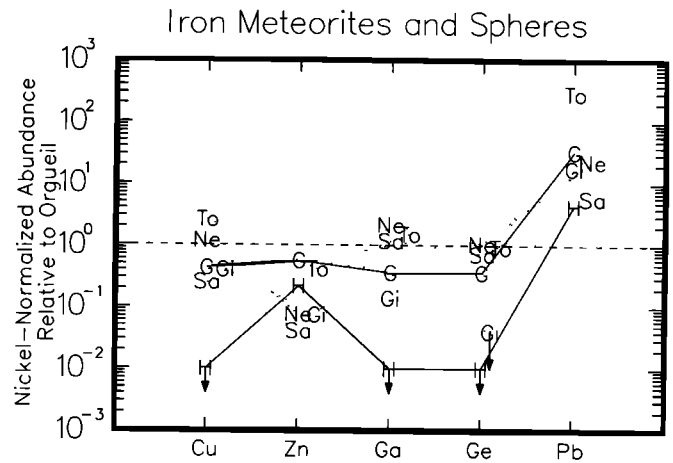


Fig. 6. Nickel-normalized abundances relative to Orgueil (K values) for iron specimens: four iron meteorites (To=Toluca, Ne=Negrillos, Sa=Sarepta and Gi=Gibeon) and two iron spheres (Greenland = G, Deep sea = H).

los and Gibeon). Nickel, Zn, Cu, Ga, and Ge were detected in all samples (Table 1) as well as a fluorescence line at 10.55 keV tentatively identified as Pb L α (the alternative identification, As K α , was ruled out since its companion K β has been observed in no energy dispersive spectra at Brookhaven). (Selenium was also observed in Orgueil and 2 of the chondritic Greenland spheres.) The results for Orgueil are in good agreement with literature values [Buchwald, 1975] with the exception of Pb, whose measured value is an order of magnitude too high

The results for the four iron meteorites are generally in poor agreement with bulk literature values especially for Cu, Zn and Pb whose contents are systematically high. The cause for these discrepancies is not understood at this time, although terrestrial contamination is one possibility. However, the fact that these specimens were not polished but

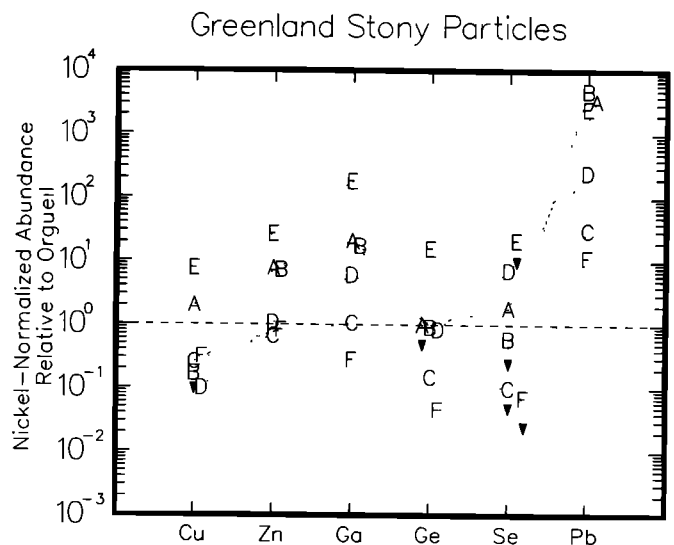


Fig. 7. Nickel-normalized abundances relative to Orgueil (K values) for six chondritic Greenland spheres (see Table 2 for symbol legend). Fractionation trends are similar in shape but vary in magnitude. An anticorrelation exists between the magnitude of the trend and the Ni content of a particle.

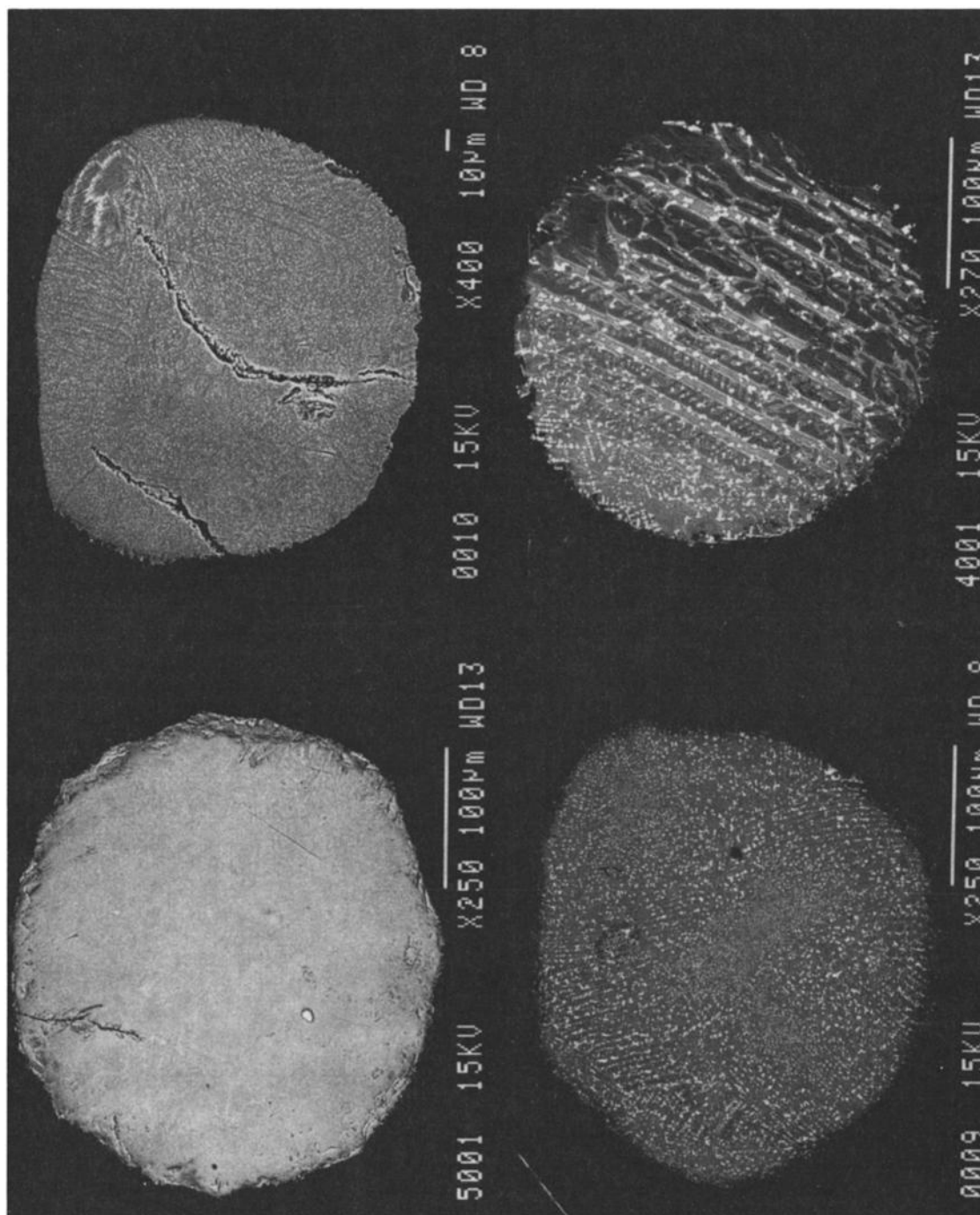


Fig. 8. SEM micrographs of Greenland chondritic spheres showing typical barred texture ranging from ultrafine grained to coarse grained.

simply split pieces suggests that such contamination is unlikely to have occurred during specimen preparation. Specimen heterogeneity is another possibility. The high concentrations of some elements (e.g., Zn and Cu in Toluca are about two orders of magnitude high) cannot be explained by errors in the deconvolution or calculation procedure

Greenland Particles

SXRF spectra obtained for iron and chondritic Greenland spheres (Figures 4a and 4b, respectively) clearly show the presence of Ni, Zn, Cu, Ga, Ge, Pb and Se. Nickel concen-

trations (Table 2) show a large variation (30 ppm to 1%) and fall within the range determined for Greenland and deep sea particles by INAA (i.e., 2-10% for iron spheres and 0.1-1% for chondritic spheres; *Bonte et al.* [1986]). Elemental abundances are for the most part depleted relative to chondritic with the exception of Pb (Figure 5). These depletions are typically one order of magnitude, but a large variation exists. The large Pb enrichments probably result from contamination by terrestrial lead, as suspected in our Orgueil analysis and previously observed in isotopic analyses of meteorites [*Oversby*, 1970]. This contamination is apparently not restricted to the surface of the specimens,

however, since recent measurements at Brookhaven on the interiors of polished Greenland spheres also show excess lead. The mechanism by which a particle can become permeated with terrestrial lead at such high levels [e.g., 1200 ppm for 5C(3.4A)] is not understood. As mentioned above, SEM observations have failed to reveal any obvious secondary phases adhering to the samples.

FRACTIONATION TRENDS IN GREENLAND SPHERULES

Relative elemental abundances have been computed by ratioing to Ni and normalizing to Orgueil [Mason, 1971; Anders and Ebihara, 1982]. In this representation, the abundance parameter K for element X is given by

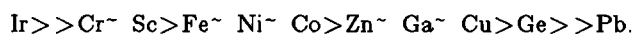
$$K(X) = \frac{(X/Ni)_s}{(X/Ni)_o} \quad (6)$$

Fractionation trends were then obtained by plotting K versus element in order of increasing atomic number.

Fractionation trends for the iron meteorite standards (To, Ne, Gi, and Sa) and two iron spheres [one from Greenland (G) and one deep sea (H)] are shown in Figure 6. The iron sphere containing a high Ni content (deep sea particle H = 7.1%) shows very low concentrations of Cu, Ga, and Ge. On the other hand, the low-Ni Greenland sphere (G = 3.4%) has high trace element concentrations comparable to those measured for the four iron meteorites. This apparent anticorrelation between Ni and trace element content was also observed for the chondritic spheres (see below).

The fractionation trends observed for the chondritic spheres (Figure 7) are remarkably similar in shape but vary by 2 to 3 orders of magnitude in absolute terms. Nickel-normalized abundances fall in the order Pb, Ga, Zn, Cu, Ge, and Se from most to least abundant. A comparison of Table 2 and Figure 7 reveals a clear anticorrelation between K value and Ni content of all detected elements with the possible exception of Se (Se was only detected in two of six chondritic particles). This observation is consistent with the trend already noted for the iron spheres.

The observed fractionation trends are apparently not determined by volatility alone. For example, the volatilities of elements rank as follows from the most refractory to the most volatile:



The corresponding fractionation trends are not observed in Figure 7. Bonte *et al.* [1986] argued from their INAA results that the fractionation trends for deep sea spheres are correlated to the geochemical character (siderophile, lithophile) of the elements. Such a correlation is difficult to observe in Figure 7. Indeed, in the chondritic spheres, Ga (a siderophile element under normal conditions) is enriched relative to two other siderophile elements, Cu and Ge.

The fractionation trends noted for siderophile and lithophile elements in the iron and chondritic Greenland spheres are not complementary in the sense that the large depletions in the stony particles, up to 2 orders of magnitude relative to chondritic abundance for Cu, Ge, and Se, are clearly not mirrored by comparable enrichments in iron spheres. This feature was also noted for a series of other lithophile (Cr, Sc) and siderophile (Ir, Co, Ni, Fe) elements in much older iron and chondritic spheres extracted from about 100,000-year-old deep sea sediments, that were analyzed by INAA [Bonte *et al.*, 1986]. Assuming the external analyses on the

iron spheres are representative of the bulk contents, the depletion trends suggest that the two iron spheres investigated in this work represent ablation products of metal-rich rather than chondritic parents. It should be stressed, however, that this conclusion is based on only two iron particles, the results for which are somewhat suspect based on the observed iron meteorite discrepancies. This conclusion is consistent, however, with the observation that ^{10}Be concentrations for large iron spheres (> 400 micrometers) are similar to the values measured for iron meteorites [Yiou *et al.*, 1985; Raisbeck *et al.*, 1986].

CHEMICAL FRACTIONATION AND MICROSTRUCTURE CORRELATIONS

Detailed studies concerning the correlation between microstructure and chemical fractionation trends have been reported by Bonte *et al.* [1986], specifically dealing with the distribution of platinum metals in deep sea spheres. In particular, it was shown that platinum metals are concentrated in highly disequibrated assemblages of nuggets, both in iron and chondritic spheres. Moreover, the segregations of magnetite in both types of spheres play a dominating role in this concentration process as all types of nuggets are found closely correlated with the various forms of magnetite segregations. Based on the deep sea particle results, magnetite segregations and/or metallic nuggets should be associated with the fractionation trends inferred from SXRF. To the contrary, no such correlation was observed in the Greenland particles.

The most abundant chondritic spheres are characterized by a typical barred texture consisting of intergrowths of olivine with an interstitial glass phase, presenting the unique property of containing magnetite segregations (Figure 8). This barred structure ranges from ultrafine to coarse-grained (Figure 8). Moreover, Fe/Ni alloy nuggets are frequently observed in olivine grains of the coarsest texture. No clear correlation between fractionation trends and microstructure has been identified in this preliminary set of specimens. Both the highest (1%) and the lowest (31 ppm) Ni contents are found in spheres showing an intermediate barred texture. The density of tiny-magnetite crystallites seems to be rather similar in both types of spheres. The Greenland iron sphere shown in Figure 2 has the smallest Ni content and yet the highest value of K ratio. K values are not necessarily correlated to magnetite content.

SUMMARY

Synchrotron X ray fluorescence is a promising technique for nondestructive trace element analyses of extraterrestrial particles with detection limits of the order of several ppm. Measurements on eight spheres from Greenland melt lakes have shown that the iron and chondritic particles possess noncomplementary fractionation patterns suggesting that they derive from separate parent micrometeoroids. An apparent anticorrelation between Ni and trace element contents has been discovered. No obvious correlation exists between fractionation pattern and microstructure.

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