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APPLICATIONS OF SYNCHROTRON X-RAY FLUORESCENCE TO EXTRATERRESTRIAL MATERIALS

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Abstract

Synchrotron x-ray fluorescence (SXRF) is a valuable technique for trace element analyses of extraterrestrial materials permitting minimum detection limits less than 1 ppm for 20 micrometer spots. SXRF measurements have been performed on iron meteorites and micrometeorites using white synchrotron radiation and an energy dispersive x-ray detector at the National Synchrotron Light Source (X-26C), Brookhaven National Laboratory (N.Y.). Partitioning of Cu between troilite (FeS) and metal in the nine iron meteorites studied suggests sub-solidus re-equilibration in these objects. A technique has been developed for determining self-absorption corrections for filtered, continuum excitation of small specimens, such as stratospheric particles and refractory inclusions in meteorites.

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Introduction

Extraterrestrial materials offer unique opportunities to study the effects of the physio-chemical processes which controlled the formation of the Sun, Earth and other solar system objects. Several new, important sources of such materials have recently been discovered, expanding and complementing the meteorite and lunar sample collections. First, the recent discovery of meteorite concentrations in Antarctica has increased the world's collection several-fold and yielded specimens of new meteorite types including several lunar meteorites [1] and suspected Martian fragments [2]. Second, micrometeorites several hundred micrometers in size have been recovered from deep sea sediments [3] and Greenland melt lakes [4]. Third, micrometer-sized particles of extraterrestrial origin, some likely to be cometary debris, are being collected from the stratosphere by high flying aircraft [5]. Sample return missions to Mars and a comet nucleus are being planned.

Trace element and isotopic compositions have proved to be valuable in deciphering the histories of extraterrestrial materials [e.g., 6]. Partitioning of elements between co-existing phases, such as sulfide and metal in iron meteorites, constrains the environment that existed at the time of solidification and cooling. Of special importance are rare, typically small (micrometer-sized) samples, for example, refractory inclusions in meteorites and stratospheric particles, thought to be condensates from the primitive solar nebula. Non-destructive analytical techniques with high sensitivity and spatial resolution are essential for studying these specimens.

Synchrotron x-ray fluorescence (SXRF) can provide elemental analyses with minimum detection limits of less than 1 ppm for 20 micrometer beam spots [7-9]. The purpose of this paper is to describe the important considerations in SXRF

analyses of these small samples and some recent applications to iron meteorites and micrometeorites on the white light beamline X-26C at the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York.

Experimental Procedures

A. Apparatus

Specimens are mounted vertically on a Klinger "x-y-z- θ " stepping motor stage and viewed by a Dage MTI TV camera attached to a horizontally mounted Nikon SMZ-10 stereozoom binocular microscope. To minimize scattered radiation, the x-ray detector (Si(Li)) is positioned within the electron storage ring plane and normal to the synchrotron beam. Beam sizes down to 20 micrometers are obtained using motor-driven tantalum slits. X-ray spectra are acquired with a LeCroy System 3500M. Data acquisition, stage and slit motions and spectral deconvolution are performed with a MicroVAX II equipped with CAMAC interface. Alignment procedures and the use of filters, essential for highest elemental sensitivity, are discussed in an accompanying paper [10].

B. Minimum Detection Limits

Minimum detection limits (MDL) depend on a number of factors including mass, atomic number, absorption cross section, fluorescence cross sections, incident flux and geometry. Empirical MDLs were determined for a variety of standard materials, e.g., NBS glass. In each case, specimens were "infinitely thick", i.e., thick compared to the characteristic absorption depth for the x-rays of interest. Absorbers were used on both the incident beam and detector to discriminate against major elements and the spot size was adjusted to yield an overall countrate of a few thousand counts, typically 20-70 micrometers. Counting times were 10 minutes. An x-ray spectrum for the Orgueil carbonaceous

chondrite (figure 1) reveals peaks due to the trace elements Zn (308 ppm), Ga (10 ppm), Ge (32 ppm), Se (18 ppm), Br (4 ppm), Rb (2 ppm), Sr (8 ppm) and Pb (2 ppm). Under these conditions, MDLs for most materials range from 0.5 to 10 ppm for elements between Fe and Sr. The anticipated installation of a 1:1 focussing mirror will reduce detection limits by about an order of magnitude, i.e., 50 ppb to 1 ppm. Further sensitivity enhancements will be achievable with an 8:1 mirror, monochromator and crystal spectrometer planned for beamline X-26A. Experiments are also being designed to run on a future superconducting wiggler line which will permit the efficient excitation of K-lines of high Z elements.

C. Interferences

There are several important interferences in SXRF analyses. Some are common obstacles in all micro-analytical techniques (e.g., contamination during specimen preparation) but several are unique to SXRF and the particular geometry employed. First, the excitation depth is typically comparable to or larger than the sample thickness. Consequently, specimens must be mounted on ultraclean materials, such as Kapton or ultrapure silica, with clean epoxies. Second, since the specimen is irradiated at a 45 degree angle, care must be taken to avoid excitation of adjacent, undesirable material, such as a different mineral within a rock section. Third, peaks may occur in an x-ray spectrum which are due to diffraction [11]. Diffraction from well-ordered specimens such as mineral grains is a particularly significant interference with the apparatus used here (white light/energy dispersive) since lattice planes merely diffract incident photons of the proper wavelength to satisfy Bragg's law. This problem has been overcome by mounting the specimen on a motor-driven rotation stage and obtaining x-ray spectra at different orientations. In this situation, diffraction peaks change

energy and intensity whereas fluorescence peaks remain unaltered.

Small Particle Analysis

The definition of a small particle in the present context is one with dimensions comparable to or less than those of the incident x-ray beam but in which absorption effects may be significant. These are particles roughly less than several hundred micrometers in size. Satisfactory mounting substrates for such samples are crucial since scattered and fluorescence x-rays can be expected to be detected from this material. Preferred substrate materials are 1/3 mil Kapton and Nuclepore filters. Particles in the 10 micrometer range will adhere to these substrates electrostatically but larger ones require the use of adhesive, primarily because of the vertical orientation of the sample (several epoxies are sufficiently clean for this purpose, including Buehler's Araldite and Devcon's 5-minute).

Minimum detection limits for particles can be estimated from MDLs for thick samples in the following way. To a first approximation, the intensities of fluorescence and scattered radiation from a particle will be those for an infinitely-thick specimen scaled by the ratio of the excited volumes in each case. The excitation volume for the thick sample is approximately the product of the cross sectional area of the beam and the characteristic excitation depth (the inverse of density times total absorption coefficient). Thus, assuming the beam is larger than the particle, the scaling factor δ is particle volume/(spot size*excitation depth). MDL will scale as $\delta^{0.5}$. For example, MDL for Se in the thick Orgueil sample was 1 ppm (figure 1) for a square beam 50 x 50 micrometers. Since the excitation depth for Se K α x-rays in this material is 70 micrometers, δ for a 10 micrometer particle is 0.002 [i.e., $(4\pi(5)^3/3)/(50 \times 50 \times 70)$] and the MDL in the particle will therefore be about 20 ppm [i.e., $(.002)^{0.5} \times 1$].

Accurate correction for self-absorption in particles excited by filtered continuum radiation is essential to obtain quantitative elemental concentrations. Both theoretical and empirical approaches are being pursued to determine these corrections. The absorption correction factor F is defined as the fraction of fluorescence x-rays exiting the sample compared to that for an "infinitely-thin" specimen of the same mass. Because of the experimental geometry, it is convenient to consider particles to consist of horizontal, parallel plates of varying lateral dimension. In the case of spherical particles, for a characteristic x-ray of energy E_f emitted within a particle of mean atomic number A , density ρ and radius R excited by monoenergetic x-rays of energy E , F is given by

$$F(E_f, E) = \frac{\int_0^{r_0} \int_0^{2\pi} \int_0^\pi e^{-\rho[\mu(E, A)z_1 + \mu(E_f, A)z_0]} d\phi dr d\theta}{4\pi R} \quad (1)$$

where, $\mu(E, A)$ = total mass absorption coefficient for x-rays of energy E in matrix A

ϕ = azimuthal angle

θ = inclination angle

r = radial distance within a disk

r_0 = disk radius = $R \sin \theta$

z_1 = absorption depth for incident x-rays = $(R^2 - r^2 \sin^2 \theta)^{0.5} - r \cos \theta$

z_0 = absorption depth for fluorescence x-rays = $(R^2 - r^2 \cos^2 \theta)^{0.5} - r \sin \theta$

The total effective absorption correction for a particular fluorescence x-ray is then obtained by integrating equation (1) over the incident energy spectrum. Solutions to equation (1) are obtained numerically by dividing each sphere into 10,000 regions of equal mass. Some initial results of these calculations for spheres of various sizes composed of the carbonaceous chondrite Orgueil (nominal composition = 46.4% O, 18.5% Fe, 10.7% Si, 9.7% Mg, 5.3% S, 3.5% C, 2.0% H, 1.1%

Ni and 0.9% Al [12]; $\rho=2.3 \text{ g cm}^{-3}$) are shown in figure 2. Empirical verification of the calculated absorption factors will be attempted by pulverizing, fusing and grinding meteoritical material after which particles of various sizes will be selected for SXRF measurements.

Applications

A. *Cu and Ni Partitioning between Metal and Troilite in Iron Meteorites*

Trace element analyses using SXRF and PIXE were performed on metal and troilite from 9 iron meteorites representing 5 geochemical groups, IAB, IIICD, IIB, IIIA, and IVA [13]. Fe, Ni, Cu, Ga and Ge were detected in all metal specimens and Fe, Ni, Cu and Se were detected in all troilite specimens. Cu and Ni distribution coefficients (troilite/metal) correlated positively with kamacite band width and correlated negatively with bulk Ni content (figure 3). The most significant finding in these measurements was the observation of Cu distribution coefficients less than 1 for Ni-rich meteorites. Such Cu enrichments in metal are not likely to have resulted from eutectic or cotectic crystallization alone since laboratory experiments demonstrate that Cu exhibits a chalcophilic character under such conditions [14]. These results, therefore, provide evidence for re-equilibration under sub-solidus conditions.

B. *Greenland and Deep Sea Particles*

The trace element signatures of particles extracted mechanically from Greenland melt lakes are being studied in collaboration with scientists at Orsay, France. These particles show much less weathering than do extraterrestrial particles collected magnetically from deep sea sediments, primarily a result of younger terrestrial ages and the less corrosive nature of water in the melt lakes. The Orsay and Brookhaven SXRF instruments are somewhat complementary, the

French apparatus using a 1 mm monochromatic beam at 14 keV and a wavelength dispersive detector in contrast to the 20 micrometer white beam and energy dispersive detector at Brookhaven. In some initial experiments at Orsay on whole, unpolished particles, K lines due to Ni, Zn, Cu, Ga, Ge, Se and a peak corresponding to either Pb $L\alpha$ or As $K\alpha$ were detected in most stony particles [15]. All elements with the exception of the Pb/As were depleted relative to C1 meteorites suggesting that ablation/melting during atmospheric entry has modified the chemical composition of the parent material. Fractionation patterns for stony and iron particles were not complementary suggesting that they do not derive from common parents. An apparent negative correlation between Ni and trace element contents was observed. No clear correlation exists between trace element content and the microstructure revealed at high magnification in the SEM.

X-ray spectra obtained at Brookhaven also showed excesses in Pb/As and the presence of Pb $L\beta$, $L\gamma$, demonstrating that large Pb excesses exist at least in some particles. The Pb enrichments may result from terrestrial contamination although this has been difficult to prove. SEM observations have failed to reveal any obvious secondary "precipitates" or reaction products adhering to the samples. The contamination may not be restricted to the surface of the specimens, however, since lead was also detected in the interior of a polished particle.

In related work, 6 deep sea particles were analyzed in collaboration with G. Herzog (Rutgers University). X-ray spectra revealed only Fe, Ni, Cu and Zn. The preliminary results of these measurements are similar to those of the Greenland particles. That is, most elements are qualitatively depleted, often below the detection limits of several ppm, but large Pb contents are observed.

Conclusions

Synchrotron x-ray fluorescence permits non-destructive, elemental analyses with minimum detection limits less than 1 ppm for 20 micrometer spots. The technique is well-suited for trace element studies of extraterrestrial materials and some valuable geochemical data on meteorites has already been obtained. Trace element measurements on small extraterrestrial particles, such as micrometeorites from deep sea sediments and Greenland melt lakes, stratospheric particles and refractory inclusions from meteorites, are a particularly important and challenging aspect of this research.

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Figure Captions

Figure 1: Synchrotron x-ray fluorescence spectra for an "infinitely-thick" specimen of the carbonaceous chondrite Orgueil obtained with the Brookhaven (continuum/energy dispersive) apparatus. A 50 micrometer square beam filtered with 275 micrometers of aluminum was used. The detector was filtered with 180 micrometers of aluminum. Acquisition time = 600 seconds.

Figure 2: Self-absorption factors for $K\alpha$ x-rays from elements between Cr and Cd in Orgueil spheres with radii between 1 and 300 micrometers assuming the experimental conditions in figure 1.

Figure 3: Copper distribution coefficient, D_{Cu} , plotted against bulk Ni content [16]. The trend intersects $D_{Cu} = 1$ at a bulk Ni content of about 9%. Meteorites with bulk Ni less than 9% have Cu-enriched troilite while those > 9% have Cu-depleted troilite.

Figure 4: Elemental abundances relative to Orgueil for 6 chondritic Greenland particles showing the marked enrichments in Pb and depletions in the other detected elements. Experimental conditions as in figure 1.

Fig 1: SXRF Spectrum for the Orgueil Chondrite

Fig. 2: Orgueil spheres— self absorption corrections

Figure 3: Cu Distribution versus Bulk Ni in Iron Meteorites

Fig. 4: Composition of Greenland Stony Particles