Reports

A Meteoritic Component Rich in Volatile Elements: Its Characterization and Implications

Abstract. *An unusual carbon-rich material found in the Abee meteorite is highly enriched in volatile elements, by factors of* 10^4 *relative to the case for nonvolatile elements. Volatile-rich material of this type might form in the solar nebula toward the end of accretion, when small amounts of residual dust acquire all the uncondensed volatile elements. The mercury enrichment factor of 8500 could explain the paradox of the excess abundance of this element in meteorites.*

The most primitive samples of planetary matter, the chondritic meteorites, consist of several components. Some of the components are conspicuous, widespread, and well studied. These include the metals, magnesium silicates, iron sulfide, and some unusual inclusions comprised of calcium-aluminum silicates. Each component carries a suite of minor and trace elements with compatible chemistries and volatilities. The metals, for example, contain most of the cobalt, nickel, and other elements more noble than iron. These components generally were blended together, just prior to accretion, to produce bulk compositions that closely match the sun (*1*). However, the relative proportions of the various components are not always identical. Families of chondrites can be resolved, each of which is depleted or enriched in whole suites of elements (*2*). This concept that planetary matter consists of several components, mixed in various proportions, has provided a useful framework with which to examine the bulk compositions of Earth, the moon (*3*), and Mars (*4*).

The volatile element inventory of a body is thought to depend primarily on the temperature (and pressure) during accretion and to be independent of the proportion of the various known components. The contents of volatile elements in chondrites vary by factors of 10^3, much greater than the variation in any known component. The only readily apparent correlation is in the carbonaceous chondrites where the volatile contents correlate with the proportion of fine-grained matrix material (*5*). This correlation suggests that the volatile elements condensed on the finer grained dust in the nebula, presumably owing to its higher ratio of surface area to volume. With decreasing temperature, this dust (matrix) would acquire increasing amounts of volatile elements until the process was terminated by accretion. Elements that had totally or partially condensed would become incorporated in the accreting body, whereas the fraction that remained gaseous would not (*2*). Of special interest are the elements partially condensed at the time of accretion. In principle, their concentrations can be used to estimate accretion temperatures.

To further explore this possibility, a comprehensive study was begun about 10 years ago to measure the concentrations of some key elements (silver, bismuth, indium, and thallium) in a representative sample of 40 to 50 meteorites (*6, 7*). In about 90 percent of the samples studied, the elemental concentrations fell into the predicted patterns. But in several meteorites the volatile elements showed extreme enrichments. The most notable case was the Supuhee meteorite, which was enriched in some elements by a factor of 500 over the expected amounts and by factors of 2 to 3 relative to C1 carbonaceous chondrites, the most volatile-rich meteoritic material known at the time.

Supuhee is a brecciated meteorite, consisting of a mixture of light and dark pieces. Other similar meteorites that have been studied are enriched in volatile elements, especially the noble gases, in the darker colored portions (*8*). However, some of the dark pieces in Supuhee are unique; not only are they more enriched in the volatile elements, but also they are not gas-rich (*9*). It was therefore suggested that Supuhee, along with a few other meteorites, contains an unusual component, facetiously named "mysterite" (*7*).

We recently undertook a study of minerals unique to enstatite chondrites, an unusual group of meteorites characterized by highly reduced mineral assemblages. One of the first materials studied is enormously enriched in volatile elements to an extent that far exceeds any material studied before. This sample, along with several other minerals, was handpicked from some gently crushed fragments of the Abee meteorite. We reversed the normal procedure of first identifying minerals in sections and then extracting them for study because it is well known that some of the more interesting minerals from enstatite chondrites are easily lost during sectioning. This approach, although it requires that one return to sections for further petrographic study, was more than justified in the case of this sample. The material has an unusual microscopic appearance; it occurs as aggregates of thin, delicate strands with a yellow tint. It seems unlikely that this material would persist through normal sectioning procedures. Considerable care would have to be taken if this material were to be studied in situ. Several aggregates, weighing a total of about 5 μg, were irradiated (along with several standards of known elemental content) with 3.1 mmole of thermal neutrons per square centimeter. The concentrations of all the elements in Table 1 were determined nondestructively by gamma-ray counting. The material apparently disaggregated during irradiation and became much blacker in color.

The elemental composition of the sample is compared to that of C1 chondrites (a group of primitive meteorites that best represent the solar system or cosmic abundances of chemical elements) in Fig. 1. The first six relatively nonvolatile elements occur in nearly their cosmic proportions, although depleted by a factor of 30. The remaining ten elements, arranged in the order of increasing enrichment, are more volatile than the first six. In most chondritic materials they are depleted by factors of 2 to 10^3. To our knowledge, such extreme enrichments of volatile elements over nonvolatile elements have never been observed before.

There have been several recent attempts to isolate and characterize this mysterious volatile-rich component (*10*). The abundances of antimony, silver, zinc, and bromine in two volatile-rich portions from Supuhee meteorite coparallel the enrichment pattern observed in our sample. It appears that the two Supuhee samples consist of a mixture of average H5-6 material (Supuhee is classified as an H5-6 chondrite) and the volatile-rich material. But the amount of the mysterious component appears to be on-

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Table 1. Abundances of trace elements in the volatile-rich material collected from Abee meteorite. Uncertainties quoted are based on 2σ counting statistics (σ is the standard deviation). Sample weight, 5 μg; ppb, parts per billion; ppm, parts per million.

Element	Sample	C1 chondrites	Sample relative to C1 chondrites
Iridium (ppb)	13.1 ± 4.7	514	0.025
Scandium (ppm)	0.29 ± 0.02	5.10	0.056
Iron (%)	0.384 ± 0.008	17.1	0.023
Cobalt (ppm)	13.3 ± 0.2	483	0.028
Nickel (%)	0.047 ± 0.008	1.03	0.046
Chromium (ppm)	96.6 ± 1.2	2250	0.043
Selenium (ppm)	17.3 ± 8.0	19.5	0.89
Sodium (%)	0.624 ± 0.010	0.511	1.22
Cesium (ppb)	280 ± 160	192	1.46
Arsenic (ppm)	3.84 ± 0.60	1.81	2.11
Gold (ppm)	0.99 ± 0.01	0.152	6.50
Bromine (ppm)	38.0 ± 1.0	3.67	10.4
Mercury (ppm)	117 ± 23	5 (0.3)*	23.4 (390)*
Zinc (%)	3.46 ± 0.01	0.030	114
Silver (ppm)	60.4 ± 10.2	0.182	332
Antimony (ppm)	79.2 ± 0.4	0.138	574

*The value in parentheses is the expected concentration based on solar system abundances computed from nuclear systematics (*13*).

ly a few percent in sample 4J and no more than 10 percent or so in sample 2D. The order of enrichment (Sb>Ag>Zn >Br) seems characteristic of all samples. The extreme enrichment in antimony, first noted by Higuchi *et al.* (*10*) but disregarded as being so extreme that contamination of the sample was suspected, actually appears to be diagnostic of the material.

Our sample also must consist largely of elements not listed in Table 1 because, even though the volatile elements are enriched, they still do not comprise more than about 5 percent (by weight) of the material. To further characterize the material, we examined about half of it with the electron microprobe and scanning electron microscope (SEM). By centering the beam on individual particles (20 μm) and monitoring the characteristic x-rays with the solid-state detector in a SEM, we detected distinct peaks for chlorine, sulfur, potassium, and sodium along with smaller peaks for iron, nickel, and zinc. Moreover, K_α radiation from carbon was observed in the electron microprobe, an indication of the presence of carbon. Semiquantitative analysis with a pure graphite standard revealed that our sample consists largely of carbon ~ 90 percent (by weight) which perhaps should also be considered an enriched volatile element [25 times the C1 abundance of 3.5 percent (by weight)].

The problems associated with the origin and evolution of a rare, volatile-rich component with peculiar physical properties are immense. Even if it were possible to obtain a complete picture of the chemistry and mineralogy of this component, the fact that it contains the most volatile, and hence most easily mobilized, elements raises the question of how primitive the material is likely to be. Any thermal event, however mild, might be sufficient to alter the original composition to some extent. For example, the mercury concentration could easily have been much higher than observed.

On the other hand, it seems unlikely that enrichments in volatile elements such as those observed could be the result of secondary processes. Although the Abee meteorite displays evidence of shock and thermal metamorphism, such processes redistribute elements according to their chemical properties, not their volatilities. For example, noble metals such as gold become concentrated in the metal whereas selenium and zinc enter the sulfide phase. The enrichment in all volatile elements thus points to a more primitive process, one that leads to high concentration of all the volatile elements.

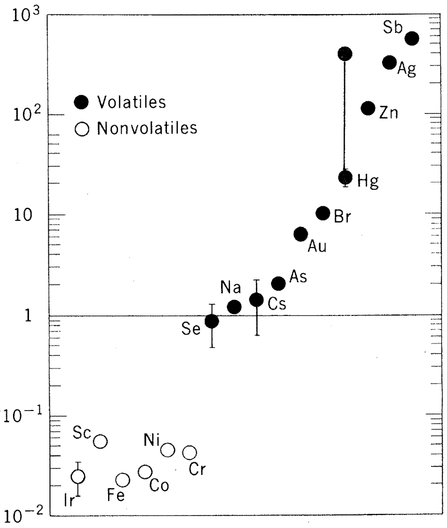

Fig. 1. Elemental abundances in the volatile-rich material from the Abee meteorite are strongly fractionated relative to those in C1 carbonaceous chondrites (1 on the vertical scale). The first six nonvolatile elements are depleted by an average factor of 30, whereas the remaining more volatile ones display a progressive enrichment, with the antimony enrichment factor of 575 being the extreme. The abundance of mercury is compared to both its measured value in C1 meteorites (lower point) and its predicted concentration based on solar system abundances (upper point). Such extreme enrichments in the volatile elements have never been observed before in any primitive solar system material.

Upon their initial discovery, Laul *et al.* (*7*) suggested that such material might represent the last residual dust to accrete. Enrichments in volatile elements by a factor of 500 or so would thus imply that only about 1 part in 500 of the condensable dust was left unaccreted and acquired all the remaining volatile elements. In its simplest form, this model predicts a correlation between enrichment factors and predicted condensation temperatures. But from the outset it has been clear that other factors must be considered. Enrichments in silver, bismuth, and thallium were observed, but indium, which should condense at the same temperature, was not enriched. Some mineralogical factor was suspected; possibly only those elements which condense as metals but not sulfides (InS) are enriched. However, in our sample enrichments are observed for a variety of elements including ones expected to form sulfides (selenium and zinc), silicates (sodium and cesium), and metals (silver, arsenic, gold, mercury, and antimony). If a mineral is present in addition to the carbon, it must be rich in zinc (~ 3 percent of the total or 30 percent of the material excluding carbon). Perhaps an unusual sulfide, or even a halide, is the dominant mineral. On the other hand, carbon might behave as an extremely efficient and highly discriminatory "getter," analogous to activated charcoal.

One of the outstanding problems in cosmochemistry is the apparent overabundance of mercury in planetary materials. Because of its high volatility, mercury would be expected to be strongly depleted in most meteorites (*11*). It is deficient in some meteorites by a factor of 1000, but the pattern is not as regular as that for other volatile elements (*12*). Occasional enrichments are observed in meteorites in which other volatile elements are depleted. Moreover, its abundance in C1 chondrites is quite variable [2 to 200 parts per million (ppm)], and it appears to be overabundant with respect to estimates of its solar system abundance based on nuclear systematics (*12*, *13*). This overabundance in C1 chondrites is unique because all other volatile elements are present in the predicted amounts.

We have compared the mercury content of our sample to both the observed (*12*) and predicted (*13*) mercury concentrations in C1 meteorites (Table 1 and Fig. 1). For the predicted concentration, 0.3 ppm based on nuclear systematics, our sample is enriched by about a factor of 400 (by 8500 when the data are normalized to nickel). This would make mercury the second most enriched element, exceeded only by antimony. Thus, if C1 meteorites contain only 1 part in 400 (or 1 part in 8500 excluding carbon) of this material, inhomogeneously distributed, this would account for both the excess abundance and the peculiar distribution of mercury. Somewhat smaller amounts of this element in other chondritic material could equally well account for its anomalous abundance there. Since this component is so enriched in mercury, only a small amount is required to account for the total amount of mercury present. At these low concentrations, enrichments or inhomogeneous distributions of only the most strongly enriched elements would be apparent. Interestingly, silver and bromine display considerable variations in C1 meteorites although the same pattern is not exhibited by zinc and antimony (*14*).

If the volatile-rich component present in Abee as well as other meteorites is a primary late condensate from the solar nebula, then it would provide valuable information on the cooling of the solar nebula. Fortunately, the primary nature of this material is not beyond verification. The observed overabundances of chlorine and bromine require that other halogens also be overabundant. The identification of an extinct radionuclide (17×10^6-year ^{129}I) in this material would not only establish the antiquity of this component but also provide chronometric information on the time scale associated with the cooling of the solar nebula. The primary nature of this material would also indicate that efficient accretion of dust and not the dissipation of gas terminated the meteorite parent-body formation.

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Tetrachlorodibenzo-*p*-Dioxin Quantitation in Stack-Collected Coal Fly Ash

Abstract. *Gas chromatography–high resolution mass spectrometry has been used to quantitate tetrachlorodibenzo-*p*-dioxin (TCDD) in fly ash collected from the stack of a typical commercial coal-fired power plant. No TCDD was detected in this fly ash, but minute traces may be present below the detection limit of 1.2 parts per trillion (by weight). This finding indicates that this type of fossil-fueled power plant is not a large source of this compound in environmental samples, in contrast to the conclusions presented in a recent industrial report.*

The projected increase in the combustion of coal for the generation of electric power poses potential adverse environmental and human health problems because of the release of fly ash into the atmosphere. It has been estimated that during 1974 2.4×10^9 kg of fly ash were emitted in the United States as a result of the burning of coal (*1*).

In a recent industrial report (*2*, p. 3) it was concluded that "refuse incinerators and fossil-fueled powerhouses are sources of both airborne and waterborne particulates which contain chlorinated dioxins." The conclusions of this report have been extensively discussed in the popular scientific press (*3*).

Chlorinated dibenzo-*p*-dioxins, particularly the 2,3,7,8-isomer of tetrachlorodibenzo-*p*-dioxin (TCDD), are well recognized as potential hazards to human health. It has been shown that 2,3,7,8-TCDD is fetotoxic in several species, teratogenic in mice, and carcinogenic in rats (*4*) and is toxic at exceedingly low levels in primates (*5*).

The presence of highly toxic materials such as TCDD in airborne particles, if coupled with the potential widespread aerial distribution of particles emitted from power plants, would pose serious hazards to the health of the general public in industrialized nations.

The problem is quantitative and centers on the rate of emission of TCDD on airborne particles. In the industrial study (*2*), the concentration of TCDD was determined on particles collected from the stack of a chemical plant powerhouse burning fuel oil and coal. Various TCDD isomers were found at a concentration of 38 parts per billion (ppb), with a detection limit of 20 ppb; the 2,3,7,8-isomer was not detected at a detection limit of 10 ppb. Concentrations of 2, 4, and 24 ppb of hexa-, hepta-, and octachlorodibenzo-*p*-dioxins, respectively, were also found.

The industrial report includes extensive descriptions of modern analytical techniques that have been used to quantitate chlorinated dibenzo-*p*-dioxins from a variety of samples. These samples include a large number of combustion products, such as refuse incinerator emissions, gasoline-powered automobile exhausts, fireplace soot, charcoal grills, cigarette smoke, and particulate emissions from a chemical plant powerhouse. From these analytical data, it was concluded that measurable amounts of chlorinated dibenzo-*p*-dioxins can be found in the products from many types of combustion, including powerhouses that burn fossil fuels. In order to evaluate the extrapolation to other fossil-fueled power plants, we have quantitated TCDD in stack-collected fly ash from a typical commercial coal combustion facility.