



## Extracts of impact breccia samples from Sudbury, Gardnos, and Ries impact craters and the effects of aggregation on C<sub>60</sub> detection

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**Abstract**—Fullerenes have been detected in carbonaceous chondrite meteorites and in breccia samples from meteorite impact craters, but questions have been raised about contradictory results from similar samples and the sensitivities and accuracies of different analytical methods. We analyzed samples from three impact craters and detected C<sub>60</sub> in samples from several locations; we also observed differences in the detection capabilities of various analytical techniques used in the search for fullerenes. The presence of C<sub>60</sub> in rocks from the Onaping Formation of the Sudbury impact crater was confirmed. Low levels of C<sub>60</sub> were also detected for the first time in samples from the Gardnos (Norway) and Ries (Germany) impact structures.

We detected C<sub>60</sub> in these samples using surface-enhanced laser desorption/ionization (SELDI), but the related technique of microprobe laser-desorption, laser-ionization mass spectrometry ( $\mu\text{L}^2\text{MS}$ ) did not observe C<sub>60</sub> above detection limits. We attribute the absence of  $\mu\text{L}^2\text{MS}$  signal to aggregate formation caused by phthalic acid esters, which appear to easily contaminate samples either during storage or demineralization in plastic containers. The  $\mu\text{L}^2\text{MS}$  technique is incapable of detecting aggregated C<sub>60</sub>, but aggregation does not suppress detection in SELDI. Phthalate-induced aggregation did, however, enhance SELDI detection of C<sub>60</sub> in some cases, and we suggest that this enhancement may help explain previously reported differences in C<sub>60</sub> detection from natural samples between laser desorption mass spectrometry (LDMS), a technique analogous to SELDI that has detected fullerenes in meteorite and impact breccia samples, and high-pressure liquid chromatography (HPLC). This work highlights the effects of phthalates and other indigenous compounds or contaminants on certain mass spectrometric techniques and lends support to the idea that several complementary analytical methods should be employed to investigate complex natural samples. Copyright © 2005 Elsevier Ltd

### 1. INTRODUCTION

The discovery of the fullerene molecule C<sub>60</sub> (Kroto et al., 1985) and its subsequent detection in the carbon-rich terrestrial rock shungite (Buseck et al., 1992) created much interest in searching for naturally occurring instances of this compound. Subsequent reports cited the detection of C<sub>60</sub> and higher fullerenes in meteorite impact craters on spacecraft (di Brozolo et al., 1994) and on Earth (Becker et al., 1994b; Becker et al., 1996; Mossman et al., 2003), in carbonaceous chondrites (Becker et al., 1994a; Becker and Bunch, 1997; Becker et al., 1999; Pizzarello et al., 2001), in fulgurite rocks (Daly et al., 1993), and in sediments from the Cretaceous-Tertiary and Permian-Triassic boundaries (Heymann et al., 1994b; Heymann et al., 1994a; Chijiwa et al., 1999; Becker et al., 2001; Poreda and Becker, 2003).

Controversy over these reports has arisen, however, as samples reported to contain C<sub>60</sub> have produced contradictory results when analyzed by different techniques and groups (Ash et al., 1991; de Vries et al., 1991; Gilmour et al., 1991; de Vries et al., 1993; Heymann, 1995; Becker et al., 1996; Heymann, 1997; Becker et al., 2000; Taylor and Abdul-Sada, 2000; Becker et al., 2001). In multiple investigations of the Allende meteorite, for example, studies carried out by Becker and

co-workers identified C<sub>60</sub> at levels of 5–100 ppb (Becker et al., 1994a; Becker and Bunch, 1997), whereas studies by other researchers failed to detect C<sub>60</sub> (Ash et al., 1991; de Vries et al., 1991; de Vries et al., 1993; Heymann, 1995; Heymann, 1997). Similarly, Becker and co-workers reported detection of C<sub>60</sub> in samples from the Sudbury impact structure at levels of 1–10 ppm, but other researchers either failed to detect fullerenes or observed much lower levels (~5 ppb) (Becker et al., 1994b; Becker et al., 1996; Heymann et al., 1999; Mossman et al., 2003). These findings have been attributed to a variety of causes, including differences in sample preparation, abilities of analytical techniques, and heterogeneities within the samples. We have taken up the challenge of finding a clear and reproducible answer to the question of C<sub>60</sub> presence in natural samples.

The low levels at which fullerenes occur in natural samples place constraints on the analytical methods suitable for their analysis. Most reports of naturally occurring fullerenes have used a combination of demineralization and extraction to remove and concentrate these compounds from their original solid host materials. Extreme caution is required during the demineralization/extraction procedure to avoid contamination that might interfere with or overwhelm the indigenous C<sub>60</sub> signal (Taylor and Abdul-Sada, 2000; Braun et al., 2001). The most widely used analytical techniques are high-pressure liquid chromatography (HPLC) and laser desorption mass spectrometry (LDMS). Both have potential drawbacks; HPLC may

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Table 1. Results of SELDI analysis.

Sample	Description	Sample weight	C <sub>60</sub> content (this work) <sup>a</sup>	Previous C <sub>60</sub> measurements
NGF-96-137 <sup>b</sup>	Gardnos suevite	24 g	n.d.	n/a
NGF-96-137 <sup>c</sup>	Gardnos suevite	20 g	~60 ppb	n/a
NGF-96-121 <sup>b</sup>	Gardnos black-matrix breccia	18 g	~25 ppb	n/a
NGF-96-121 <sup>c</sup>	Gardnos black-matrix breccia	10 g	n.d.	n/a
GER-6 <sup>b</sup>	Ries suevite	27 g	~2 ppb	n/a
CSF-94-7A <sup>c</sup>	Sudbury Black Onaping	10 g	~15 ppb	n/a
NMNH 112666-34 <sup>b</sup>	Sudbury Black Onaping, High Falls	10 g	n.d.	6–7 ppm <sup>d</sup>
NMNH 112666-35 <sup>b</sup>	Sudbury Black Onaping, High Falls	26 g	n.d.	n.d. <sup>e</sup>
NMNH 112666-41 <sup>b</sup>	Sudbury Black Onaping, High Falls	20 g	~2 ppb	10 ppm <sup>d</sup> , n.d. <sup>e</sup>
NMNH 112666-42 <sup>b</sup>	Sudbury Black Onaping, High Falls	23 g	n.d.	n.d. <sup>e</sup>
NMNH 112666-47 <sup>b</sup>	Sudbury Black Onaping, High Falls	22 g	~4 ppb	n.d. <sup>e</sup>
NMNH 112668-183 <sup>b</sup>	Sudbury Black Onaping, High Falls	18 g	n.d.	1 ppm <sup>d</sup> , n.d. <sup>e</sup>

n/a—no previous analyses available.

n.d.—not detected.

<sup>a</sup> Concentrations are estimates within a factor of two.

<sup>b</sup> Demineralized by HF/HCl method.

<sup>c</sup> Demineralized by HF/BF<sub>3</sub> method.

<sup>d</sup> Becker et al., 1994b; correlation between samples in this work and in Becker et al. provided by B. French (personal communication)

<sup>e</sup> Heymann et al., 1999.

suffer from misinterpretations caused by compounds with identical retention times (although this effect can be reduced by the use of preseparation or multiple HPLC columns), whereas laser desorption has been shown to create fullerenes under certain circumstances (Kasuya et al., 2001; Kano et al., 2003). In several cases C<sub>60</sub> was detected in samples using LDMS but was not observed with HPLC, even when LDMS results suggest C<sub>60</sub> concentrations well above the level of HPLC detectability and show no evidence of laser-induced fullerene formation (Becker et al., 1994a; Becker et al., 1994b; Heymann, 1995; Heymann, 1997; Heymann et al., 1999).

The contradictory results and difficulties inherent to fullerene detection have led to a call for more research using a wider range of analytical methods to investigate the distribution of naturally occurring fullerenes (Buseck, 2002). In this paper, we report the detection of C<sub>60</sub> in samples from three impact craters: Sudbury, Ontario; Gardnos, Norway; and Ries, Germany. The analyzed samples include portions of some Sudbury samples studied by other researchers (Becker et al., 1994b; Heymann et al., 1999); differences in C<sub>60</sub> levels detected in this work and published values are observed. We note that differences in preparative techniques can affect detection in unpredictable ways. We also compare surface-enhanced laser desorption/ionization (SELDI), a technique analogous to LDMS, with the related yet distinct technique of microprobe laser-desorption, laser-ionization mass spectrometry ( $\mu\text{L}^2\text{MS}$ ), and discuss how the wide range of compounds in extracts from natural samples can create interferences for  $\mu\text{L}^2\text{MS}$  by causing C<sub>60</sub> aggregation during sample preparation.

## 2. MATERIALS AND METHODS

### 2.1. Samples

Ten samples from three impact craters were analyzed for the presence of C<sub>60</sub>. These include seven impact breccias from the “Black Member” of the Onaping Formation in Sudbury (the location of reported fullerenes), a suevite breccia and a black-matrix breccia from the Gardnos impact site, and a suevite from the Ries crater. Sudbury

samples were obtained from the Smithsonian Institution’s National Museum of Natural History (Table 1; “NMNH” samples). Additional Sudbury and Gardnos samples were obtained from Bevan M. French (Smithsonian Institution; Table 1; “CSF” and “NGF” samples). The Ries sample was acquired from Don Lowe (Stanford University).

The Sudbury impact structure, in southern Ontario, Canada, is ~1.85 billion years old and has been deformed and metamorphosed since formation, making it difficult to know its original size (Wichman and Schultz, 1993). The structure contains several distinct impact-produced geologic units, including the carbon-bearing “Black Member” of the Onaping Formation, a 1600-m-thick unit of heterolithic breccias formed by deposition in the crater immediately after impact (for descriptions, see French, 1968; Muir and Peredery, 1984; Avermann, 1994; Heymann et al., 1999). Samples of the “Black Member” (Table 1) were collected from the informally but generally recognized “type locality” at Onaping High Falls in Dowling Township, in the northwestern part of the Sudbury Basin. Most samples were collected from a highway roadcut at High Falls, which exposes the massive, non-bedded lower part of the “Black Member”; one sample (NMNH 112668–183) was collected from an outcrop of the same unit ~1.6 km to the SE. Another sample (CSF-94–7A) was collected from the poorly—but definitely—bedded upper part of the “Black Member,” where it is exposed on a highway near Capreol, in the northeastern part of the basin.

The Gardnos crater, located in southern Norway and ~5 km in diameter, is estimated to be 400–700 million years old (French et al., 1997). The Gardnos and Sudbury craters are the only two known impact craters whose impactites contain significant amounts of carbon (French et al., 1997; Gilmour et al., 2003). Two samples were analyzed (see Table 1); one (NGF-96–121) is a carbon-rich “black-matrix breccia” from the shattered granitic target rocks immediately beneath the crater floor; the other (NGF-96–137) is a glass-bearing suevite breccia deposited in the crater after impact, collected from immediately above the crater floor.

The Ries crater is located in Bavaria, Germany. It has a diameter of 24 km and was formed ~15 million years ago (for descriptions, see Pohl et al., 1977; von Engelhardt and Graup, 1984; von Engelhardt, 1997). The analyzed sample of suevite was collected from a quarry near the town of Amerdingen on the southwest side of the crater at 48°43′20″N, 10°29′20″E.

All samples were crushed to a fine powder. Each powder was then placed in a polypropylene centrifuge bottle, and 50 mL of hydrochloric acid was added slowly to remove carbonates. An additional 50 mL of 48% hydrofluoric acid was then added to remove silicates and other minerals. The resultant mixture was allowed to stand overnight, after

which the acids were removed, and the remaining carbon-rich residues were rinsed three times with Milli-Q water. In addition, unprocessed portions of three samples (two Gardnos and one Sudbury) were sent to Luann Becker (University of California at Santa Barbara) and were demineralized in her laboratory using a method that utilizes a combination of HF and BF<sub>3</sub> to prevent the formation of water-insoluble fluorides in the residue (Robl and Davis, 1993; Becker et al., 1996). All acid-demineralized residues were Soxhlet extracted in toluene for 24 hours and then concentrated to a final volume of 500  $\mu$ L. To prevent contamination, extraction glassware was cleaned by overnight soaking in a base bath followed by baking in an oven at 550°C for 24 hours. Procedural blanks were run at all stages, with no C<sub>60</sub> detected.

Standard solutions of C<sub>60</sub> used for comparison with the rock extracts were prepared by dissolving known quantities of commercially purchased C<sub>60</sub> in toluene. Aggregation experiments were carried out by spiking the toluene-C<sub>60</sub> solutions with dimethyl phthalate. All chemicals were purchased from Sigma Aldrich (Milwaukee, WI) at >99% purity.

## 2.2. SELDI Analysis

Surface-enhanced laser desorption/ionization (SELDI) analysis was carried out at Ciphergen Biosystems (Fremont, CA). Two microliters of each sample were spotted onto a general-purpose NP20 ProteinChip Array (with silicate functionality), which was then loaded into the vacuum chamber of a Ciphergen ProteinChip Biology System PBSIIc. This instrument uses a nitrogen laser (337 nm) to desorb and ionize molecules from the sample spot, with subsequent detection of the ions in a linear time-of-flight mass spectrometer. Laser powers between 20 and 50  $\mu$ J/mm<sup>2</sup> were used. Although the SELDI technique permits modification of the sample substrate to selectively enhance desorption of certain compounds, we did not use such modification in this work. The SELDI technique is similar to the LDMS technique used to detect fullerenes in other studies (e.g., Becker et al., 1994b; Becker et al., 1996; Becker and Bunch, 1997), using the same combination of laser wavelength, one-step desorption/ionization, and time-of-flight mass spectrometry. In terms of the sample interaction with the nitrogen laser, we expect that the processes should be comparable.

Quantitative estimates were made by comparing the signal strength of sample extracts with those measured from standard solutions of C<sub>60</sub> in toluene over the concentration range from 10 ng/mL to 100  $\mu$ g/mL. SELDI gives good correlation of peak response to concentration for these solutions, with a linear fit ( $R^2 = 0.9945$ ) between intensity and log (concentration) over three orders of magnitude of concentration. Heterogeneities caused by the evaporation of the natural samples, however, limits the accuracy of the estimated concentrations to a factor of two. Extract volume and original sample weight were then used to convert solution concentration to ppb in the solid rock samples. Detection limits for the laser fluences used in this work were estimated to be 10 ng/mL of C<sub>60</sub> in toluene, although it is expected that lower detection limits could be achieved under different conditions. For example, this study used a chemically underivatized substrate surface to match typical LDMS samples; SELDI ProteinChip Arrays are, however, available with multiple chemistries designed for optimization of sample concentration and cleanup. In addition, higher laser powers could be used to enhance sensitivity, although this may cause a smaller linear dynamic range.

Laser-induced creation of fullerenes has been suggested to potentially occur during one-step desorption/ionization. To determine the possibility of fullerene creation in this work, we analyzed all extracts using laser powers of 158  $\mu$ J/mm<sup>2</sup>, which is a much higher intensity than that used for the quantitative estimates. No additional instances of C<sub>60</sub> were detected; the samples without C<sub>60</sub> signal under low power also showed no signal under this higher power. The main difference observed at high fluences was the presence of a series of high-mass peaks in four of the samples (two Sudbury, two Gardnos). These peaks extended up to 5000 Da, with regular spacings of 24 or 214 Da. The most probable origin of these peaks is simply a greater liberation from the substrate due to the higher laser fluence. We found no evidence to indicate that one-step desorption/ionization produces C<sub>60</sub> from these carbonaceous residues at the laser fluences used in this work.

## 2.3. $\mu$ L<sup>2</sup>MS Analysis

Samples for  $\mu$ L<sup>2</sup>MS analysis were prepared by evaporating 10  $\mu$ L of each extract onto a glass sample platter. The  $\mu$ L<sup>2</sup>MS technique is described in detail in Clemett and Zare (1997). It differs from SELDI and LDMS by temporally and spatially separating desorption and ionization and by the laser wavelengths employed. Desorption is accomplished by a pulsed, focused infrared laser (10.6  $\mu$ m), which creates a plume of neutral molecules from the sample surface. This plume is subsequently intersected by a pulsed ultraviolet (UV) laser tuned to selectively ionize the molecules of interest. For detection of fullerenes, the UV laser is tuned to 212.8 nm (the 5<sup>th</sup> harmonic of a Nd:YAG laser), a wavelength that promotes direct ionization of C<sub>60</sub> (Zhang and Stuke, 1993). The resulting ions are analyzed in a reflectron time-of-flight mass spectrometer. The detection limit of C<sub>60</sub> by  $\mu$ L<sup>2</sup>MS was characterized using standard C<sub>60</sub> solutions and was  $\sim$ 100 ng/mL in toluene.

## 2.4. Chromatographic Techniques

Gas chromatography/mass spectrometry (GC-MS) was carried out on extracts from three of the impact breccia samples (GER-6, CSF-94-7A, and the HF/BF<sub>3</sub>-demineralized NGF-96-137). Analysis was performed with an Agilent Technologies 5973N Model G2589A Mass Selective Detector with a 6890N Model G1530N GC system (Agilent Technologies, Palo Alto, CA) equipped with a 0.32 mm  $\times$  30 m  $\times$  0.25  $\mu$ m DB-5 column. A splitless injection of 1  $\mu$ L was used, and the GC temperature was ramped from 90 to 300 °C at 4°C/min. Compound identifications were made by comparison of mass spectra with the Wiley Registry of Mass Spectral Data (7<sup>th</sup> ed.) (McLafferty, 2000).

The effect of aggregate-inducing compounds on HPLC detection was also investigated. The HPLC apparatus consists of two Beckman 110B Solvent Delivery Modules, an injection volume of 100  $\mu$ L, a 4.6 mm  $\times$  150 mm reverse-phase C18 column, and a Beckman 166P Detector measuring absorbance at 330 nm. The mobile phase was 1:1 toluene:methanol at a flow rate of 1 mL/min (Heymann et al., 1994b).

# 3. RESULTS AND DISCUSSION

## 3.1. SELDI Analysis

Table 1 presents the results of SELDI analysis for the impact breccia rock samples, as well as a comparison with reported analyses of these same samples. C<sub>60</sub> was detected in six extracts at estimated concentrations of 0.01–0.6  $\mu$ g/mL, corresponding to concentrations in the original rock samples of 2–60 ppb by weight. Figure 1 presents SELDI spectra from the six samples in which C<sub>60</sub> was detected, as well as two standard solutions and a sample without detectable C<sub>60</sub>.

Three of the seven Sudbury samples contain detectable levels of C<sub>60</sub>, with estimated concentrations in the solid rocks of 2–15 ppb. These values agree well with those reported by Mossman and co-workers, who detected  $\sim$ 5 ppb of C<sub>60</sub> in a sample of Sudbury Onaping “Black Member” from the same High Falls location as the rocks analyzed here (Mossman et al., 2003). In contrast, earlier values of C<sub>60</sub> concentration in some of the samples analyzed in this work were reported as 1–10 ppm (Becker et al., 1994b), orders of magnitude higher than those observed in this study. In addition, the level of C<sub>60</sub> detected appears inconsistent; three analyses of sample NMNH 112666-41 by different researchers, for example, produced measurements of 10 ppm,  $\sim$ 2 ppb, and undetectable levels (Becker et al., 1994b; Heymann et al., 1999 and this work). These results suggest that either sample preparation and detection methodology strongly influence detected levels of C<sub>60</sub>, or the C<sub>60</sub> in these samples is inhomogeneously distributed on the centimeter scale (Heymann et al., 1999).

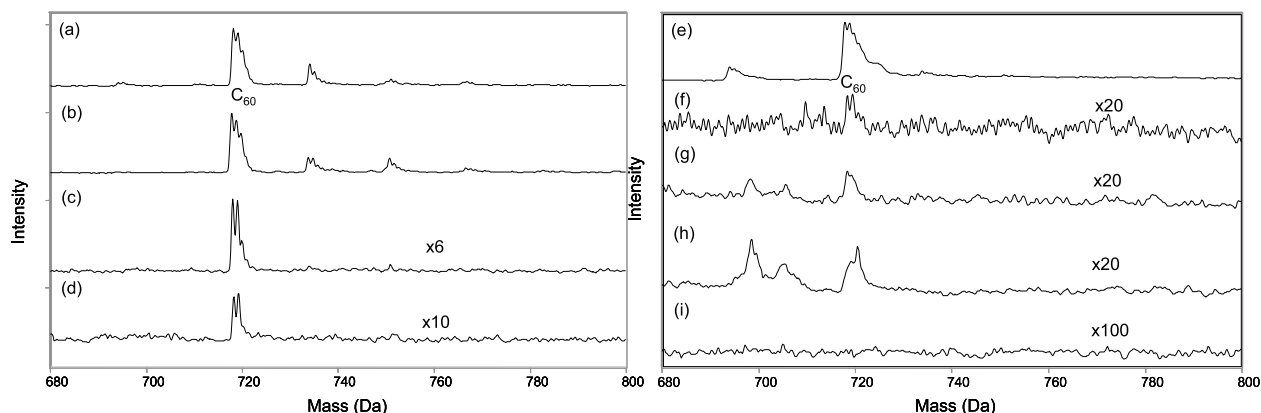


Fig. 1. SELDI spectra of  $C_{60}$ -containing solutions. The left panel shows spectra taken with a laser energy of  $2.5 \mu\text{J}$  for: (a) standard solution of  $1 \mu\text{g/mL}$   $C_{60}$  in toluene; (b) extract of Gardnos sample NGF-96-137 (HF/BF<sub>3</sub> demineralization); (c) extract of Gardnos sample NGF-96-121 (HF/HCl demineralization); and (d) extract of Sudbury sample CSF-94-7A. The right panel displays spectra taken with a laser energy of  $5 \mu\text{J}$  for: (e) standard solution of  $0.1 \mu\text{g/mL}$   $C_{60}$  in toluene; (f) extract of Ries sample GER-6; (g) extract of Sudbury sample NMNH 112668-41; (h) extract of Sudbury sample NMNH 112666-47; and (i) extract of Sudbury sample NMNH 112668-183 (no  $C_{60}$  detected). Some peaks from  $C_{60}$  oxidation are observed in (a)–(c), whereas fragmentation is seen in (e), (g), and (h).

$C_{60}$  was also detected in both samples from the Gardnos structure, at levels of 25–60 ppb. Although the character of the organic materials in these samples has been studied (Gilmour et al., 2003), no analyses for  $C_{60}$  have yet been reported. The method of demineralization strongly influenced  $C_{60}$  detection in these cases. For the suevite sample, a relatively strong  $C_{60}$  signal was detected only in the portion that was demineralized by Becker using the HF/BF<sub>3</sub> method. For the black-matrix breccia sample the reverse was true;  $C_{60}$  was observed in the sample demineralized using HF/HCl but not in the HF/BF<sub>3</sub> portion. These disparate results likely arise from two different causes. In the suevite sample, the difference in signal may be caused by increased efficiency of the HF/BF<sub>3</sub> method in concentrating and releasing the organic materials. In the breccia sample, however, the two analyzed portions were not equal in mass; the HF/HCl method was used on 18 g of rock, whereas only 10 g were processed with HF/BF<sub>3</sub>. The level of  $C_{60}$  detected in the HF/HCl extract was near the limit of detection for the SELDI technique, suggesting that the amount of  $C_{60}$  in the smaller portion may have been below detectable levels, even with the seemingly more efficient HF/BF<sub>3</sub> method. There is no indication that systematic contamination during sample demineralization is responsible for the disparate results; each laboratory produced one residue that gave rise to  $C_{60}$  signal upon extraction and analysis and one residue that did not. In view of the fact that once a sample is demineralized and extracted it cannot be reprocessed, further investigation into the effect of demineralization must wait until new samples are obtained.

The Ries crater suevite contains  $C_{60}$  at levels of  $\sim 2$  ppb. No previous investigations into fullerenes in the Ries crater have been reported, and previous analyses of Ries suevite did not indicate significant levels of carbonaceous material (von Engelhardt, 1997). Given the heterogeneity in  $C_{60}$  distribution observed in samples from the Sudbury crater and the low levels detected here, there is a need for analysis of additional Ries samples to determine if  $C_{60}$  is abundant or widespread in suevites from this crater.

### 3.2. $\mu\text{L}^2\text{MS}$ Analysis

Microprobe laser desorption laser ionization mass spectrometric ( $\mu\text{L}^2\text{MS}$ ) analysis was carried out on the same extracts used in the SELDI experiments.  $C_{60}$  was not detected in any of the samples, even those that gave relatively strong SELDI signals (e.g., NGF-96-137 demineralized with HF/BF<sub>3</sub>). To verify the ability of the  $\mu\text{L}^2\text{MS}$  technique to detect fullerenes, standard solutions of  $C_{60}$  in toluene were analyzed; a detection limit of  $\sim 100$  ng/mL was observed. This detection limit is an order of magnitude higher than that seen with SELDI, but low enough to detect  $C_{60}$  in the concentrations expected in at least one rock extract (the NGF-96-137 portion demineralized with HF/BF<sub>3</sub>). Surprisingly, even when toluene extracts of powdered, demineralized rocks were spiked with relatively high levels of  $C_{60}$  ( $100 \mu\text{g/mL}$ ), no  $C_{60}$  signal was observed upon  $\mu\text{L}^2\text{MS}$  analysis (Figs. 2a and 2b). The same spiked rock extracts exhibited strong  $C_{60}$  signals upon SELDI analysis (Figs. 2c and 2d), which suggests that something in the extracts interfered with  $\mu\text{L}^2\text{MS}$  detection of  $C_{60}$ . Given that literature reports on the detection of  $C_{60}$  in natural samples have raised concerns about technique-specific limitations and abilities (Buseck, 2002), this difference in detection capabilities was explored in some detail.

Signal inhibition was confined to  $C_{60}$  and  $C_{70}$  (the only fullerenes investigated); the signal strengths of polycyclic aromatic hydrocarbons, such as phenanthrene and coronene, were not affected by the presence of rock extracts. Filtration of the fullerene-spiked extracts using a  $0.2 \mu\text{m}$  PTFE syringe filter was used to determine if small particles were responsible for the signal suppression; no effect on signal inhibition was seen. We attempted to duplicate the observed signal suppression in standard solutions of  $C_{60}$  in toluene on the assumption that finding a way to artificially reproduce the effects of the rock extract would provide information on the cause of the suppression. Changes to the pH, water content, and solvent composition of the standard solutions did not suppress  $C_{60}$  signal. Addition of small amounts (as low as 0.1%) of phthalic acid

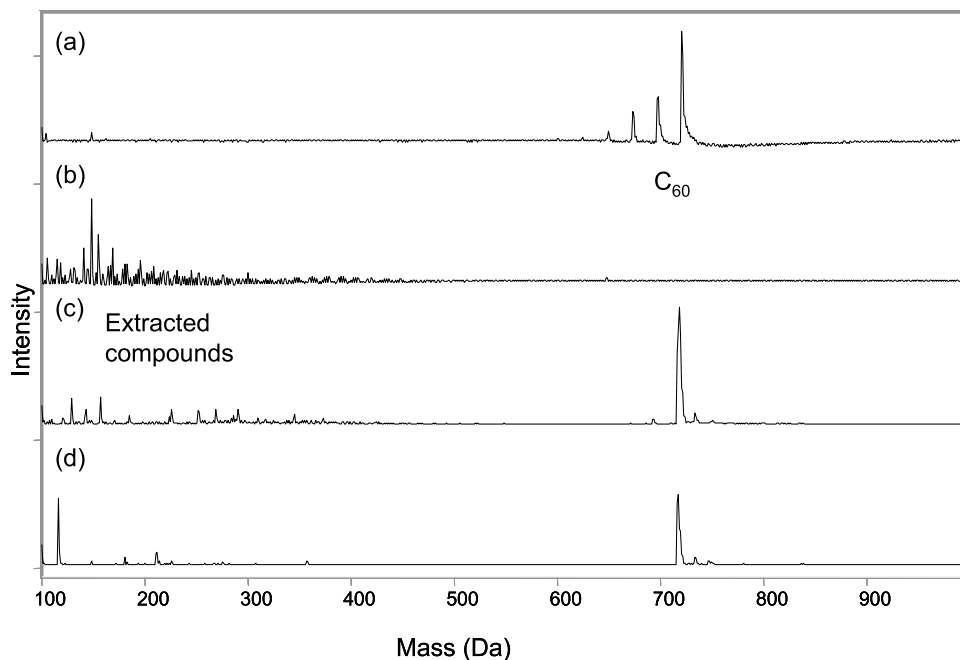


Fig. 2. (a)  $\mu\text{L}^2\text{MS}$  spectrum of  $100\ \mu\text{g}/\text{mL}$   $\text{C}_{60}$  in toluene; (b)  $\mu\text{L}^2\text{MS}$  spectrum of the toluene extract of CSF-94-7A spiked with  $100\ \mu\text{g}/\text{mL}$   $\text{C}_{60}$ ; (c) SELDI spectrum of  $100\ \mu\text{g}/\text{mL}$   $\text{C}_{60}$  in toluene; (d) SELDI spectrum of the toluene extract of CSF-94-7A spiked with  $100\ \mu\text{g}/\text{mL}$   $\text{C}_{60}$ . Traces (a) and (b) have identical intensity scales based on  $\mu\text{L}^2\text{MS}$  detection units, whereas (c) and (d) have identical intensity scales based on the SELDI instrument.

esters such as dimethyl phthalate to solutions of  $\text{C}_{60}$  in toluene, however, was observed to inhibit  $\mu\text{L}^2\text{MS}$  detection of  $\text{C}_{60}$  without affecting the signal of coronene (Fig. 3). The possible causes and implications of sample contamination by phthalate esters are discussed below (Section 3.3.).

$\text{C}_{60}$  signal suppression appears to have a physical cause—the formation of  $\text{C}_{60}$  aggregates. Evaporation of the solutions of  $\text{C}_{60}$  in 1% dimethyl phthalate and the  $\text{C}_{60}$ -spiked rock extracts onto glass substrates produces microscopic clusters of  $\text{C}_{60}$ . Evaporation of a solution of  $\text{C}_{60}$  in toluene at the same con-

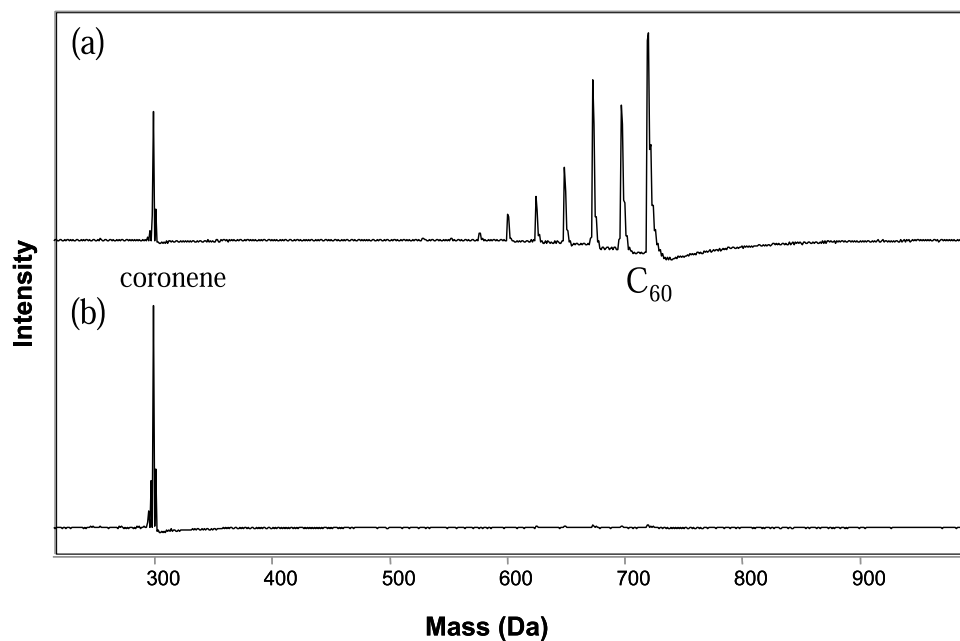


Fig. 3.  $\mu\text{L}^2\text{MS}$  spectra of coronene and  $\text{C}_{60}$  ( $100\ \mu\text{g}/\text{mL}$ ) in (a) pure toluene and (b) toluene containing 1% dimethyl phthalate.

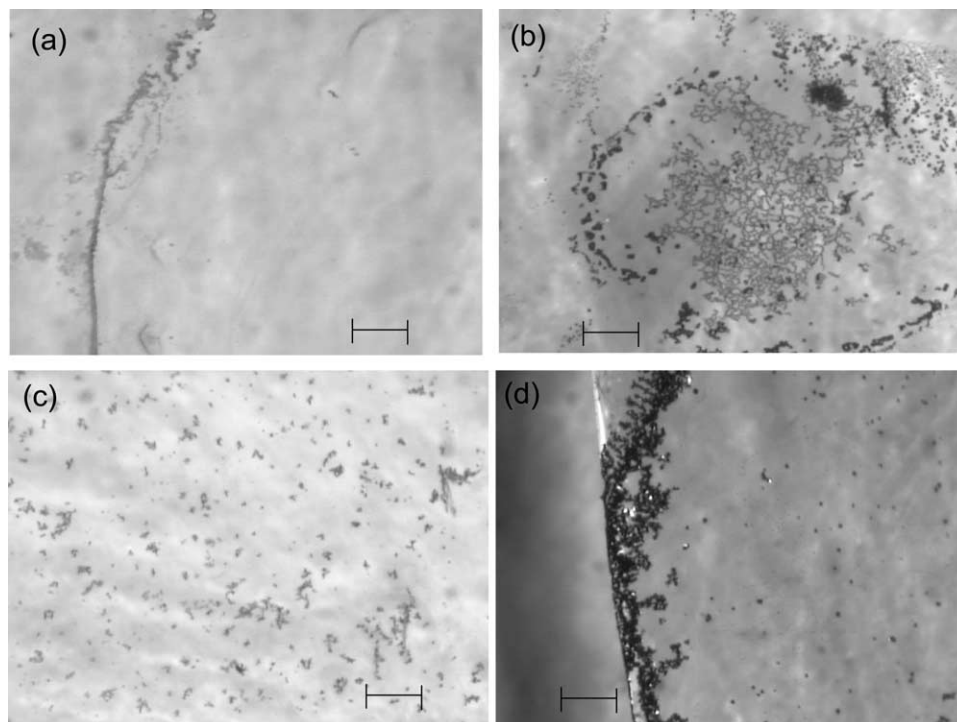


Fig. 4. Optical microscope photographs of residues formed on glass substrates by evaporation of (a)  $C_{60}$  in pure toluene, 100  $\mu\text{g/mL}$ ; (b)  $C_{60}$  (100  $\mu\text{g/mL}$ ) in toluene containing 1% dimethyl phthalate; (c)  $C_{60}$  (100  $\mu\text{g/mL}$ ) in toluene extract of GER-6; and (d)  $C_{60}$  in pure toluene, 1 mg/mL. The scale bar in all photographs represents 100  $\mu\text{m}$ . A thin film is observed in (a), whereas aggregation of  $C_{60}$  is observed in (b), (c), and (d).

centration, by contrast, produces a relatively even film, although a more concentrated solution also produces aggregates (Fig. 4). Aggregation of  $C_{60}$  and other fullerenes has been well documented and is linked to  $C_{60}$  concentration and to the dielectric constant of the solvent (Sun and Bunker, 1993; Ghosh et al., 1996; Nath et al., 2000; Nath et al., 2002). Dimethyl phthalate has a higher dielectric constant (8.5) than toluene (2.4) as well as a higher boiling point, implying that as the sample solution is heated, toluene will evaporate first, leaving behind a solution with an increasing dielectric constant.  $C_{60}$  aggregation occurs when the critical values for dielectric constant and  $C_{60}$  concentration are reached, producing the residues shown in Figure 4. Thus, aggregation happens only during the evaporative preparation of samples for analysis and does not appear in bulk solution.

The  $\mu\text{L}^2\text{MS}$  technique does not detect  $C_{60}$  when it is clustered; attempts to analyze solid  $C_{60}$  powder also failed. Solutions of 1 mg/mL  $C_{60}$  in toluene (as in Fig. 4d) produce only weak signals. The cause of this phenomenon is the laser wavelength used for desorption and the thermal desorption mechanism integral to  $\mu\text{L}^2\text{MS}$ . When a thin film of a sample is deposited on glass, the infrared radiation of the desorption laser is absorbed by the glass substrate, which is rapidly heated and “kicks” analyte molecules from the thin film into the gas phase (Maechling, 1995). If the sample of  $C_{60}$  to be analyzed is clustered, as occurs in aggregate formation or in  $C_{60}$  powder, the desorption mechanism breaks down because there is not sufficient energy to allow these high-mass clusters to escape into the gas phase. Additionally,  $C_{60}$  does not have an infrared

absorption at the 10.6  $\mu\text{m}$  wavelength used for desorption (Krätschmer et al., 1990), so it cannot act as its own substrate to absorb and be heated by the desorption laser pulse. This problem does not occur with the SELDI or LDMS techniques, however, because both SELDI and LDMS use a 337-nm desorption/ionization wavelength produced by a nitrogen laser. This wavelength is absorbed well by  $C_{60}$ , which has a strong absorption at 339 nm (Krätschmer et al., 1990).

The phthalate-induced aggregation was reversible; when residues such as that shown in Figure 4b were redissolved in toluene and re-evaporated, films similar to those of Figure 4a were formed, and  $\mu\text{L}^2\text{MS}$  analysis resulted in  $C_{60}$  detection. Rock-induced aggregation, however, was not reversible, suggesting that although phthalate addition to toluene solutions provides a reasonable model for the rock extracts, for the rock samples themselves the overall effect is either not caused by or not confined to the presence of phthalates. This difference is not surprising, as the carbonaceous rock extracts contain a wide variety of toluene-soluble organic and inorganic compounds that may influence aggregation (see discussion of GC-MS analysis in Section 3.3). The solutions used to test aggregation were simple by comparison, containing only dimethyl phthalate.

### 3.3. Causes and Effects of Phthalate Contamination

Phthalic acid esters (often referred to as phthalates) are plasticizers commonly used as additives to soften plastics. They are prevalent environmental contaminants with a propensity to

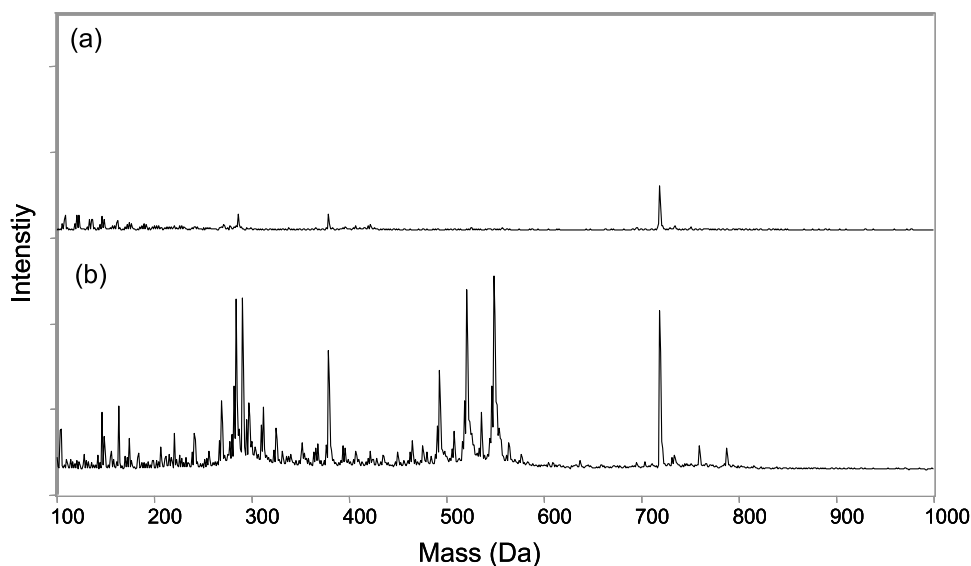


Fig. 5. SELDI spectra of 100  $\mu\text{g/mL}$   $\text{C}_{60}$  in (a) pure toluene and (b) toluene containing 1% dimethyl phthalate. Intensity scales are identical in both spectra; the  $\text{C}_{60}$  peak in (b) is approximately three times larger than that in (a).

leach from discarded plastics. In laboratory settings, phthalates have been observed in high-grade solvents and in O-rings, tubing, and other common apparatus (Asakawa and Gnjida, 1970; Verge and Agnes, 2002). Most relevant to our current work, phthalates have also been shown to leach from polypropylene bottles into stored water samples (Holm and Charlou, 2001) and to contaminate carbonaceous chondrite meteorites (Cronin and Pizzarello, 1990). The impact breccia samples studied in this work were stored in plastic bags, and demineralization was carried out in polypropylene bottles. Phthalates or related compounds could have been introduced to the samples via these containers. It is unknown whether phthalate contamination occurred during sample storage (which would have implications for all samples stored in plastic containers) or during demineralization (which would affect only samples that are acid-processed in plastic containers).

GC-MS analysis was performed on three extracts (GER-6, CSF-94–7A, and the HF/BF<sub>3</sub>-demineralized NGF-96–137). Both the GER-6 (Ries) and NGF-96–137 (Gardnos) extracts contained a complex mixture of compounds with more than twenty peaks observed, including several phthalates (diethyl phthalate, di-*n*-octyl phthalate, di(2-methylethylpropyl) phthalate, and benzyl butyl phthalate). The CSF-94–7A (Sudbury) extract did not show phthalate peaks, but did contain other toluene-soluble compounds such as long-chain acids and esters that may cause similar aggregation effects. These GC-MS results lend support to the claim that phthalates or other high-dielectric-constant compounds are a likely cause of the problematic detection of  $\text{C}_{60}$  by  $\mu\text{L}^2\text{MS}$  in various samples.

SELDI analysis of phthalate-spiked  $\text{C}_{60}$  solutions (100  $\mu\text{g/mL}$   $\text{C}_{60}$ , 1% dimethyl phthalate in toluene or in rock extracts) exhibited strong  $\text{C}_{60}$  signals, with no evidence of suppression. On the contrary, in some cases the  $\text{C}_{60}$  signal strength for phthalate-containing solutions was larger than the signal observed in  $\text{C}_{60}$ /toluene solutions without phthalate (Fig. 5). This signal enhancement was, however, not always observed (e.g., Fig. 2c and 2d). It is possible that aggregation produced stron-

ger signals by allowing the desorption of more  $\text{C}_{60}$  in each laser shot, or that the aggregated  $\text{C}_{60}$  provided a better substrate for desorption with the 337-nm laser.

Because of the numerous reported differences between  $\text{C}_{60}$  detection by LDMS and HPLC, we investigated the effects of phthalate contamination on HPLC analysis of  $\text{C}_{60}$ -containing samples. HPLC carried out on standard  $\text{C}_{60}$ /toluene/dimethyl phthalate solutions showed no evidence of signal suppression; signal strengths were comparable to those produced in phthalate-free  $\text{C}_{60}$ /toluene solutions. Because of the limited sample size of the impact breccia extracts, we could not analyze them by HPLC. A test rock sample, consisting of the  $\text{C}_{60}$ -spiked toluene extract of a demineralized piece of greywacke (Stanford, CA), was analyzed by  $\mu\text{L}^2\text{MS}$ , GC-MS, SELDI, and HPLC. The  $\mu\text{L}^2\text{MS}$ , GC-MS, and SELDI results mirrored those of the impact breccia rock extracts; HPLC analysis produced a strong  $\text{C}_{60}$  signal, with no evidence of signal suppression or enhancement.

Phthalate-induced aggregation by the mechanisms suggested here would produce clustering only upon evaporation of the samples and would not cause aggregation in the bulk solutions. The GC-MS and HPLC analyses of the bulk solution support this mechanism; phthalates were observed in the GC-MS data, but no evidence of aggregated  $\text{C}_{60}$  (such as signal suppression or peaks corresponding to aggregates) was observed by HPLC analysis. The signal enhancement observed in some SELDI analyses of phthalate-containing solutions provides additional evidence for aggregation; it also suggests one possible cause of discrepancies in previous LDMS/HPLC analyses. It is possible that such aggregation caused enhancement of the  $\text{C}_{60}$  signal observed in LDMS, leading to higher estimates of  $\text{C}_{60}$  concentration in natural samples when compared with phthalate-free standards. Differences between the estimated and actual values of  $\text{C}_{60}$  could place  $\text{C}_{60}$  levels below the detection limits of HPLC analysis, which does not exhibit such signal enhancement. The full extent and probability of aggregate-induced signal enhancement in LDMS, however, is not yet known.

### 3.4. Origin and Formation of Impact-Related Fullerenes

The origin and formation mechanisms for the fullerenes detected in these samples from three impact structures are still uncertain. Possible origins for the fullerenes include: (1) pre-impact presence and survival of fullerenes in possibly carbonaceous impacting bodies; (2) formation of fullerenes from the impactor, from carbonaceous target rocks, or from atmospheric gases, in the high-temperature impact environment; and (3) formation or introduction of fullerenes into the rocks during later postimpact metamorphic events.

The preimpact presence of fullerenes in the Sudbury impactor has been proposed (Becker et al., 1996), based on the reported presence of extraterrestrial gases (helium) trapped within the fullerenes, but the presence of such trapped helium in natural fullerenes remains controversial (Farley and Mukhopadhyay, 2001). In addition, calculations based on the reported fullerene contents of 1–100 ppm (Becker et al., 1994b) indicate that this mechanism requires an impactor of implausibly large size and/or carbon content (Heymann et al., 1999), a conclusion that holds true even with the lower concentrations of 2–15 ppb suggested by our work and that of Mossman et al. (2003). Production of fullerenes from terrestrial preimpact target rocks is problematic because of the apparent absence of appropriate carbonaceous target rocks in the presently exposed Sudbury and Gardnos structures (French, 1968; Pye et al., 1984; French et al., 1997; Gilmour et al., 2003). In any case, the long-term geological survival of fullerenes, no matter how formed, at Sudbury and other impact structures, is also problematic given the significant metamorphic temperatures (300 to 400 °C) to which the rocks at Sudbury and Gardnos have been subjected for possibly millions of years after the impact event itself (French, 1968; French et al., 1997; Heymann et al., 1999).

Clearly, a number of questions remain difficult to answer even after this study has been completed. The inconsistencies in reported C<sub>60</sub> concentrations from impactites, especially from the same samples, only add to the problems remaining to be solved.

## 4. CONCLUSIONS

Our SELDI results confirm the presence of C<sub>60</sub> in rocks from the “Black Member” of the Onaping Formation of the Sudbury impact structure. A comparison of analyses of the same samples by different researchers shows inconsistent reports of detected C<sub>60</sub> levels (Becker et al., 1994b; Heymann et al., 1999; Mossman et al., 2003). These differences could be caused by heterogeneities in C<sub>60</sub> distribution or by the effects of sample preparation and technique. We also detected low concentration levels of C<sub>60</sub> in samples from the Gardnos and Ries craters. These observations indicate that further analyses of rocks from these impact structures may be useful in determining if C<sub>60</sub> and higher fullerenes are widespread in these craters. We also observed differences in extracts prepared by different demineralization methods, which suggests that the liberation and concentration of C<sub>60</sub> depends upon preparative conditions, although a definitive correlation was not observed.

C<sub>60</sub> was detected in these extracts only using the SELDI technique, which is analogous to the LDMS techniques used in the only other reports of fullerenes in Sudbury (Becker et al.,

1994b; Mossman et al., 2003). Phthalate-induced aggregation may underlie the signal suppression in C<sub>60</sub>-containing samples analyzed by  $\mu\text{L}^2\text{MS}$ . Such aggregation also appeared to enhance SELDI signal detection in some cases, and we suggest that this enhancement may have played a role in previous LDMS analyses of natural rock extracts. Extracts of demineralized rocks were shown to contain many compounds, including aromatic and aliphatic hydrocarbons, phthalates, and other toluene-soluble species. The mechanism we propose for C<sub>60</sub> aggregation (evaporation of toluene resulting in higher-dielectric-constant solutions and aggregate formation) could be caused by phthalates, which may easily contaminate samples, or by other indigenous compounds possessing the necessary boiling points and dielectric constants. It is worth noting that although such contamination can produce a “false negative” when analyzing C<sub>60</sub>-containing samples, we have not observed any mechanism for producing a “false positive” result with the analytical methods used in this work.

The work reported here explains the differences between detection capabilities of  $\mu\text{L}^2\text{MS}$  and SELDI; it also suggests one possible explanation for previously observed differences between HPLC and LDMS measurements. This work also carries a larger message. Natural samples are often complex mixtures of compounds, and the influences of one set of compounds on C<sub>60</sub> or other analytes of interest are not always well characterized and may differ from one technique to the next. For that reason, results from different analytical techniques and preparative methods should be viewed as complementary. We suggest that a wide range of such methods should be applied to the analysis of such complex and interesting natural samples.

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