The search for fullerenes in rocks from the Ries impact crater

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Abstract—Since their discovery, fullerenes have been reported from various geological environments. One group of these findings has been related to bolide impacts, e.g., the Sudbury crater and the K-T and P-T boundaries. Impact rocks of the Ries crater, Germany, including samples of suevites, metamorphosed crystalline clasts, and glass bombs, have been collected in the Otting, Alteberg, and Seelbronn quarries. No fullerenes in concentrations above 1 ppb have been found in analyzed samples. Laser desorption time-of-flight mass spectrometry (LD-TOF-MS) confirmed the absence of fullerenes in the analyzed samples. These results support the concept that the Ries impactor was a stony meteorite.

INTRODUCTION

This paper describes the results of a search for fullerenes in rocks from the Ries crater, Bavaria, Germany. There are generally two basic hypotheses about the origin of fullerenes from meteorite-related occurrences. One involves the formation of fullerenes during impact, the other proposes their extraterrestrial origin. We searched for fullerenes in the Ries impact structure, where the target rocks are carbon-rich and thus could have been a source for the carbon of fullerenes, had they formed during the impact. Impact diamonds were first reported from this crater by Rost et al. (1978). Subsequently, impact diamonds have been investigated in the Ries crater by several groups. They were found in suevite whole-rock samples (Hough et al. 1995, Abbott et al. 1998), in glass bombs (Rost et al. 1978, Abbott et al. 1996, Siebenshock et al. 1998), and in highly shocked crystalline fragments (El Goresy et al. 1999). According to Schmitt et al. (1999) the major carriers of diamonds in Ries are glass bombs of the fallout suevite formed by melting at shock pressures above 60 GPa, and the source of impact diamonds seems to be highly shocked graphite-bearing gneisses. Other carbon phases are also known from the Ries crater, e.g., chaoite (El Goresy and Donnay 1968) and silicon carbide (Hough et al. 1995).

The only crater with fullerenes reported so far is the Sudbury basin, Ontario, Canada (Becker et al. 1994a, 1996; Mossman et al. 2003). It is a 1.85 Ga old multi-ring impact crater (see Heymann et al. 1999 and references therein) with estimated diameter of ~180–250 km. The impact breccias of the Onaping formation that are enclosed within the Sudbury igneous complex are traditionally subdivided into four members: the igneous-matrix basal member, the gray member polymict suevitic breccias, the green member, and the black member, a redeposited suevitic-breccia unit. The gray, green, and black members contain recrystallized glass fragments (Dressler et al. 1996). Masaitis et al. (1997) observed shock-produced diamonds in the breccias of the black member.

The reports on naturally occurring fullerenes have been summarized by Buseck (2002) and by Heymann et al. (2003). Fullerenes have been reported in rocks that experienced unique geological events under high-energy conditions, such as lightning (Daly et al. 1993), meteorite impacts in Chicxulub, Mexico, at the Cretaceous-Tertiary (K-T) boundary (Heymann et al. 1994, 1996, 1998), at the Permian-Triassic boundary (Becker et al. 2001), and at Sudbury, Canada (Becker et al. 1994a, Mossman et al. 2003). At Sudbury, the extraterrestrial origin of fullerenes was deduced from the isotopically anomalous composition of helium trapped in carbonaceous cages (Becker et al. 1996). Heymann and co-authors reported the occurrence of fullerenes at the New Zealand K-T boundary sites of Woodside Creek and Flaxbourne River, at Caravaca (Spain), Sunbar and Maliyi Balkan (Turkmenistan), Stevens Klint (Denmark), and Brazos River (Texas). The fullerene concentrations in the rocks of these sites were about 0.1 to 11 ppb. Heymann et al. (1996)
suggested that the K-T boundary fullerenes were formed during global wildfires after the impact of a meteorite in Chixculub, Mexico. Taylor and Abdul-Sada (2000) have not found fullerenes in a single sample from K-T boundary. Becker et al. (2001) reported that sediments from the Permian-Triassic (P-T) boundary contain fullerenes with an isotopically distinct extraterrestrial signature of noble gases. Farley and Mukhopadhyay (2001) measured 3He values in samples from the P-T boundary and suggested a terrestrial distribution. In view of the fact that other inconsistencies bring into doubt the precise origin of the studied samples (Isozaki 2001) and considering the ambiguous process when detecting fullerenes and endohedral 3He inside fullerenes (Braun et al. 2001), the published findings concerning the P-T boundary remain controversial.

Similarly, the presence of natural fullerenes in shungite (highly carbonized carbonaceous matter of Precambrian age) has been a matter of speculation for some time. They were initially reported by Buseck et al. (1992) in a sample from Shunga, Karelia (Russia). Other samples of shungite, as well as similar thucholite and anthraxolite materials, were examined unsuccessfully for the presence of fullerenes by Heymann (1995a), Gu et al. (1995) and Ebbesen et al. (1995). However, Parthasarathy et al. (1998) reported fullerenes in shungite from Kondopoga, Karelia, thus supporting the original findings of Buseck et al. (1992). Natural fullerenes in low concentration have been reported from the Bohemian Massif in hard solid bitumens (rocks similar to shungites) from Mitov (Jehlička et al. 2000, 2003).

The presence of fullerenes in space or extraterrestrial bodies also remains to be confirmed. Di Brozolo et al. (1994) found C_{60} and C_{70} in and around a micrometeorite impact pit on the skin of the LDEF (Long Duration Exposure Facility) spacecraft and concluded that the fullerenes had been formed from C of the micrometeorite. Becker et al. (1994b) and Becker and Bunch (1997) reported fullerenes in the Allende meteorite, but Heymann (1995b) detected no fullerenes in Allende meteorite samples and concluded that the fullerene content in the meteorite calculated by Becker is either overestimated or the distribution of fullerenes in the mineral matter is inhomogeneous. The search for fullerenes in Murchison meteorite (deVries et al. 1993) and in lunar samples (Heymann 1996) proved unsuccessful.

MATERIALS AND METHODS

Geological Setting

The Ries crater (48°51′06″N, 10°29′23″E) lies in southern Germany. It is an approximately circular structure with an inner diameter of 25 km. The target rocks at the time of impact consisted of ~580 m thickness of sedimentary rocks, including 190 m of Upper Jurassic limestone, 50 m of Middle Jurassic (sandstone, marlstone, limestone), 15 m of Lower Jurassic (sandstone, marlstone, limestone), and 250 m of Upper and Middle Keuper (sandstone, siltstone, marlstone, and claystone). The southern half of the present basin was covered by ~25 m of unconsolidated Upper Miocene sands, marls, and clays (Engelhardt 1997). This sedimentary rock sequence is underlain by crystalline rocks (gneisses, granites, metabasites) of Hercynian age (Engelhardt 1997 and references therein). Two major groups of impact rocks can be distinguished using the classification of Stöffler (1974): low shock level ejecta, shocked by pressures <10 GPa (Bunte breccia, blocks of sedimentary and crystalline rocks, and monomict crystalline breccias) and high shock level breccias, containing materials shocked by pressures exceeding 10 GPa (polymict breccias and suevites). Bunte breccia is, by volume and area, the most extensive ejecta formation. Together with large blocks of sedimentary rocks, mainly Upper Jurassic limestone, the Bunte breccia represents all material originating from the 580 m thick sedimentary sequence. The only impact formations of the Ries structure that contain rock clasts in all stages of shock metamorphism, together with pieces of vitreous and devitrified impact melts, are the suevites (for the classification of suevites, see Stöffler et al. 1974). Fallout suevites occur on the surface beyond the crater ring, while crater suevite fills the crater cavity and is covered by post-impact lake sediments. Fallout suevites (Engelhardt et al. 1995, Engelhardt 1997) occur today in numerous isolated patches from a few meters up to 30 m thick outside the inner ring at distances between 6 and 20 km from the crater center. Distribution of fallout suevites is shown in Fig. 1. Fallout suevites were deposited as last ejecta on top of earlier ejecta formations such as Bunte breccia and megablocks of limestone and crystalline rocks. Therefore, fallout suevites were the first of all ejecta formations to be removed by erosion so that the occurrences (i.e., Alteburg, Seelbronn, Otting) shown in Fig. 1 must be regarded as remnants of the original suevite ejecta blanket (Engelhardt 1997).

The glass bombs in the Ries suevite have an 40Ar/39Ar and a fission track age of 15.0 Ma (see Stöffler et al. 2002 and references therein) as do moldavites, which are tektites found in various places in Central Europe. They can be interpreted as condensates of vaporized, surficial sediments (Engelhardt et al. 1995).

Samples Collection

In the Ries crater, samples of suevites were collected at the Otting, Seelbronn, and Alteburg quarries. Our focus was on fresh, non-weathered samples with possibly higher glass contents. Whole rock samples were used for the analysis. As for composition of crystalline rocks in suevites, according to Engelhardt (1997), Otting suevite contains mostly granite clasts (17.4%), biotite-plagioclase gneiss (15.3%), and granodiorite (12.5%), while the majority of clasts are shock
The search for fullerenes in Ries metamorphosed in stage II (classification of Stöffler 1974) in the pT range of 35–45 GPa and 300–900 °C. Alteburg suevite contains mostly biotite-plagioclase gneiss (34.8%), amphibolite (21.7%), kersantite (11.6%), and granite (10.1%).

Measurements of Total Carbon and Organic Carbon Content

Powdered samples of whole rock suevites have been analyzed for total carbon and organic carbon content using the ELTRA CS 1000 analyzer. The total carbon has been measured by burning the samples at 1250 °C in air. The organic carbon content was calculated by subtracting the mineral carbon content that has been measured by decomposition in H_3PO_4 at 100 °C.

Demineralization, Extraction, and Analysis

Four demineralized samples of suevites (OttHF1 and OttHF2 from Otting, SeelHF from Seelbronn and AbHF from Alteburg) and three non-demineralized samples of suevite (Ott0, Seel0 and Ab0) were examined only by high-performance liquid chromatography (HPLC). For OttHF2, the sample consisted of one clast of glassy suevite (130 g). OttHF1, SeelHF and AbHF are 1 kg selections of more clasts.
that contain both the glass bombs and crystalline rocks. Ott0, Seel0 and Ab0 are samples weighing approximately 100 g of the same composition as the demineralized ones.

For mass spectroscopic measurements of fractions separated by HPLC, another set of samples (Ott2 from Otting, Ab2 from Alteburg and Seel2 from Seelbronn) was selected and demineralized.

Concentrated hydrofluoric and hydrochloric acids (p.a. grade, Lachema a.s.) were used for the demineralization. In the first step, samples were divided into parts no larger than 200 g and treated with 1 liter of HF:HCl (2:1) mixture for one day at room temperature. Particles lighter than the solution were carefully collected, and then the liquid phase was separated. The insoluble residue was treated with pure HF three times, eight hours each time, then repeatedly washed with distilled water and dried at room temperature.

Toluene (HPLC grade, Merck AG) was used for the extraction. The toluene/rock ratio was approximately 2–3 ml/g. The samples were treated in an ultrasonic bath for two hours. Then they were later filtered through a 0.45 µm PTFE filter. The remaining extracts were evaporated under vacuum to 1 ml.

High-performance liquid chromatography was used for the fullerene analysis with a Cosmosil Buckyprep Analytical Column (250 × 4.6 mm) and toluene as the mobile phase. The retention spectra were taken on a photo-diode-array detector. Before each run, instrumental blanks were run. C_{60} fullerene standard (99.5% purity, provided by Xillion, Germany) was used for calibration and determination of the detection limit.

To ensure that the fullerenes were not destroyed during the demineralization and extraction procedures, special spiked samples were prepared. The OttSP sample was prepared by mixing 46 g of Otting suevite matter and 25 µg of C_{60} standard evaporated from a toluene solution. This sample was then demineralized and extracted in the same manner as the other samples.

To prevent possible contamination of fullerenes, all the glassware used was heated at 400 °C for 12 hours. Instrumental blanks were run prior to each run in HPLC.

For separation prior to mass spectroscopy measurements, Cosmosil Buckyprep Semipreparative Column (250 × 10 mm) equipped with guard column Cosmosil Buckyprep (20 × 10 mm) was used. Fractions from the area of C_{60} elution in retention time range 12.30–14.30 min were collected from two runs. The solvents were evaporated at reduced pressure to dryness and redissolved in HLPC grade toluene (10 µl). The samples (1 µl) were deposited on a metallic target and sample directly ionized with a laser pulse.

The target was measured on a MALDI-TOF instrument (ToFSpec 2E, Micromass, Manchester, UK) operated in a reflectron mode using delayed extraction. Desorption and ionization was accomplished using nitrogen UV laser
The search for fullerenes in Ries

(337 nm, 4 ns pulses of 180 µJ). Formed positive ions were subjected to a 25kV accelerating potential and detected by a dual microchannel plate (MCP) detector. Scans were accumulated using 10 laser shots and obtained spectra are an average of at least 100 consecutive scans. Smoothed and baseline subtracted data were centered and calibrated using calculated mono-isotopic masses of \([C_{60}]^+\) and \([C_{74}]^+\) peaks where needed. Data were collected and analyzed with MassLynx software running on a PC workstation. The sensitivity of measurement was checked using C60 standard (10 ppm).

RESULTS

No fullerenes were detected by HPLC in toluene extracts of natural samples in concentrations exceeding the detection limit of 10 ppb in toluene solutions. The chromatograms of OttHF1, OttHF2 and OttSP from the analytical column are shown in Fig. 2 (a, b, and c, respectively). In OttHF1 sample, sign of a peak emerging at 7.9 min can be possibly attributed to C60. However, we were not able to reproduce this result, even when analyzing extracts obtained from higher amounts of rock like OttHF2. Table 1 summarizes the samples, their weights before demineralization and extraction, and limits of their C60 content. The detection limit for each sample is calculated from its weight prior to demineralization for AbHF, SeelHF, OttHF1, OttHF2, and OttSP, and prior to extraction for Ab0, Seel0, and Ott0. This calculation considers 88% extraction efficiency that was obtained from OttSP analysis with added C60 fullerene standard. The area of the C60 peak at 7.9 minutes from OttSP has been measured and compared to the areas of the C60 peaks from the prepared standard calibration solutions. The yield of extracted C60 from spiked OttSP was 22 µg, corresponding to 88% efficiency.

The fractions collected on the semipreparative column from the samples Ott2, Ab2, and Seel2 were concentrated and analyzed by LD-TOF-MS. The obtained spectra did not show any peak around \(m/z\) 720.

The total carbon content of whole rock samples from Alteburg, Seelbronn, and Otting was 0.64, 0.06, and 0.49 wt%, respectively. Organic carbon content did not exceed 0.06 wt% in these samples. Table 2 summarizes the total and organic carbon contents in the samples.

DISCUSSION

The absence of detectable amount of fullerenes in analyzed samples can be attributed to several factors. The role of impactor and target stratigraphy will be discussed first, then the low stability of fullerenes exposed to high pressures and its consequences for possible carbon phase transitions in the target rocks. The last part will mention the susceptibility of fullerenes to weathering.

The only occurrence so far of fullerenes reported from an impact crater on the Earth is from the Sudbury impact structure (Becker et al. 1994a, 1996; Mossman et al. 2003). The first hypothesis advanced was that this occurrence was due to fullerene synthesis within the vapor plume from carbon in the bolide (Becker et al. 1994a). Results of subsequent measurement of helium isotopes encapsulated in fullerenes from Sudbury, however, are taken to indicate their extraterrestrial origin (Becker et al. 1996).

Similarly, the occurrence of C60 in a microcrater on the LDEF satellite (di Brozolo et al. 1994) is attributed to a carbonaceous chondrite. That same paper included the results of experiments of hyper velocity impacts of man-made fullerenes on alumina targets, showing that fullerenes had not been destroyed at impact velocities of 6.1 km s\(^{-1}\). However, similar experiments with organic acids did not produce fullerenes at these impact velocities, a result which favors the suggested extraterrestrial origin of fullerenes on the LDEF microcrater. The theoretical probability of occurrence of fullerenes in an impact crater on the Earth is reduced to either extraterrestrial origin from carbonaceous chondrites or some gas-phase formation process that incorporates helium atoms from the impactor into the fullerenes.

Solid state formation of fullerenes from an organic precursor, as suggested by Heymann et al. (2003) for

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Table 1. Detection limits of C\(_{60}\) for analyzed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Locality</th>
<th>Weight before demineralization (g)</th>
<th>Weight before extraction (g)</th>
<th>Limit of C(_{60}) content in sample (ppb)</th>
<th>Analysis method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab 0</td>
<td>Alteburg</td>
<td>non-demineralized</td>
<td>91.8</td>
<td>0.62</td>
<td>HPLC</td>
</tr>
<tr>
<td>Seel 0</td>
<td>Seelbronn</td>
<td>non-demineralized</td>
<td>111.9</td>
<td>0.51</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ott 0</td>
<td>Otting</td>
<td>non-demineralized</td>
<td>96.3</td>
<td>0.59</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ab HF</td>
<td>Alteburg</td>
<td>1061.6</td>
<td>8.8</td>
<td>0.05</td>
<td>HPLC</td>
</tr>
<tr>
<td>Seel HF</td>
<td>Seelbronn</td>
<td>1000.6</td>
<td>7.7</td>
<td>0.06</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ott HF1</td>
<td>Otting</td>
<td>130.6</td>
<td>9.5</td>
<td>0.44</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ott HF2</td>
<td>Otting</td>
<td>991.2</td>
<td>79.4</td>
<td>0.06</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ott SP</td>
<td>Otting</td>
<td>46.2</td>
<td>6.6</td>
<td>1.23</td>
<td>HPLC</td>
</tr>
<tr>
<td>Ab 2</td>
<td>Alteburg</td>
<td>554.3</td>
<td>11.8</td>
<td>0.02</td>
<td>HPLC, LD-TOF-MS</td>
</tr>
<tr>
<td>Seel 2</td>
<td>Seelbronn</td>
<td>753.9</td>
<td>22.9</td>
<td>0.02</td>
<td>HPLC, LD-TOF-MS</td>
</tr>
<tr>
<td>Ott 2</td>
<td>Otting</td>
<td>328.2</td>
<td>27.6</td>
<td>0.03</td>
<td>HPLC, LD-TOF-MS</td>
</tr>
</tbody>
</table>
fullerenes in Shunga, Mítov and perhaps Sudbury, could be probably ruled out in the case of the Ries crater. This hypothesis demands a possible biogenic precursor and thermal alteration maybe with the presence of elemental sulfur. The precursor could have been derived from Posidonia Shale (Lias ε), which was part of the target area stratigraphy and comprises a sequence of organic matter-rich black shales deposited in an oxygen deficient, shallow marine environment (see Hofmann et al. 2001 and references therein). The total organic carbon content in Posidonia shale can reach up to 15% (Frimmel et al. 2004). However, thermal overprint in samples of Posidonia shale from Bunte breccia studied by Hofmann et al. (2001) is not very strong and does not suggest much higher temperatures of alteration than temperatures of sedimentary burial (40–60 °C). For comparison, the temperature supposed for pyrolysis of organic matter in Mítov could well be around 1000 °C (Jehlička et al. 2003).

The low stability of fullerenes under high non-hydrostatic pressure is well known. Rapid transformation of C60 to diamond at pressures of 20 ± 5 GPa at room temperature was first documented by Regueiro et al. (1992). The precursor to diamond at pressures of 20 GPa at high temperature has been documented by Hodeau et al. (1994). Wasa et al. (2000) described irreversible amorphization of C70 at pressures above 35 GPa, while the amorphization is reversible between 12.5 and 35 GPa.

In suevites of the Ries impact crater, high-pressure and high-temperature induced effects on target rocks have been well documented. According to description by Stöffler et al. (1974), the impact glass (suevite type IV) occurs in the pressure range of 60–80 GPa; only vaporization takes place above this pressure. Glass is very abundant in our samples, but clasts of all other stages of shock-metamorphism are present. As earlier summarized, transition from graphite to diamond occurs in various suevite types. El Goresy et al. (2001) estimate the peak pressure of graphite-diamond transition in gneisses at 30–40 GPa. Other findings of diamonds in glass bombs (Rost et al. 1978, Abbott et al. 1996, Siebenschock et al. 1998) indicate transition pressures of 60–80 GPa. Covering all the range of suevites of type II to type IV, the principal carbon phase transformation in the solid state in Ries suevites seems to be graphite-diamond. The presence of chaote (El Goresy and Donnay 1968) has not been successfully explained.

Gardnos structure, another interesting impact site where various carbon phases occur, was described recently by Gilmour et al. (2003). Platey microdiamonds as well as moderately to poorly crystalline graphite were observed in suevites. The authors suggest at least two distinct phases for carbon emplacement in Gardnos suevites: the first was related to the carbon shock transformation during the impact, the second was probably related to post-impact cooling process or later regional metamorphism. There is no information about fullerene occurrence in these rocks.

Based on the results of Abbott et al. (1998), the source of the carbon for diamonds in the Ries suevites was derived either from a mixture of C sources or from a heterogeneous single C source such as graphite (Hough et al. 1995). The basement graphite also provided a suitable C source to yield lighter C isotopic compositions for diamonds found in the shock-produced glasses (Abbott et al. 1998). The total C content in Otting suevite was 1.6% with δ13C of ~11.9 per mil and in Seelbronn suevite 3.9% with δ13C of ~7.9 per mil (Abbott et al. 1998). These data indicate that a mixing of sedimentary C primarily as carbonates with basement-derived graphite results in the final C composition of the whole-rock suevites. However, these results on measured total C contrast with the results of our measurements on whole rock suevite samples. We have found 0.64, 0.06, and 0.49 wt% for Altebûrg, Seelbronn, and Otting samples, respectively, with organic carbon content 0.06 wt% and less (Table 2). The probable reason for our lower carbon content is the higher amount of glass bombs in our suevites, which have significantly lower C content than the whole rock suevites (Abbott et al. 1998). These results substantially lower the probability of finding fullerenes in our samples. The source of carbon for the fullerenes at Sudbury has not been successfully explained yet, though it seems that the target rocks contained little carbon (Heymann et al. 1999). This suggestion was made upon a remarkable observation that “shock metamorphosed carbons,” such as chaote and diamond, are very rare at Sudbury (Masaitis et al. 1997). Also the distribution of fullerenes in Sudbury is very heterogeneous (Heymann et al. 1999).

Another important reason for absence of fullerenes can be the state of collected samples that were more or less weathered. As documented by Chibante and Heymann (1993) and Juha et al. (2000), fullerenes are susceptible to decomposition caused by oxygen, especially in the form of O3. The crystalline clasts of collected suevites are heavily shocked and have many deformational aspects, which allow more intense weathering and are very permeable to gases. In shungites and hard solid bitumens at Mítov (Bohemian Massif), where fullerenes were found e.g., by Buseck et al. (1992) and Jehlička et al. (2003), respectively, fullerenes are thought to be enclosed in a glass-like carbonaceous matrix that is quite gas-impermeable. For fullerenes at Sudbury, the role of the sulfide-silicate matrix in preservation of fullerenes was probably substantial as well (Becker et al. 1994a).

The nature of the impacting body has not been solved. Since known occurrences of fullerenes associated with meteorites, e.g., Sudbury (Becker et al. 1994a, 1996), LDEF

<table>
<thead>
<tr>
<th>Sample</th>
<th>C_{total} (wt%)</th>
<th>C_{org} (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altebûrg</td>
<td>0.64</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Seelbronn</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>Otting</td>
<td>0.49</td>
<td>0.05</td>
</tr>
</tbody>
</table>
facility (diBrozolo et al. 1994), and Allende (Becker et al. 1994b, Becker and Bunch 1997), are all associated with carbonaceous chondrites, our negative results support the concept raised by El Goresy and Chao (1997) that the Ries impactor was a stony meteorite.

CONCLUSION

No fullerenes have been found in toluene extracts of demineralized natural samples of suevites from the Ries crater, Germany. Their absence indicates either that the P/T conditions were not favorable for their formation, or that if they were formed (e.g., in the vapor plume), they must have been exposed to weathering and thus should have decomposed. In addition, our negative results are in good agreement with generally accepted theory of a stony meteorite impactor.

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