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Distribution and origin of impact diamonds in the Ries crater, Germany

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ABSTRACT

The distribution and origin of impact diamonds in the ejecta blanket of the Ries crater, Germany, was investigated. Impact diamonds are present in the fallout suevite, whereas the cataclastic crystalline breccias, lithic impact breccia (Bunte Breccia) and clast-rich impact melt rock do not contain diamonds. No regional concentrations of impact diamonds in the fallout suevite could be detected. The average concentration of diamonds is ~0.1–0.2 ppm. The carriers of impact diamonds are specific suevite components, such as graphite-bearing crystalline rock fragments of shock stage III, and most likely small fragments thereof in melt fragments and suevite matrix. Impact diamonds occur as pseudo-hexagonal, transparent, and birefringent plates, which reach sizes up to 300 µm. Their color is commonly greenish, but can also be black, gray, yellow, or colorless. Most of the impact diamonds have a fibrous or spongy internal structure and extensional microfractures, which lead to a characteristic porosity. This is the result of a volume decrease due to the phase transformation of graphite to diamond. The Raman characteristics of these impact diamonds are discussed in detail. The strong morphologic similarity of impact diamonds to the precursor graphite from the crystalline target rocks indicate a solid state martensitic phase transformation which occurs at shock pressures of 45–55 GPa.

Key words: impact diamonds, Ries crater.

INTRODUCTION

Diamonds produced by shock metamorphism were discovered for the first time by Yerofeev and Lachinov (1888) in the ureilite Novo Urei. In 1891, Foot described impact diamonds in fragments of the Canyon Diablo iron meteorite associated with the Meteor (Barringer) Crater in Arizona, USA. In this case, polycrystalline diamonds were formed by shock transformation of carbonaceous matter that occurred within the projectile. Impact diamonds are generally different from kimberlite or lamproite diamonds due to their µm-sized, polycrystalline structure. Moreover, X-ray investigations revealed the occurrence of the hexagonal carbon phase lonsdaleite (Frondel and Marvin, 1967; Hannemann et al., 1967) in many of these impact diamond grains. Since these findings, impact diamonds were frequently reported from other iron meteorites and especially from ureilites (e.g., Anders, 1965; Frondel and Marvin, 1967; Vdovykin, 1970; Berkley et al., 1980; Bischoff and Stöffler, 1992).

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Diamonds synthetically produced by shock compression were for the first time described by DeCarli and Jamieson (1961). They used mixtures of graphite and metal, and shock-loaded them at pressures above 15 GPa. Impact diamonds are produced if the shock temperature of the samples is above 1300 K and the post-shock temperature below 2000 K (DeCarli, 1995, 1998). A successful experimental shock transformation of graphite to diamond in natural graphite-bearing gneiss was reported by Kenkmann et al. (2002) above 45 GPa.

Impact diamonds in shocked terrestrial target rocks were first discovered in the Popigai crater, northern Siberia, Russia (Masaitis et al., 1972, 1995; Masaitis, 1998; Koeberl et al., 1995, 1997; Vishnevsky et al., 1997). In this crater, impact diamonds are found in shocked graphite-bearing gneiss clasts in suevite and impact melt rocks, in the suevite matrix, and in impact melt rocks. These diamond grains reach sizes up to 1 cm in diameter. They are yellow, gray, or black in color and rarely colorless. The diamond grains display the original shape of the precursor graphite, yet they are aggregates and consist of microcrystals with diameters of <1–5 µm. For such diamond grains, the term paramorphs was introduced (Shafranovsky, 1985). Impact diamonds are also found in alluvial deposits at Popigai due to weathering of the impactites and in this case, the grains are broken or have irregular shapes. Subsequently, impact diamonds were found in the Kara and Puchezh-Katunki craters in Russia (Vishnevsky et al., 1997), in the Ilyinets, Obolon, Ternovka, and Zapadnaja craters in Ukraine (Valter et al., 1992; Gurov et al., 1995, 1996; Masaitis et al., 1995; Vishnevsky et al., 1997), in Sudbury, Canada (Masaitis et al., 1997), in the Cretaceous-Tertiary boundary layer of Mexico, USA, and Canada (Hough et al., 1997a, 1997b), in the Lappajärvi crater in Finland (Masaitis et al., 1998; Hough et al., 1999; Moroz et al., 2003) and the Gardnos crater in Norway (Gilmour et al., 2003). The shape and size of the impact diamonds depend strongly on the shape and size of the precursor carbon phase (e.g., graphite, coal) in the respective target rocks, e.g., in the Sudbury crater impact, diamonds are generally anhedral. None of these craters contains impact diamonds suitable for commercial exploration.

GEOLOGY OF THE RIES CRATER

The Ries crater, Germany (diameter ~24 km; age 14.3–14.4 Ma; Fig. 1) occurs in a target of up to 0.75 km thick Cenozoic and Mesozoic sediments (limestone, shale, sandstone) overlying a complex Variscan crystalline basement (e.g., Graup, 1978; Stöffler and Ostertag, 1983, and references therein; Engelhardt, 1990; Hüttner and Schmidt-Kaler, 1999a, 1999b; Buchner et al., 2003; Laurenzi et al., 2003). The base of the ejecta deposits consists of a lithic, clastic matrix breccia (Bunte Breccia) with a thickness of up to 200 m and a radial extent of up to 42 km from the crater center (Stöffler and Ostertag, 1983; Engelhardt, 1990). This polymict breccia is dominated by material (shock stages 0–II) from the sedimentary cover mixed with locally derived material, especially in the outer parts of the ejecta blanket. Near to the crater rim and in the megablock zone between the crater rim and the inner ring (diameter ~12 km) crystalline breccias (shock stages 0–II) occur as irregular bodies within or on top of the lithic breccia (Stöffler and Ostertag, 1983; Engelhardt, 1990). These crystalline and polymict breccias are covered locally by patches of fallout suevite (Engelhardt, 1997, and references therein). In contrast to the Bunte Breccia, the suevite consists mainly of crystalline basement material of shock stages 0–IV (Engelhardt, 1997) and impact melt that is dispersed in form of melt fragments (“glass bombs”) of up to 50 cm in size and of small, chilled melt particles within the matrix (Engelhardt, 1997; Osinski et al., 2003). The chemical composition of this impact melt reflects a mixture of crystalline target rocks, mainly granite and biotite-plagioclase-gneiss, and is rather homogeneous in composition across the entire Ries crater (Stähle, 1972; Engelhardt and Graup, 1984; Engelhardt, 1997). Melt fragments contain abundant mineral, crystalline, and sedimentary rock fragments of different shock stages. Inside the inner ring, a suevite lens (crater or fallback suevite), up to 400 m thick and deficient in melt fragments, was found

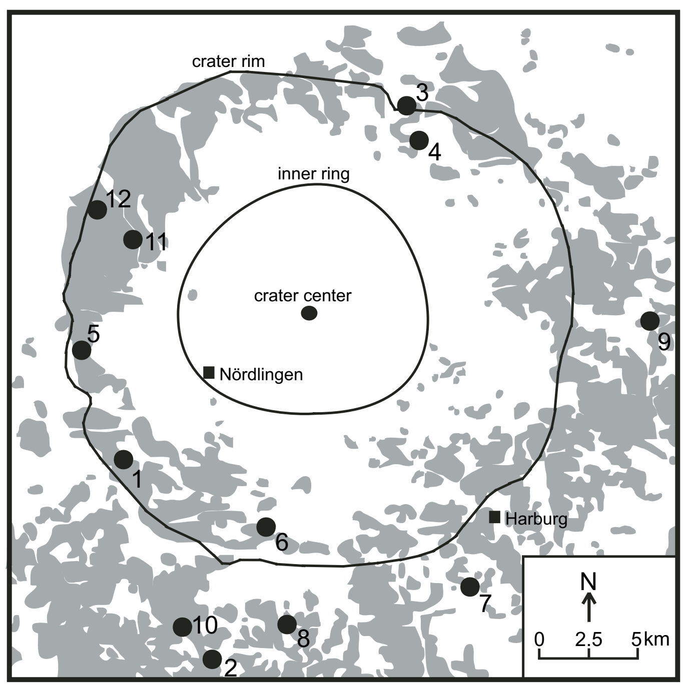

Figure 1. Simplified map of the Ries crater, Germany. The ejecta deposits (cataclastic crystalline breccias, lithic clastic impact breccia, fallout suevite, and clast-rich impact melt rock) are shown in gray. The crater rim (diameter ~24 km) and the inner ring (diameter ~12 km) are indicated by solid lines. Due to the erosion, ejecta deposits occur preferentially in the megablock zone between the inner ring and the crater rim, and in the southern and eastern surroundings of the crater. The diamond-bearing suevite localities are marked by filled circles: 1—Altenbürg, 2—Amerdingen, 3—Aumühle, 4—Hainsfarth, 5—Heerhof, 6—Hohenaltheim, 7—Mauren, 8—Oberringingen, 9—Otting, 10—Seelbronn, 11—Unterwilflingen, 12—Zipplingen. Map modified after Schmidt-Kaler (1978).

by drilling (Gudden, 1974; Bayerisches Geologisches Landesamt, 1977; Stöffler and Ostertag, 1983). The crater suevite is covered by up to 330 m thick, post-impact lake sediments. An impact melt rock layer does not occur in the central depression, although two small outcrops of red, clast-rich, recrystallized impact melt rock occur near to Polsingen and Amerbach at the eastern crater rim (Engelhardt et al., 1969; Stöffler and Ostertag, 1983; Hüttner and Schmidt-Kaler, 1999a, 1999b).

IMPACT DIAMONDS FROM THE RIES CRATER

The first impact diamonds in the Ries crater were discovered by Rost et al. (1977) in melt fragments from the suevite of Otting. Masaitis et al. (1995) described impact diamonds extracted from shocked gneiss fragments from the suevite deposits Otting and Aumühle, which occur in the form of paramorphs after graphite. Also, Abbott et al. (1996) found impact diamonds in a melt fragment from the Otting suevite. In the crater suevite of the scientific drill core Nördlingen 1973, Abbott et al. (1998) reported impact diamonds in suevite samples from depths of 384 and 494 m. Valter et al. (1998) and Thiele and Scherer (2000) extracted impact diamonds from suevite whole-rock samples from the Otting quarry. All of these findings show a similar appearance of the impact diamonds, closely resembling the impact diamonds occurring in the Popigai crater. The diamonds are flat platelets of variable color, 20–400 µm in size, which are interpreted as paramorphs after the precursor graphite. El Goresy et al. (2002, 2003) described a potentially new carbon phase of similar appearance from a shocked gneiss fragment of the suevite.

Different types of diamonds were discovered by Hough et al. (1995), who reported µm-sized skeletal aggregates of diamonds and diamond-silicon carbide intergrowths from a suevite whole-rock sample of the Otting quarry. These grains were interpreted as chemical vapor deposited from the ejecta plume. Still another type of diamond was detected by El Goresy et al. (2001), who found µm-sized grains of diamond together with graphite at graphite-garnet, graphite-sillimanite, and graphite-rutile interfaces in shocked garnet-cordierite-sillimanite and garnet-biotite-gneiss fragments of shock stage II from the Ries suevite.

The aim of our study was a systematic investigation of the distribution and abundance of impact diamonds in the various types of impactites and their components within the ejecta blanket of a complex impact structure. We chose the Ries crater because it exposes all types of ejecta deposits (e.g., lithic impact breccia, cataclastic crystalline breccia, fallout suevite, clast-rich impact melt rock). In contrast to previous studies at the Ries crater, this is the first systematic investigation that is based on a larger number of samples from widely different localities representative of the whole ejecta blanket. Therefore, we were able to assess the regional distribution of diamonds in the ejecta blanket and to provide quantitative estimates of the diamond concentration in different types of impactites. Another focus of our work was a systematic Raman investigation of a large number of impact diamonds from the Ries crater.

SAMPLES AND ANALYTICAL METHODS

Samples

For this study, 32 whole-rock samples of impactites (lithic impact breccia, cataclastic crystalline breccia, fallout suevite, clast-rich impact melt rock) from different localities in the ejecta blanket of the Ries crater were chosen (Table 1; Fig. 1). All major fallout suevite and lithic impact breccia deposits from the ejecta blanket were investigated during this study. The crater or fallback suevite was not analyzed because sufficient sample material was not available from the drill cores. Field samples of impactites were additionally split in the laboratory into their components and analyzed separately: 7 matrix samples of fallout suevite, 24 melt fragments from the suevite, and 70 crystalline fragments of different shock stages from the fallout suevite and the clast-rich impact melt rock (Table 1). During the preparation of melt fragments and matrix samples, all fragments with a diameter >0.5 cm were discarded. Each sample was mechanically processed, split by a hydraulic press with breaking jaws of stainless steel and subdivided into three aliquots for (1) thin section preparation, (2) chemical analysis, and (3) extraction of diamonds. Possible contamination by industrial diamonds and silicon carbide grains from saw blades and grinding devices were eliminated by avoiding any sawing and grinding during the dividing and processing of the aliquots used for the diamond extraction.

Petrographic and Geochemical Investigations

Thin sections were used for shock and rock classification, especially for the unshocked to moderately shocked crystalline fragments. The shock stage of the crystalline fragments was determined after Stöffler (1971). Shock stage 0 (shock pressure <10 GPa) is characterized by quartz and feldspar grains which display only fracturing. In shock stage I (shock pressure 10–35 GPa) quartz and feldspar show planar deformation features and reduced refractive index. Shock stage II (shock pressure 35–45 GPa) is indicated by diaplectic quartz glass with coesite and diaplectic feldspar glass, whereas rocks of shock stage III (shock pressure 45–60 GPa) display mainly vesiculated feldspar glass together with coesite-bearing diaplectic quartz glass. The whole-rock texture of shock stage III is generally porous to pumice-like. Major element chemistry of crystalline fragments was measured by X-ray fluorescence spectrometry to establish the chemical signature of heavily shocked fragments in comparison with a database of Ries crystalline rocks (Engelhardt and Graup, 1984). Based on the SiO_2 versus $Na_2O + K_2O$ diagram after Le Maitre (1984), precursors of granitic, granodioritic, and monzonitic to dioritic composition could be distinguished. Due to the large number of different crystalline rocks in the Ries crater (Graup, 1978; Engelhardt and Graup, 1984), a detailed rock classification based only on the composition of major elements was not possible in the present study.

Extraction of Diamonds

The extraction of impact diamonds was carried out by a cyclic acid dissolution technique. To accelerate the extraction procedure we did not use large, uncrushed whole-rock samples. Our starting material had a grain size of 90–560 µm, which was produced using a cutting mill (breaking jaws of stainless steel) and a planetary ball mill (stainless steel grinding jars), followed by sieving on a vibratory sieve shaker. Due to this procedure, most of the separated impact diamond grains were broken. The basic extraction procedure of impact diamonds was as follows: The silicates were dissolved by alternating cycles of HF–HCl and HCl mixtures at room temperature. Acids were cycled every 24 h by decanting. This procedure was repeated for 10–14 cycles. Afterwards most of the silicates were dissolved and the sample was treated with a HCl–H_3BO_3 mixture for 24 hours to completely remove HF, followed by a pure water cycle for 24 hours. The residues (~0.2–0.5 wt% of the initial sample mass) were filtered and inspected under the optical microscope. The residues contain the carbon polymorphs (graphite and impact diamonds) together with some partially dissolved minerals (e.g., zircon). Due to the filter paper used and the handling methods, only diamond grains with a diameter greater than 15–20 µm could be extracted and investigated with this method. For each sample, a minimum initial sample mass of 30 g was used for the extraction procedure. Depending on the size of the samples, up to 100 g of material was dissolved. The detection limit based on 30 g sample was ~0.02 ppm diamond assuming a homogeneous distribution of diamond grains with an average weight of 0.5 µg within the sample.

Investigation of Impact Diamonds

For the identification of impact diamonds, the grains in the acid dissolution residues were investigated by Micro Raman spectroscopy (DILOR LabRam; HeNe laser beam 632.8 nm; laser power on sample 0.65 mW·µm^{-2}; 50 × objective lens). This is the best method to distinguish impact diamonds from other, optically similar, phases. Confirmed impact diamond grains were analyzed under the optical microscope for size, shape, color, and birefringence. For an estimation of the diamond concentration

TABLE 1. COMPILATION OF SAMPLE MATERIALS FROM THE RIES CRATER USED IN THE PRESENT STUDY

Locality	Whole-rock samples	Matrix	Melt fragment	Crystalline fragment SIII	Crystalline fragment SII	Crystalline fragment SI/0
Lithic impact breccia (Bunte Breccia)						
Aumühle	2 / 0					
Otting	1 / 0					
Ronheim	1 / 0					
Cataclastic crystalline breccia						
Appetshofen	1 / 0					
Langenmühle	5 / 0					
Meyers Keller	1 / 0					
Unterwilflingen	3 / 0					
Fallout suevite						
Altenbürg	1 / 1	1 / 0	1 / 0	3 / 0		
Amerdingen	1 / 1					
Aumühle	4 / 0		2 / 2	17 / 0	8 / 0	1 / 0
Bollstadt			2 / 0			
Christgarten			1 / 0			
Hainsfarth			1 / 1			
Heerhof			2 / 1			
Hohenaltheim	1 / 1	1 / 1	1 / 1			
Mauren	1 / 1					
Oberringingen	1 / 1	1 / 1	3 / 3			
Otting	1 / 0	1 / 1	3 / 2	2 / 0	1 / 0	
Seelbronn	3 / 2	2 / 0	3 / 1	27 / 1		
Unterwilflingen	1 / 0	1 / 1	4 / 1			
Zipplingen	2 / 0		1 / 1	1 / 0		
Clast-rich impact melt rock						
Amerbach	1 / 0					
Polsingen	1 / 0			4 / 0	4 / 0	1 / 0
Total	32 / 7	7 / 4	24 / 13	52 / 1	16 / 0	2 / 0

Note: The samples are listed according to the type of impactite. The number before the slash gives the total number of samples investigated per locality and the number after the slash gives the number of diamond-bearing samples (see Table 2).

within the samples, each diamond grain was weighed with an ultra-microbalance (SARTORIUS SC 2). Chemical composition, shape, and surface of the impact diamonds were investigated with a scanning electron microscope (SEM; JEOL JSM 6300 with RÖNTEC EDX system).

RESULTS

Investigation of Impactite Whole-Rock Samples

The investigation of whole-rock samples from different impactites (cataclastic crystalline breccias, lithic impact breccia, fallout suevite, clast-rich impact melt rock) from the ejecta blanket of the Ries crater show clearly that impact diamonds were observed only in the fallout suevite (Fig. 2A; Tables 1 and 2). Impact diamonds were found in ~45% of the suevite whole-rock samples. In contrast to the Popigai crater (Masaitis, 1998), a preferred regional distribution of impact diamonds in the fallout suevite of the Ries crater could not be observed (Fig. 1). However, the concentration of impact diamonds in the fallout suevite displays great variability, even in single outcrop, ranging between <0.02 (proposed detection limit) and 0.26 ppm diamond (Fig. 2B; Table 2). If all of our analyzed suevite whole-rock samples were taken into consideration, the mean diamond concentration of the Ries fallout suevite could be estimated at ~0.1–0.2 ppm.

Distribution of Impact Diamonds in the Fallout Suevite

The distribution of impact diamonds in the fallout suevite was investigated by subdividing whole-rock samples into their specific components: matrix (clasts and melt fragments >0.5 cm diameter were discarded), crystalline, and melt fragments (Table 1). The results are shown in Figure 3A and Tables 1 and 2.

Impact diamonds were found in ~50% of the analyzed matrix samples and melt fragments. The large melt fragment Au-G from the suevite of Otting was subdivided for the diamond extraction into a core sample (Au-G-core; rich in vesicles) and a rim sample (Au-G-rim; poor in vesicles and rich in mineral and rock clasts). Both fractions reveal similar diamond concentration, which indicates that the diamonds are relatively homogenously distributed within this melt fragment. The melt fragment SIE988 from the dike suevite of Unterwilflingen was completely transformed into kaolinite and montmorillonite due to pervasive post-impact hydrothermal alteration. This sample contains impact diamond grains which have a similar appearance in comparison to impact diamonds from only slightly altered melt fragments. Therefore the impact diamonds are stable under the conditions of hydrothermal alteration.

In contrast to the matrix samples and melt fragments, only one diamond-bearing crystalline fragment of shock stage III could be detected, whereas ~50% of the fragments in this shock stage contain still recognizable graphite (Fig. 3A). Figure 3B indicates that the analyzed suite of crystalline fragments represents all major lithological units of the crystalline basement (Graup, 1978; Engelhardt and Graup, 1984; Engelhardt, 1997): (*a*) Granitic composition (22 samples) compared to 22% granites and 7% orthogneisses in the crystalline clast population of the suevite; (*b*) granodioritic composition (24 samples) compared to 21% biotite-plagioclase-gneiss, 10% mixed-, blastomylonite- and migmatic-gneisses, and 7% granodiorite in the crystalline

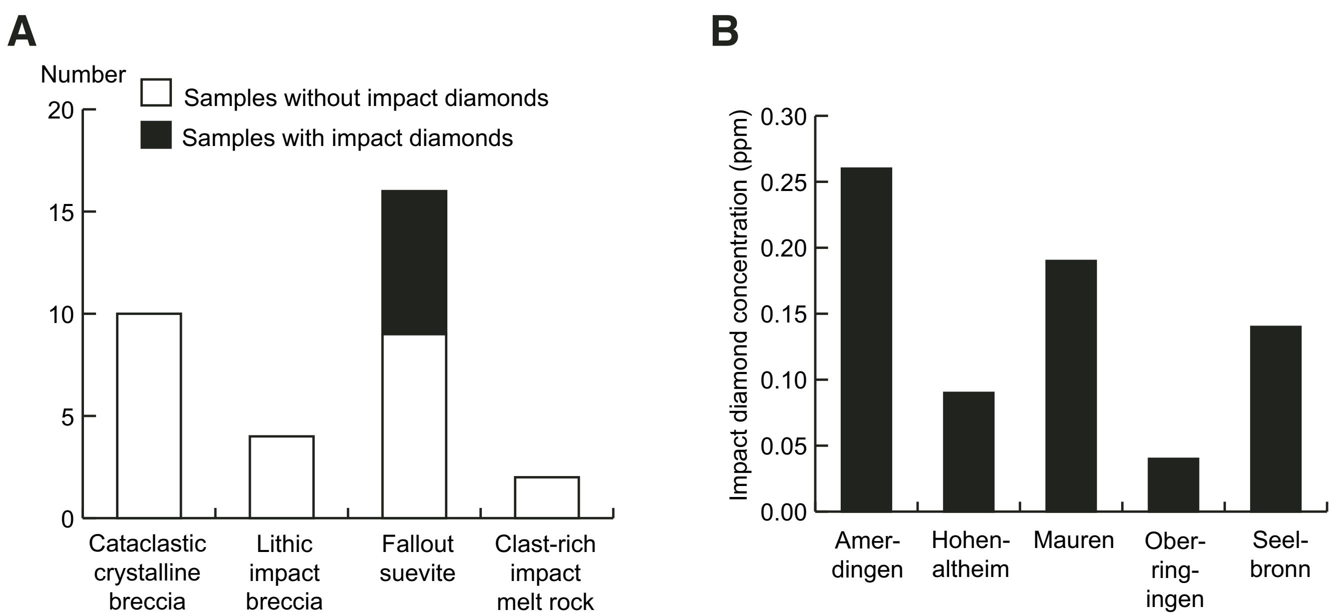

Figure 2. (A) Distribution of impact diamonds in the different lithological units (cataclastic crystalline breccias, lithic impact breccia, fallout suevite, clast-rich impact melt rock) of the Ries ejecta blanket; see also Tables 1 and 2. (B) Estimates of impact diamond concentrations in suevite whole-rock samples of selected localities (see Fig. 1 and Table 2).

TABLE 2. COMPILATION OF DIAMOND-BEARING SAMPLES

Locality	Lithology	Sample type	Sample number	Diamond concentration (ppm)	Number of diamond grains
Altenbürg	Suevite	Whole rock	SIE97121	n.d.	1
Amerdingen	Suevite	Whole rock	La9930 Am	0.26	3
Aumühle	Suevite	Melt fragment, core/rim	Au-G core/rim	0.04 / 0.02	4 / 3
Aumühle	Suevite	Melt fragment	SIE9781	0.21	15
Hainsfarth	Suevite	Melt fragment	Ha-G1	0.20	5
Heerhof	Suevite	Melt fragment	SIE97103	0.03	1
Hohenaltheim	Suevite	Whole rock	SIE97132	n.d.	1
Hohenaltheim	Suevite	Matrix	SIE97132M	0.03	1
Hohenaltheim	Suevite	Melt fragments	SIE97132G	0.10	4
Mauren	Suevite	Whole rock	La9934 Mau	0.19	6
Oberringingen	Suevite	Whole rock	La9928 Ob	0.04	1
Oberringingen	Suevite	Matrix	La9928M Ob	0.39	3
Oberringingen	Suevite	Melt fragment	La9927a Ob	1.48	24
Oberringingen	Suevite	Melt fragment	La9927b Ob	0.61	4
Oberringingen	Suevite	Melt fragment	La9927c Ob	0.17	7
Otting	Suevite	Matrix	SIE97120M	0.09	1
Otting	Suevite	Melt fragment	Ot-G	0.14	1
Otting	Suevite	Melt fragment	Ot-G3	0.02	2
Seelbronn	Suevite	Whole rock	SIE97123	n.d.	1
Seelbronn	Suevite	Whole rock	SIE985	0.14	1
Seelbronn	Suevite	Melt fragment	SIE9721	0.10	10
Seelbronn	Suevite	Crystalline fragment SIII	Se-2	0.62	31
Unterwilflingen	Suevite	Matrix (hydrothermally altered)	SIE983	0.42	9
Unterwilflingen	Suevite	Melt fragment (hydrothermally altered)	SIE988	0.37	5
Zipplingen	Suevite	Melt fragment	Zi-G1	0.33	22

Note: n.d.—no data

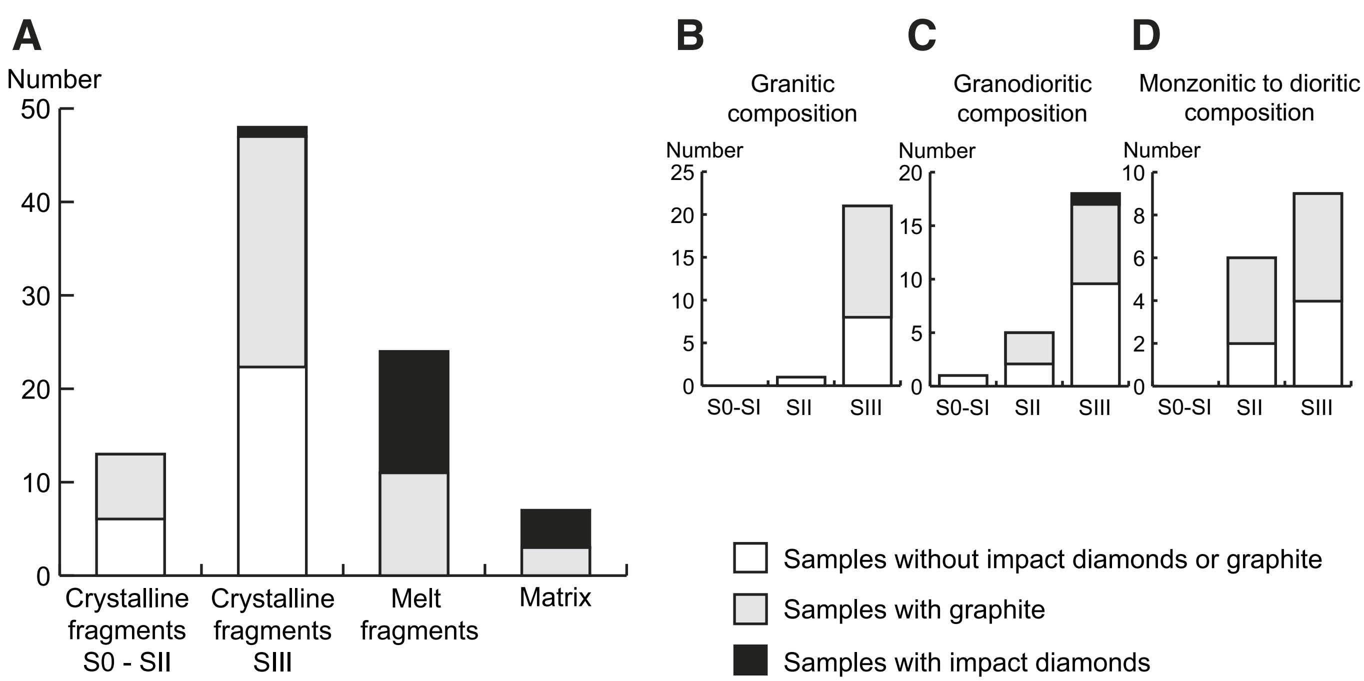

Figure 3. Distribution of impact diamonds and graphite in the different suevite components and shocked crystalline fragments of different chemical composition (see Tables 1 and 2). (A) Number of samples with and without impact diamonds or graphite from melt fragments, matrix samples and crystalline fragments of shock stage 0 to II and III. Note that the diamond-bearing melt fragments and matrix samples contain also graphite. (B–D) Samples with and without impact diamonds or graphite in shocked crystalline fragments of variable chemical composition. (B) Granitic composition includes granites and orthogneiss. (C) Granodioritic composition includes biotite-plagioclase-gneiss, mixed-, blastomylonite-, and migmatic-gneisses and granodiorite. (D) Monzonitic to dioritic composition includes amphibolite, sphene-fleck-rock, monzonite, diorite, gabbro, cordierite- and granulitic-gneisses, and dike rocks.

clast population of the suevite; and (*c*) monzonitic to dioritic composition (15 samples) compared to 14% amphibolite, 8% sphene-fleck-rock, 5% monzonite, diorite and gabbro, 3% cordierite- and granulitic-gneisses, and 3% dike rocks in the crystalline clast population of the suevite. Crystalline fragments that have high, primary contents of carbon (e.g., cordierite-gneisses) are rare within the suevite. They constitute ~2% of the crystalline clast population of the fallout suevite (Graup, 1978; Engelhardt, 1997), and these fragments are distinctly smaller in comparison to other crystalline clasts, e.g., granite. Therefore the probability of finding such highly shocked fragments containing impact diamonds is also rather low.

The diamond concentrations show great variability in the specific components of the fallout suevite similar to the suevite whole-rock samples (Fig. 4). The highest observed diamond concentration in this study was 1.48 ppm in a melt fragment from Oberringingen (sample La9927a Ob). Average diamond concentrations estimated on the basis of all analyzed samples are 0.3 ppm for the melt fragments and 0.2 ppm for the matrix samples.

Diamond-Bearing Crystalline Fragment Se-2

The diamond-bearing crystalline fragment Se-2 (Figs. 5A and 6A) from the suevite of Seelbronn was originally ~8 cm in diameter. This sample shows a pumice-like texture and the primary texture is largely destroyed. A relic gneiss foliation is indicated by a succession of white and dark schlieren. The high degree of shock metamorphism can be easily recognized macroscopically due to the pumice-like texture. This fragment belongs to shock stage III according to Stöffler (1971). Under the microscope, recrystallized feldspar melt, partially recrystallized diaplectic quartz glass, which contains tube-like coesite, and biotite, which displays birefringence and kink bands as well as thermal decomposition, have been observed (Fig. 6A). The shock features of the minerals indicate a shock pressure of 45–55 GPa (Stöffler, 1971, 1972; Stöffler and Langenhorst, 1994). Secondary mineralizations consist of quartz, calcite, and chlorite. The chemical analysis (Siebenschock et al., 1998) shows a granodioritic composition for this sample. Low TiO_2, P_2O_5, Cr, and V concentrations indicate that this fragment was originally most likely a biotite-plagioclase-gneiss when compared with chemical data of Engelhardt and Graup (1984). The only carbon phase observed in the extraction residue of this fragment is impact diamond. Therefore the phase transformation of graphite to diamond was complete.

Diamond-Bearing Melt Fragments of the Fallout Suevite

Diamond-bearing melt fragments (e.g., Figures 5C and 6B) show a fluidal texture, irregularly distributed vesicles, and numerous mineral and rock clasts of different shock stages, which are mainly derived from the crystalline basement. Mineral and rock clasts were discarded during the preparation, if possible. The matrix of all analyzed melt fragments is more or less recrystallized indicating that these samples come from the central, slowly cooled part of the suevite layer. In most of the analyzed melt fragments, schlieren-like zones of highly shocked mineral assemblages were observed, which consist of recrystallized or rare glassy feldspar and quartz melt, coesite and thermally decomposed biotite (Fig. 6B). In the melt fragment La9927b Ob, graphite could be observed within such a schlieren-like zone. The shock pressure estimated for the schlieren-like zones is similar to that of the crystalline fragment Se-2. Most likely these schlieren-like zones within the melt fragments are the carrier of impact diamonds. A test of this hypothesis would be the in situ detection of diamonds in such zones, but this was not successful during this study. In all extraction residues of melt fragments, the carbon phases were graphite and diamond.

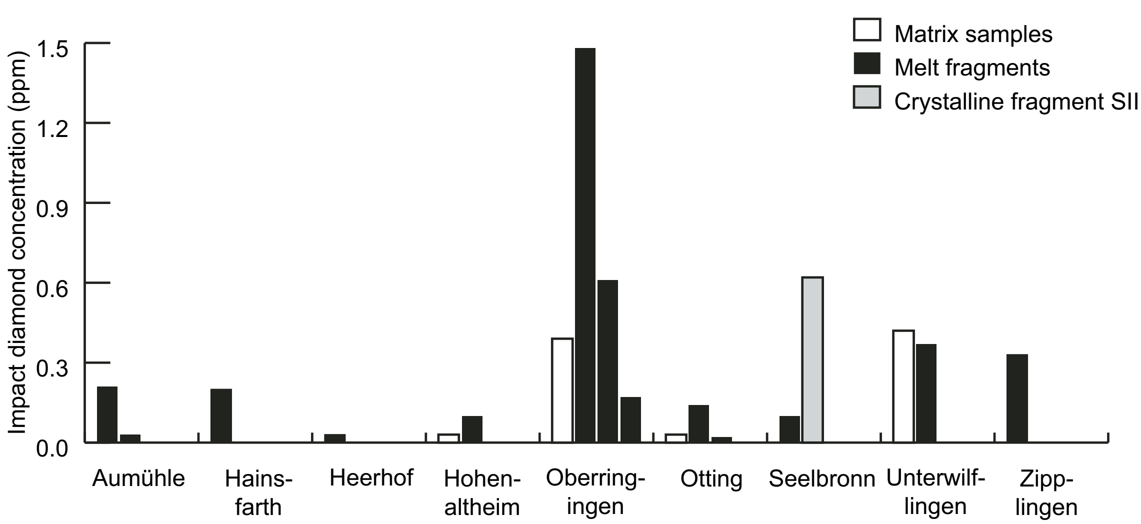

Figure 4. Estimates of impact diamond concentrations in crystalline fragments, melt fragments, and matrix samples of the fallout suevite from different localities (see Fig. 1 and Table 2).

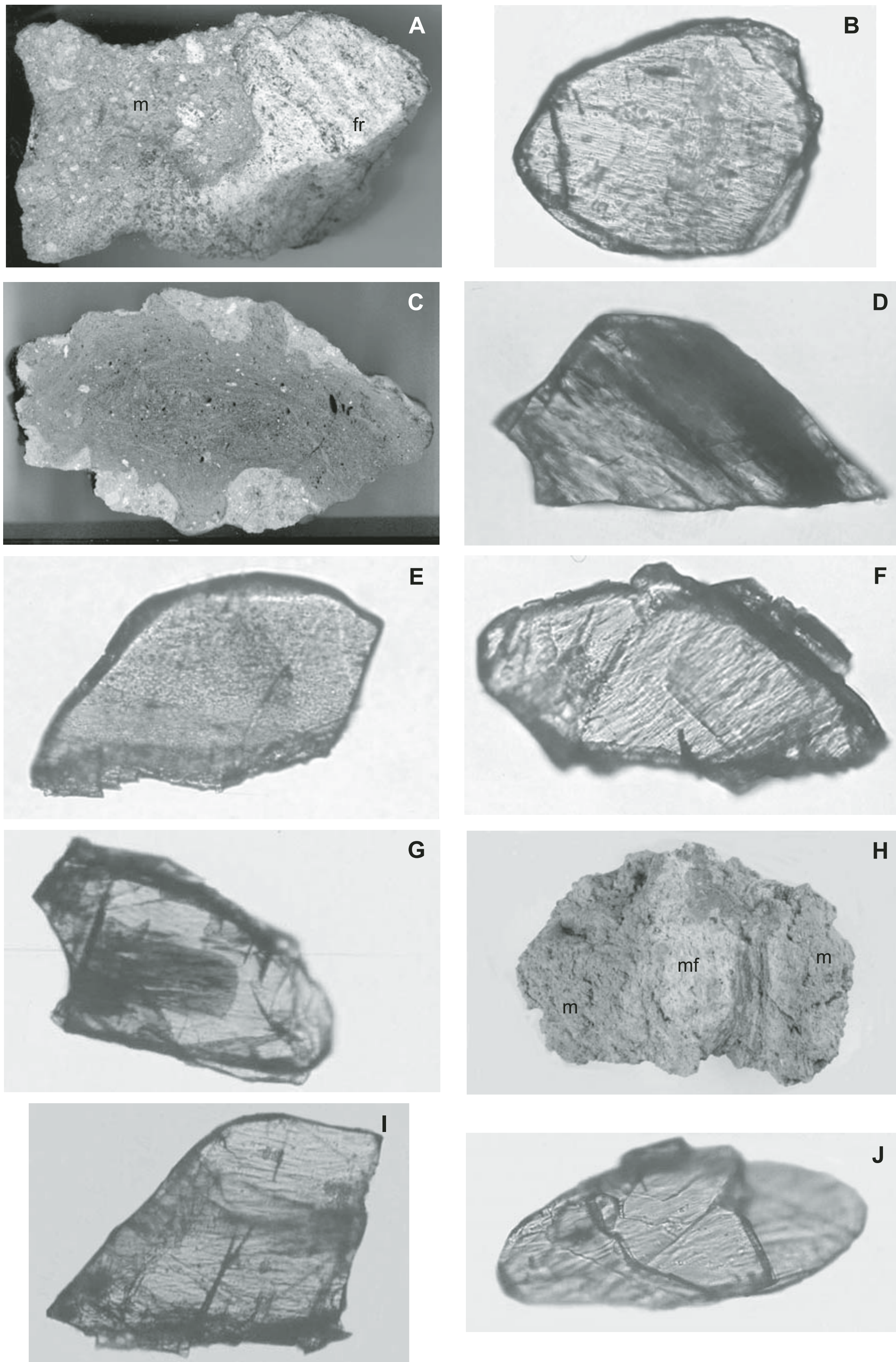
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Figure 5. Host rocks of impact diamonds and associated diamonds from the Ries crater. (A) Diamond-bearing crystalline fragment (fr; size 3.5 × 3 cm; sample Se-2) of shock stage III displaying relic metamorphic foliation embedded in the suevite matrix (m); Seelbronn. (B) Greenish diamond grain extracted from Se-2 (see A; Se-2/grain 11; diameter ~105 µm). (C) Melt fragment (size 27 × 11 cm) in the suevite displaying fluidal textures especially in the center of the fragment (sample Au-G; Aumühle quarry). For diamond extraction, this sample was subdivided into a core sample (Au-G-core; rich in vesicles) and a rim sample (Au-G-rim; poor in vesicles and rich in mineral and rock clasts). (D, E) Diamond grains extracted from the Au-G-rim sample (see C). (D) Olive-green diamond grain with some dark areas on the right hand side of the grain (Au-G-rim/grain 1; size 100 × 60 µm). (E) Light-olive-green diamond grain (Au-G-rim/grain 2; size 50 × 40 µm). (F) Large, olive-gray diamond grain from a melt fragment of the suevite of Mauren (La9934Mau/grain 1; size 140 × 60 µm). (G) Diamond grain with a greenish-brownish color in the rim region and a dark center from a melt fragment of the suevite of Zipplingen (Zi-G1/grain 2; size 120 × 75 µm). (H) Dike suevite sample from Unterwilflingen (9 × 7 cm). This sample consists of a greenish colored matrix (m; sample SIE983) and a heavily altered, white-colored melt fragment (mf; sample SIE988) displaying a relic fluidal texture. (I) Olive-brownish diamond grain extracted from the heavily altered melt fragment of the dike suevite (SIE988/grain 5; size 90 × 90 µm). (J) Light greenish diamond grain extracted from the matrix of the dike suevite (SIE 983/grain 3; size 85 × 35 µm). All diamond grains in this figure are shown in plane polarized light under the optical microscope.

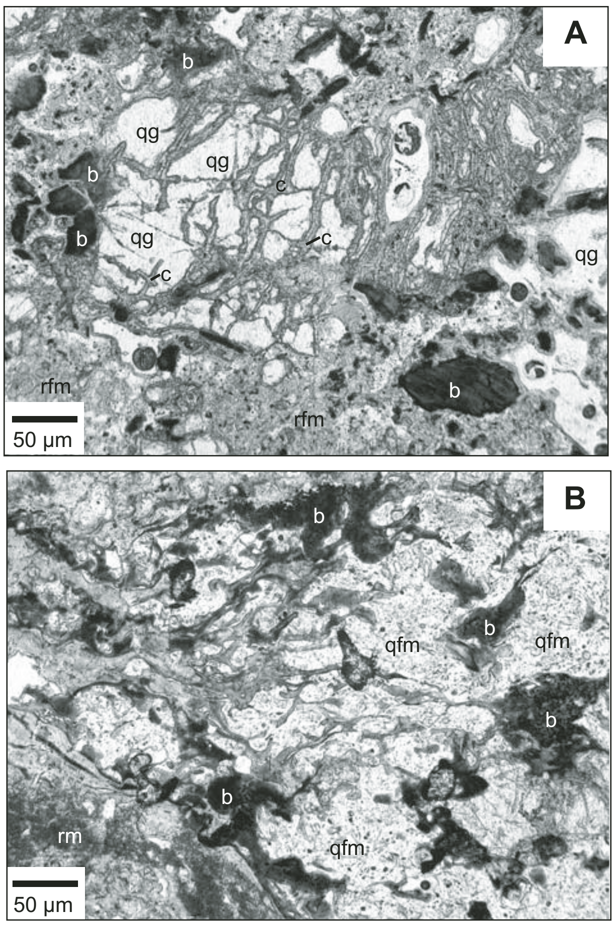

Figure 6. (A) Thin section of the highly shocked, diamond-bearing crystalline fragment Se-2 from the suevite of Seelbronn. The sample consists of diaplectic quartz glass (qg) with tube-like coesite aggregates (c), recrystallized feldspar melt (rfm) and biotite (b) which is (at the rims) partially thermally decomposed. This paragenesis indicates shock stage III after Stöffler (1971) and corresponds to a shock pressure of 45–55 GPa. (B) Schlieren-like zone of a highly shocked mineral assemblage in melt fragment La9927c Ob from the suevite of Oberringingen. In the recrystallized melt matrix (rm), thermally decomposed biotite (b) and recrystallized quartz and feldspar melt (qfm) can be observed. Both images in transmitted, plane polarized light.

Diamond-Bearing Fallout Suevite Matrix

The matrix of the fallout suevite is a clastic mixture of fine-grained mineral and various rock fragments of different shock stages together with fine-grained melt particles altered to montmorillonite and zeolites (Engelhardt and Graup, 1984; Osinski et al., 2003). Chemical investigations do not show great differences in composition between suevite whole-rock and matrix samples from any single locality. The diamond carrier in the suevite matrix is unknown. It is assumed that the diamond carriers could be small graphite-bearing crystalline fragments of shock stage III. Similar to the melt fragments, the residues of matrix samples show the carbon phases graphite and diamond.

Impact Diamonds

The impact diamonds show an identical appearance independent of their source (suevite whole rock, crystalline fragment, melt fragment, matrix) and locality (Figs. 5 and 7). They occur as thin, pseudo-hexagonal plates, which are composed of a parallel intergrowth of much smaller platelets. Therefore the plates show a distinct cleavage parallel to the platelets. The diameter of the diamond grains reaches up to 300 µm, but the thickness is much smaller, mostly <20 µm. Most of the grains display fractures which intersect with angles between 110° and 130° (Fig. 7C) or they are broken along such fracture systems. Some diamond grains display twinning striations in certain parts. The morphology of the impact diamond grains resembles unambiguously the precursor graphite. Due to their polycrystalline structure as shown by transmission electron microscopy (e.g., Siebenschock et al., 1999) the diamond grains are paramorphs after graphite. The term paramorphs instead of pseudomorphs is used to emphasize the internal polycrystalline structure of the diamond grains. The color is most commonly olive-green, grayish-green, or grayish-black. Yellow, pale green, brownish-black, or rarely, colorless grains were observed as well. The surface as seen in the optical microscope is uneven to rough and displays a vitreous to sub-metallic luster. Thin diamond grains are transparent and birefringent.

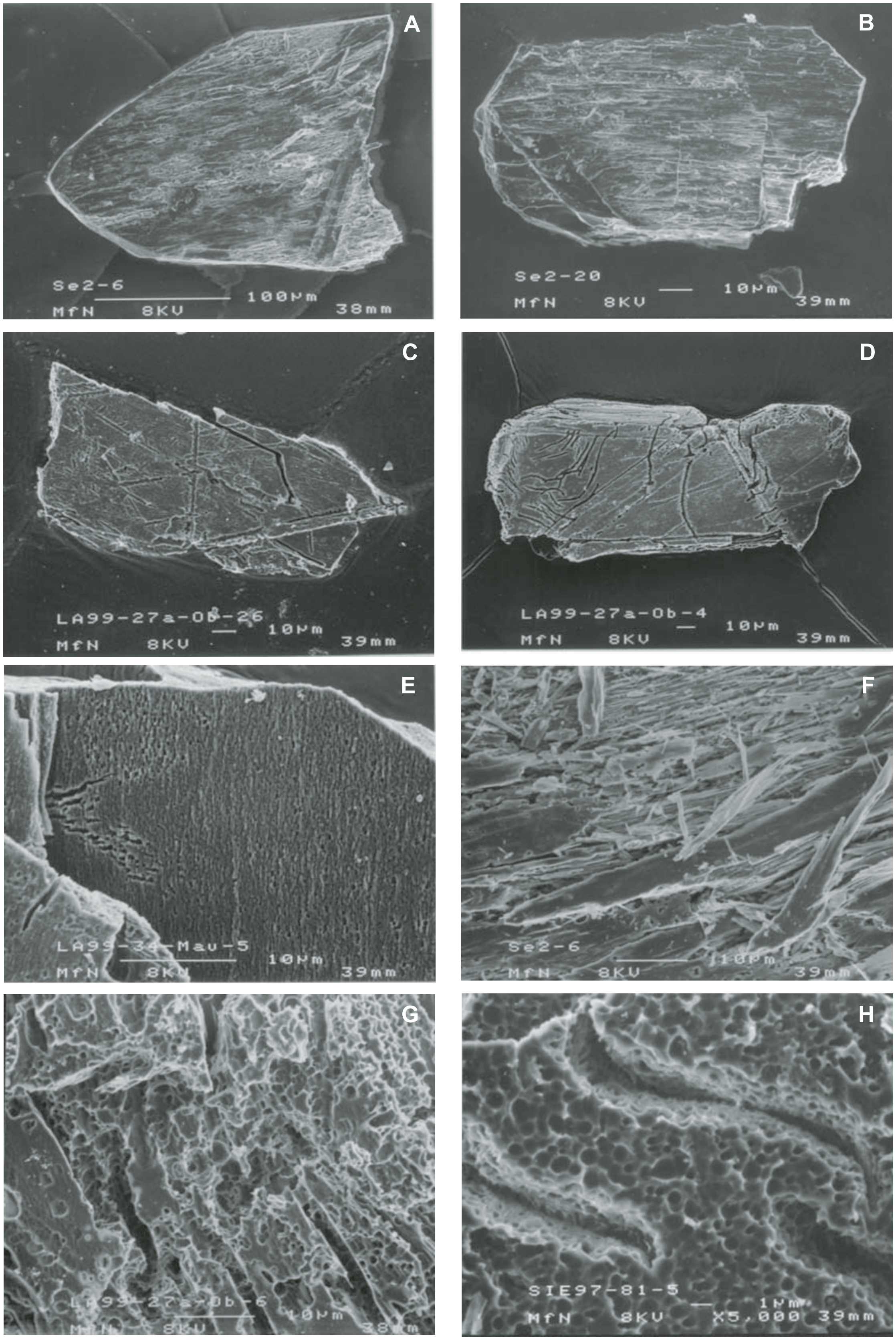

Figure 7. Scanning electron microscope images (secondary electrons) of impact diamonds from the Ries crater and their surfaces. (A, B) Impact diamonds from the crystalline fragment Se-2, suevite of Seelbronn. Both grains display a fibrous surface which is shown in detail in F. (C, D) Impact diamonds from melt fragment La9927a Ob, suevite of Oberringingen. Fracture systems could be observed in C whereas the surface of D displays in addition curved depressions. (E) Rough surface caused by small inhomogeneities; on the left-hand side occur some extensional microfractures (whole-rock sample La9934 Mau; Mauren suevite). (F) Fibrous surface and structure, enlargement of the upper right hand corner of the diamond grain shown in A. (G, H) Spongy surface and structure of diamond grains from melt fragments of the suevite (La9927a Ob from Oberringingen, and SIE9781 from Aumühle, respectively). The spongy diamond grain H is cut by two extensional microfractures.

At higher magnifications with the SEM, the surface of the impact diamond grains (Fig. 7) varies independent of their source even within one grain. The following types could be distinguished: (*a*) smooth surface; (*b*) isolated pores with diameters of ~1 µm occurring on more or less smooth surfaces; (*c*) linear or curved depressions crosscutting more or less smooth surfaces (Fig. 7D); (*d*) rough surface (Fig. 7E) caused by small inhomogeneities (diameter <1 µm) which define sometimes a lineation; (*e*) fibrous surface (Figs. 7A, 7B, and 7F) caused by elongated anhedral platelets with sizes up to 30 µm × 5 µm x < 0.5 µm; and (*f*) spongy surfaces (Figs. 7G and 7H) caused by closely arranged pores of ~1 µm diameter. Relatively frequent are the types (*e*) and (*f*), which display striped patterns and a streaky appearance, respectively, under the optical microscope. Smooth surfaces do not contain graphite based on Raman mapping and therefore cannot be interpreted as graphite coatings which were frequently observed by Masaitis (1998) on the surface of Popigai diamonds. In comparison, pure graphite grains from the crystalline basement rocks of the Ries crater have generally smooth surfaces and display sometimes striped surface patterns. Surface features similar to the types (*b*–*f*) of the impact diamonds could not be observed on graphite grains. The surface patterns (*b*–*d*) are a typical feature also of impact diamonds from other impact craters, e.g., Popigai, Puchezh-Katunki, and Lappajärvi (Vishnevsky et al., 1997; Masaitis, 1998; Masaitis et al., 1998). Such surface patterns are the result of a natural corrosion or etching process at the contact with impact melt, or of a heating process as proposed by Masaitis (1998). Cross sections of impact diamonds show that most of the grains have a fibrous or spongy internal structure similar to the surface patterns (*e*) and (*f*). This characteristic porosity is most likely the result of some specific volume decrease during the phase transformation of graphite to diamond, rather than the result of a natural corrosion or etching process. In addition to the above-described structures, the volume decrease causes relatively frequent extensional microfractures in the diamond grains (Figs. 7E and H). Compositional analysis and elemental mapping of the impact diamonds with the SEM-EDX reveal only carbon. Diamond-silicon carbide intergrowths could not be detected during this study.

Irrespective of their color, surface structure and source, ~75% of the diamond grains exhibit a strong photoluminescence (Fig. 8A), which makes the detection of Raman bands impossible. This is also a typical feature of impact diamonds from the Popigai (Phelps, 1997; Boudeulle et al., 1999) and Lappajärvi craters (Moroz et al., 2003). The remaining grains display a minor photoluminescence. A broad Raman band at 1305–1330 cm^{-1} and sometimes an additional broad Raman band at 1560–1575 cm^{-1} could be observed (Figs. 8B and 8C). The Raman band at 1305–1330 cm^{-1} is generally higher in intensity than the latter which reaches 0–90% of the intensity of the band at 1305–1330 cm^{-1}. In contrast, single crystal grains of natural (e.g., from Brasilia, sample MfN 1997–2465) as well as of synthetic diamond (e.g., diamonds from saw blade, diamond polishing paste with diamonds of 1–2 µm grain size) display a sharp Raman band at 1331–1333 cm^{-1}. This Raman band is shifted for impact diamond grains to lower frequencies (1305–1330 cm^{-1}) and reveals a FWHM (full width at half maximum) ranging from 70–170 cm^{-1} (Fig. 8D). There is no correlation between the wavenumber of this Raman band and the FWHM visible. A few impact diamonds and also highly shocked graphite grains (e.g., sample SIE9733; Lapke et al., 2000) from the Ries crater reveal a broad and strong Raman band at 1420–1440 cm^{-1} (Fig. 8E). Mapping of these grains with the SEM-EDX display only carbon, and exclude the presence of non-carbon phases. Therefore this Raman band is most likely caused by amorphous diamond-like carbon (Yoshikawa et al., 1995).

For comparison with the impact diamonds, graphite grains from crystalline breccias and crystalline fragments of the suevite of different shock stages were investigated. Graphites occur as black, non-transparent, more or less hexagonal crystals, which show a distinct cleavage. Some of the graphite grains display Veselowski twinning. The diameter of the graphite grains reaches up to 1 mm, whereas the thickness is much smaller, mostly <100 µm. Graphite grains have generally smooth surfaces and some irregular fractures. With increasing shock stage, an increasing number of parallel microfractures, oriented normal to the basal plane, were observed. As a consequence, highly shocked graphite in shock stage III displays striped surface patterns which are caused by parallel, densely packed microfractures. Graphite grains in shock stages II and III are frequently broken and occur, therefore, in form of blocky fragments. The Raman investigation (Lapke et al., 2000) of graphite of shock stage 0 (sample SIE9795) normal to the basal plane shows a sharp, strong Raman band at 1580 cm^{-1} and a weak, broad band at 1330–1345 cm^{-1} with an intensity of 5–20% in comparison to the 1580 cm^{-1} band. At shock stage I and II (samples SIE97116, SIE9777) the strong band decreases in intensity, moves to 1575–1578 cm^{-1}, and starts to broaden. The broad band at 1330–1340 cm^{-1} increases in intensity up to 30–40% of the band at 1575–1578 cm^{-1}. At shock stage III (sample SIE9733), the intensity of this band reaches 30–90% of the band at 1575–1578 cm^{-1}. Additionally, all of the graphite spectra of shock stage 0–III display a weak band at 1600–1620 cm^{-1}. None of the graphite grains show photoluminescence under the laser beam.

DISCUSSION

Formation of Impact Diamonds

Several mechanisms have been proposed for the graphite-diamond phase transition in the past including: (*a*) solid state martensitic phase transformation (Masaitis et al., 1990; Erskine and Nellis, 1991; DeCarli, 1998; Vishnevsky et al., 1997; Langenhorst et al., 1998; Masaitis, 1998); (*b*) thermally activated, diffusion controlled formation mechanism based on a solid-vapor/liquid-solid sequence of phase transformations (Kleiman et al., 1984; DeCarli, 1995, 1998; Vishnevsky et al., 1997; Kenkmann et al., 2002); (*c*) ultrafast annealing of a glassy carbon phase (Pujols and Boisard, 1970); (*d*) dissociation of twin boundaries,

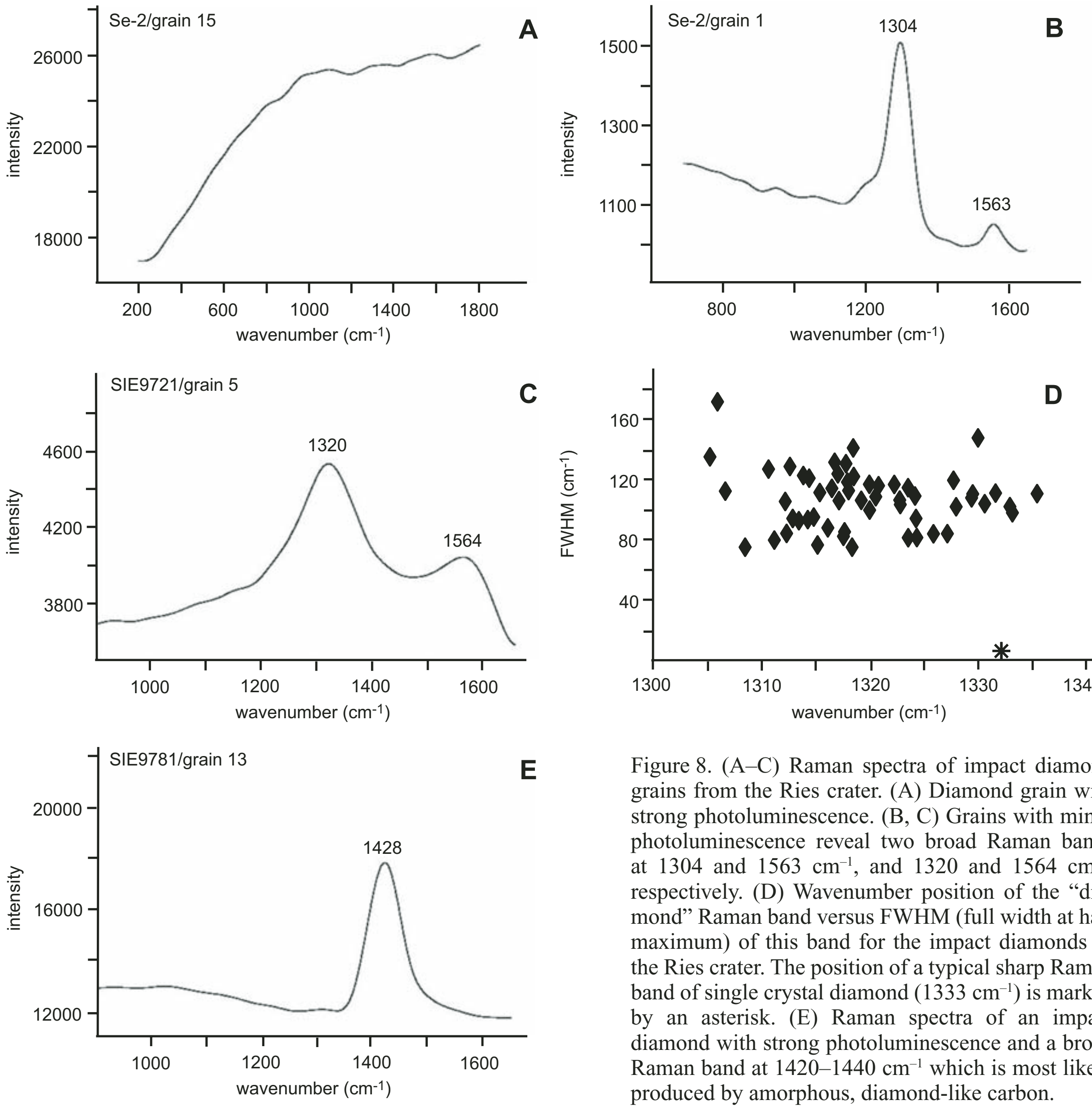

Figure 8. (A–C) Raman spectra of impact diamond grains from the Ries crater. (A) Diamond grain with strong photoluminescence. (B, C) Grains with minor photoluminescence reveal two broad Raman bands at 1304 and 1563 cm^{-1}, and 1320 and 1564 cm^{-1}, respectively. (D) Wavenumber position of the "diamond" Raman band versus FWHM (full width at half maximum) of this band for the impact diamonds of the Ries crater. The position of a typical sharp Raman band of single crystal diamond (1333 cm^{-1}) is marked by an asterisk. (E) Raman spectra of an impact diamond with strong photoluminescence and a broad Raman band at 1420–1440 cm^{-1} which is most likely produced by amorphous, diamond-like carbon.

which leads to partial dislocations and diamond-like stacking faults (Pujols and Boisard, 1970); and (*e*) vapor phase growth of diamond (Hough et al., 1995). Previous studies indicate that the completely different mechanisms (*a*) and (*b*) above should be primarily considered for the formation of impact diamonds. Erskine and Nellis (1991) propose that the mechanism (*a*) depends strongly on the shock temperature: a solid state martensitic phase transformation occurs at shock temperatures <2000 K, whereas at shock temperatures >3000 K, the transformation mechanism is thermally activated, diffusion controlled.

(1) Diamonds produced by the thermally activated, diffusion-controlled formation mechanism characteristically display aggregates of small diamond grains of single crystal structure in paragenesis with shocked graphite or other high-temperature phases of carbon, e.g., carbynes. For example, µm-sized grains of diamond displaying a sharp and unshifted Raman band were found together with graphite by El Goresy et al. (2001) at graphite-garnet, graphite-sillimanite and graphite-rutile interfaces in garnet-cordierite-sillimanite and garnet-biotite-gneiss fragments of shock stage II in the Ries crater. These rocks display an equilibrium shock pressure of 35–45 GPa and a post-shock temperature of 575–1175 K (Stöffler, 1971). Graphite grains which are not in contact with garnet, sillimanite, or rutile are shocked, but do not contain diamond. Therefore the phase transformation is controlled by the textural setting of the graphite grains in contact with minerals of high shock impedance leading to

distinct temperature spikes during the shock compression. These temperature spikes were neglected in the proposed transformation mechanism of El Goresy et al. (2001), but might reach or exceed the melting temperature of graphite (~4000 K at 20 GPa, ~3400 K at 35 GPa, and ~2800 K at 45 GPa, respectively; e.g., Zoltai and Stout, 1984). Therefore, in this case, the partial phase transformation of graphite to diamond can simply be explained by a thermally activated, diffusion-controlled process. In the shock experiments of Kenkmann et al. (2002), µm-sized single crystal grains of diamond as indicated by a sharp and unshifted Raman band were observed in contact with biotite melt, together with shocked graphite grains in contact with quartz and feldspar glass. In this case, the formation of diamond is thermally activated by the biotite melting which released water that produced hot spots during vaporization (Kenkmann et al., 2002). Close to these hot spots, the melting temperature of graphite was exceeded and the phase transformation of graphite to diamond based on a solid-vapor/liquid-solid sequence occurred at shock pressures of >45 GPa. Synthetically produced diamonds by shock loading of graphite-metal mixtures or porous graphite were formed also by this type of phase transformation at temperatures above 3000 K (Kleiman et al., 1984; DeCarli, 1998).

(2) The solid-state martensitic phase transformation of graphite to diamond is characterized by the occurrence of diamond paramorphs after graphite or other carbon phases (Shafranovsky, 1985; Masaitis et al., 1990). These paramorphs are well known as impact diamonds from many craters, all of similar appearance (Gurov et al., 1995, 1996; Masaitis et al., 1972, 1995, 1997, 1998; Masaitis, 1998; Koeberl et al., 1995, 1997; Vishnevsky et al., 1997; Valter et al., 1992). Depending on the shape of the precursor carbon phase (e.g., graphite, coal) the shape of the shock-produced diamond grains varies from pseudo-hexagonal plates to anhedral grains. These paramorphs consist internally of nm to at most µm-sized diamond grains, which possibly may also contain lonsdaleite (e.g., Vishnevsky et al., 1997; Langenhorst et al., 1998). Raman spectra of such diamond paramorphs display a characteristic broadening of the "diamond" Raman band caused by this microstructure (Masaitis et al., 1990; Yoshikawa et al., 1995; Vishnevsky et al., 1997; Boudeulle et al., 1999). Based on this microstructure, Erskine and Nellis (1991) proposed a two-stage phase transformation: the first step is a martensitic phase transformation of graphite to lonsdaleite followed by a second, possibly also martensitic phase transformation, of lonsdaleite to diamond. This type of phase transformation leads, above a certain threshold pressure, to the complete in situ transformation of the carbon precursor phase to diamond. If the post-shock temperature exceeds some threshold, a partial or complete back transformation of diamond to graphite occurs (Masaitis, 1998). In shock experiments with graphite crystals, this type of phase transformation was observed at shock pressures of 30 GPa within ~10 ns if the shock loading was applied normal to the basal planes of graphite (Erskine and Nellis, 1991). In this case the shock temperature (1800 K) was clearly lower than the melting temperature of graphite (~3550 K; e.g., Zoltai and Stout, 1984). In contrast DeCarli (1998) propose for this type of phase transformation a minimum pressure of 15 GPa, a shock temperature above 1300 K and a post-shock temperature lower than 2000 K.

This study shows unambiguously that the impact diamond grains from the Ries crater resemble the morphology of the precursor graphite. Raman spectra of these diamond grains show a broadening of the "diamond" Raman band, which is typical for microcrystalline paramorphs. Therefore, a solid state martensitic phase transformation of graphite to diamond is proposed for the formation of these impact diamonds, consistent with previous studies. The shock pressure necessary for the phase transformation is on the order of 45–55 GPa in the highly shocked Se-2 crystalline fragment, which displays a complete transformation of graphite to diamond. The impact diamonds in the melt fragments occur most probably in schlieren-like zones of highly shocked mineral assemblages which have suffered the same shock pressure as melt-rich zones of the diamond-bearing crystalline fragment Se-2. A similar source of impact diamonds is also proposed for the suevite matrix. The accompanying post-shock temperature for shock pressures of 45–55 GPa in the case of quartzo-feldspathic rocks is in the range of 1175–1775 K (Stöffler, 1971). In the Popigai crater, impact diamonds could be observed in an extended pressure range from 35 to 50 GPa and from 50 to 60 GPa as grains which were partially transformed back to graphite (Masaitis, 1998). In contrast to suevite, the shock pressures in the lithic impact breccia (Bunte Breccia) and the cataclastic, crystalline breccias of the Ries crater are too low to produce impact diamonds. In the clast-rich impact melt rock occurring at the east rim of the Ries crater, the post-shock temperature is probably too high and impact diamonds might be completely transformed back to graphite.

Silicon carbide grains with diameters up to 100 µm or diamond-silicon carbide intergrowths as described by Hough et al. (1995) could not be found in this study based on samples for which sawing and grinding procedures were avoided during the preparation. However, we found some green and blue silicon carbide grains of ~25 µm diameter in a sawed suevite whole-rock sample of Otting at the beginning of our study. These findings suggest contamination, and this sample was excluded therefore from our study. The occurrence of silicon carbide grains (Hough et al., 1995) is therefore doubtful and could neither be confirmed by our study nor by the work of other groups (Abbott et al., 1996, 1998; Valter et al., 1998; Thiele and Scherer, 2000; El Goresy et al., 2001, 2002, 2003).

Raman Characteristics of Impact Diamonds

Many impact diamond grains from the Ries crater display a strong photoluminescence, which makes the detection of Raman bands impossible. Also, impact diamonds from other craters, e.g., Popigai and Lappajärvi (Phelps, 1997; Boudeulle et al., 1999; Moroz et al., 2003) as well as many natural, endogenous diamonds display a strong photoluminescence, which is caused by impurities and lattice defects (e.g., Moroz et al., 2003).

Single crystals of natural, endogenous diamond (e.g., from Brasilia; sample MfN 1997-2465) and synthetical diamond (e.g., diamonds from saw blade, diamond polishing paste with diamonds of 1–2 µm grain size) display a sharp and intense Raman band at 1331–1333 cm^{-1}, which corresponds very generally to the main C-C bond vibration in diamond (Nasdala and Massone, 2000). In contrast, impact diamond grains (paramorphs) from the Ries crater that possess a minor photoluminescence show a broad Raman band, which is shifted to lower frequencies at 1305–1330 cm^{-1}, and an additional Raman band at 1560–1575 cm^{-1}, which is in comparison to the first one generally lower in intensity. Broadening and shifting of the "diamond" Raman band to lower frequencies is also observed in shock-produced synthetic diamonds (Yoshikawa et al., 1995), in diamonds of ureilites (Vishnevsky et al., 1997; Greshake et al., 2000; Mostefaoui et al., 2001) and the Canyon Diablo iron meteorite (Miyamoto, 1998), and in impact diamonds from the Kara crater (Vishnevsky et al., 1997). In contrast, impact diamonds from the Popigai crater reveal only a broadening of this Raman band (Masaitis et al., 1990; Vishnevsky et al., 1997; Boudeulle et al., 1999). Our standard Raman spectroscopy procedure generates unshifted and sharp Raman spectra of diamond even on isolated, single-crystal grains of 1–2 µm diameter (e.g., diamond polishing paste). Therefore, broadening and shifting of Raman bands in impact diamonds is not the result of a heating effect by the laser beam as proposed by Andreyev et al. (1992). Variations of the intensity and the exposure time of the laser beam for a single analysis point of an impact diamond grain do not influence either of these effects. Nevertheless, Raman mapping shows that the shifting and broadening varies distinctly even within one grain. One possibility for the broadening of the major Raman band is the presence of lonsdaleite within the grains (Vishnevsky et al., 1997). More likely, broadening and shifting could be explained by the small crystallite size (<1 µm) of the polycrystalline impact diamonds (Yoshikawa et al., 1995).

The additional Raman band at 1560–1575 cm^{-1} is also observed in impact diamonds from Popigai (Boudeulle et al., 1999) and shock-produced synthetic diamonds (Yoshikawa et al., 1995). In contrast, this Raman band does not occur in diamond spectra of ureilites (e.g., Greshake et al., 2000; Mostefaoui et al., 2001) or the Canyon Diablo iron meteorite (Miyamoto, 1998). This Raman band could be explained by the occurrence of graphite-like nanodomains in the impact diamond grains (Boudeulle et al., 1999).

Diamond Concentration in the Suevite of the Ries Crater

This study estimates a mean diamond concentration of the Ries fallout suevite of ~0.1–0.2 ppm, which is clearly lower than a previous estimate of ~5.5 ppm diamond by Hough et al. (1995). A simple calculation can be carried out based on the following assumptions: the crystalline target of the Ries crater contains 2 wt% graphite-bearing rocks. This assumption is based on the frequency of cordierite-gneisses in the fallout suevite (Graup, 1978; Engelhardt, 1997). The cordierite-gneisses have an average carbon concentration of ~5 wt% (estimate from an investigation of graphite-bearing rocks in the Variscan crystalline basement by Hofmann, 1989). The graphite content of the biotite-plagioclase-gneisses was neglected because their graphite content is much lower, presumably <0.1 wt%. Neglecting further a small amount of shock stage II material in the lithic impact breccia, the crystalline target material of shock stages II to IV occurs almost exclusively in the suevite. Within the fallout suevite, some 25% of the crystalline target material was shocked to shock stage III (Engelhardt, 1997) and may therefore contain impact diamonds. This leads to a potential diamond concentration of 0.25 ppm for the fallout suevite. This is in good agreement to the observed diamond concentration of ~0.1–0.2 ppm. Using the volume estimate of the fallout suevite (0.13–0.25 km^3; Stöffler, 1977) and the observed diamond concentration (0.1–0.2 ppm), a diamond content of 27–105 t could be assumed for the Ries fallout suevite. Within the fallback or crater suevite, the content of material shocked to shock stage III and the melt content is much lower (Engelhardt, 1997), and therefore the diamond concentration should be clearly lower than in the fallout suevite.

Impact Diamonds as Impact Criteria

The investigation of the highly altered dike suevite of Unterwilflingen reveals that impact diamonds have survived hydrothermal alteration without any change. In contrast, silicates typically used as shock indicators, e.g., quartz with planar deformation features, quartz or feldspar glass and coesite, were destroyed during the alteration process. Therefore, the impact origin of this dike material could simply be derived from the existence of impact diamonds if other impact criteria would be lacking. This makes impact diamonds a very diagnostic and reliable tool for the search for impact features in deeply eroded and altered or even metamorphosed impact structures.

CONCLUSIONS

Impact diamonds in the Ries crater are present in all types of suevite (fallout suevite, suevitic dikes, fallback or crater suevite) whereas the cataclastic crystalline breccias, lithic impact breccias, and clast-rich impact melt rocks do not contain diamonds. The mean diamond concentration in the fallout suevite is ~0.1–0.2 ppm. A preferred regional distribution of impact diamonds in the fallout suevite could not be detected. Impact diamonds are contained in three main components of the suevite: graphite-bearing crystalline rock fragments of shock stage III, melt fragments, and matrix. Within the latter two, the carriers of impact diamonds are most likely small graphite-bearing crystalline rock fragments of shock stage III.

Impact diamond grains show an invariant appearance independent of their source and locality. They occur as pseudo-hexagonal plates and reach sizes up to 300 µm. Their color is commonly greenish, but black, yellow, and colorless grains were also observed. Under the optical microscope, the diamond grains are transparent and birefringent. SEM shows that most of the diamond grains have a fibrous or spongy internal structure and extensional microfractures, which leads to a characteristic porosity. This is the result of a volume decrease due to the phase transformation of graphite to diamond. Internally, the diamond grains are polycrystalline (e.g., Siebenschock et al., 1999) and therefore paramorphs after the precursor graphite. Irrespective of their color, surface structure, and origin, ~75% of the impact diamond grains exhibit a strong photoluminescence, which makes the detection of Raman bands impossible. The remaining grains display a minor photoluminescence and show a broad Raman band at 1305–1330 cm^{-1} and sometimes an additional broad Raman band at 1560–1575 cm^{-1}, which is lower in intensity than the first one. This is the result of their micro-polycrystalline internal structure and the occurrence of graphite-like nanodomains. Some impact diamond grains with an additional Raman band at 1420–1440 cm^{-1} may contain amorphous, diamond-like carbon.

The impact diamonds were most likely formed by a complete in situ shock transformation of graphite in crystalline target rocks at pressures of 45–55 GPa. The accompanying post-shock temperature in the case of quartzo-feldspathic rocks is in the range of 1175–1775 K (Stöffler, 1971). In agreement with previous studies, a solid-state martensitic phase transformation of graphite to diamond is proposed due to the strong morphologic similarity of impact diamonds with the precursor graphite. Evidence for the formation of diamond by a chemical vapor deposition and the occurrence of silicon carbide as proposed by Hough et al. (1995) could not be confirmed.

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