



## Shock-metamorphosed zircon in terrestrial impact craters

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**Abstract**—To ascertain the progressive stages of shock metamorphism of zircon, samples from three well-studied impact craters were analyzed by optical microscopy, scanning electron microscopy (SEM), and Raman spectroscopy in thin section and grain separates. These samples are comprised of well-preserved, rapidly quenched impactites from the Ries crater, Germany, strongly annealed impactites from the Popigai crater, Siberia, and altered, variably quenched impactites from the Chicxulub crater, Mexico. The natural samples were compared with samples of experimentally shock-metamorphosed zircon. Below 20 GPa, zircon exhibits no distinct shock features. Above 20 GPa, optically resolvable planar microstructures occur together with the high-pressure polymorph reidite, which was only retained in the Ries samples. Decomposition of zircon to  $ZrO_2$  only occurs in shock stage IV melt fragments that were rapidly quenched. This is not only a result of post-shock temperatures in excess of  $\sim 1700$  °C but could also be shock pressure-induced, which is indicated by possible relics of a high-pressure polymorph of  $ZrO_2$ . However,  $ZrO_2$  was found to revert to zircon with a granular texture during devitrification of impact melts. Other granular textures represent recrystallized amorphous  $ZrSiO_4$  and reidite that reverted to zircon. This requires annealing temperatures  $>1100$  °C. A systematic study of zircons from a continuous impactite sequence of the Chicxulub impact structure yields implications for the post-shock temperature history of suevite-like rocks until cooling below  $\sim 600$  °C.

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### INTRODUCTION

#### Significance of Zircon as a Shock Indicator

Zircon is among the last minerals that succumb to shock deformation and the subsequent extreme temperature conditions (El Goresy 1965, 1968; Mashimo et al. 1983). It has been suggested that zircon preserves shock features even under granulite facies metamorphic conditions (Reimold et al. 2002). This allows the identification and dating of ancient impact structures, e.g., Sudbury (Krogh and Davis 1984; Krogh et al. 1996) and Vredefort (Kamo et al. 1996; Gibson et al. 1997; Reimold et al. 2002). A correlation of distal ejecta with parental impact structures was attained by the study of shocked zircons (Krogh et al. 1993a, 1993b). In spite of their importance, shock features in zircon are only occasionally described by in situ methods (El Goresy 1968; Kamo et al. 1996; Corfu et al. 2003). Grain separation from whole rocks will recover more zircons, but some shock features are commonly lost, e.g., decomposed zircon (Glass 2000; Deloule et al. 2001). Also, grain sizes below  $\sim 100$   $\mu\text{m}$  are seldom recovered (Krogh et al. 1993a, 1993b). This study

aims to constrain the occurrence and stability of shock features in naturally shocked zircon from a known petrological context. In a case study from a continuous ejecta deposit from the Chicxulub crater, implications for the temperature-time history of this sequence will be discussed.

#### Previous Studies of Shock-Induced Features in Zircon

##### *Reidite and Planar Microstructures*

Naturally shocked zircons appear turbid to opaque in color (Krogh et al. 1984; Bohor et al. 1993; Corfu et al. 2003) and exhibit a decrease of the refractive index, which indicates amorphization (Dobretsov et al. 1969). Amorphous lamellae of diaplectic  $ZrSiO_4$  glass were confirmed by transmission electron microscopy (TEM) analyses of experimentally shocked  $ZrSiO_4$  (Leroux et al. 1999). They occur as multiple sets of intersecting planes with spacings between 0.5 and 4  $\mu\text{m}$  that are optically not recordable. Optically recordable planar microstructures have been identified as microcracks and microtwinning features (Leroux et al. 1999; Reimold et al. 2002). They occur as single or multiple sets of parallel bands with a spacing below 5  $\mu\text{m}$  (Krogh and Davis 1984;

Bohor et al. 1993) and are interpreted to form along with the transition of zircon to the high pressure polymorph reidite (Kusaba et al. 1986; Leroux et al. 1999; Finch and Hanchar 2003). The shock-induced martensitic, i.e., solid-state transition of zircon to reidite starts at ~20 GPa and is complete at 52 GPa (Fiske et al. 1994). Reidite is quenchable and stable at ambient pressures and temperatures up to 1000 °C. It fully reverts to zircon if heated at ambient pressures to 1200 °C (Kusaba et al. 1985). Reidite (space group  $I4_1/a$ ) has a tetragonal structure akin to zircon (space group  $I4_1/amd$ ) and exhibits similar optical properties but is about 10% more dense (Reid and Ringwood 1969; Kusaba et al. 1985; Leroux et al. 1999; Glass et al. 2002; van Westrenen et al. 2004). Natural reidite was found in distal ejecta from the Eocene Chesapeake Bay impact, where it occurs together with tektite glass, shocked quartz and feldspar, coesite and stishovite (Glass and Liu 2001; Glass et al. 2002). The only other occurrence was reported from a suevite melt fragment of the Ries crater (Gucsik et al. 2004a, 2004b).

#### *Granular Textures*

Granular-textured zircon grains are frequently observed in impact-related lithologies (Bohor et al. 1993; Krogh et al. 1993b, 1996; Glass and Liu 2001). Such polycrystalline grains represent crystallites of zircon in a glassy  $ZrSiO_4$  matrix (Bohor et al. 1993; Kamo et al. 1996; Glass 2000) that resulted from shock-induced amorphization and subsequent recrystallization. Localized granular aggregates that were interpreted as incipient structural breakdown or recrystallization features were produced in shock experiments (Deutsch and Schärer 1990; Leroux et al. 1999).

#### *Decomposition*

The decomposition of zircon was first described by El Goresy (1965, 1968) in tektite glass and glassy melts of suevites as granular droplets of monoclinic  $ZrO_2$  (baddeleyite) at rims of zircon clasts. This author inferred temperatures for this breakdown reaction between 1775 °C–1900 °C. The presence of this decomposition feature in tektites was consequently used to infer their origin from a hypervelocity impact (Kleinmann 1969; Glass et al. 1990, 1995). It is also regarded as a feature that is diagnostic of impact melts in general (Marvin and Kring 1992; Koeberl and Reimold 2003; Wittmann et al. 2004a, 2004b). Dobretsov et al. (1969) reported the decomposition of zircon to a mixture of  $ZrO_2$  polymorphs, amorphous  $SiO_2$ , and amorphous  $ZrSiO_4$  in shock experiments. This was confirmed by Kusaba et al. (1985) in shock recovery experiments at pressures of ~90 GPa.

## **SAMPLE DESCRIPTIONS**

### **Ries Crater**

The Ries crater in Germany, which is 14.4 Ma old and

24 km in diameter, is a well-preserved complex crater (e.g., Stöffler and Ostertag 1983; von Engelhardt 1990; Laurenzi et al. 2003). Impactites from the Ries have been studied in great detail and have revealed some basic principles of impact metamorphism (e.g., Hörz 1965; Stöffler 1971a, 1974a; von Engelhardt et al. 1969, 1995; von Engelhardt 1990, 1997; Newsom et al. 1990). Various ultra-high pressure minerals were found and intensely studied in Ries impactites, e.g., stishovite, coesite (Stöffler 1971b), diamond (e.g., Hough et al. 1995; El Goresy et al. 2001a; Schmitt et al. 2005), a post-diamond carbon polymorph (El Goresy et al. 2003), baddeleyite-structured  $TiO_2$  (El Goresy et al. 2001b), and reidite (Gucsik et al. 2004a, 2004b).

We extracted highly shocked crystalline fragments from the fallout suevites of the Seelbronn, Zipplingen, and Aumühle locations in the Ries crater. Macroscopically, their high degrees of shock metamorphism are indicated by pumice-like textures. Microscopically, crystallized feldspar melt, diaplectic quartz glass with tube-like coesite, and thermally decomposed biotite are present in the Zipplingen and Seelbronn fragments. Following the shock classification of Stöffler (1971a), this suggests lower shock stage III conditions with equilibrium shock pressures of 45–50 GPa and post-shock temperatures of 900–1100 °C, given that feldspar melt is recrystallized but no ballen quartz crystallized and coesite is retained (Dworak 1969; Stöffler 1971b; Stöffler and Langenhorst 1994; Grieve et al. 1996). The only carbon phase observed in the Seelbronn fragment is impact diamond (Schmitt et al. 2005). Feldspar and quartz occur as diaplectic glasses in the fragment from Aumühle. This is diagnostic for shock stage II conditions of shock pressures between 35–45 GPa and post-shock temperatures <900 °C (Dworak 1969; Stöffler 1972; von Engelhardt 1990).

Two additional samples of the fallout suevites of Seelbronn and Aumühle represent inhomogeneous shock stage IV melt fragments that indicate peak shock pressures in excess of 60 GPa and post-shock temperatures >1500 °C (Stöffler 1971a; von Engelhardt 1990). The Aumühle sample is taken from a grey melt fragment with an aerodynamic, contorted shape. In thin section, the melt rock matrix appears almost completely crystallized with intergrown plagioclase phenocrysts and abundant cryptocrystalline Ti-Fe oxides. Pyroxene is missing as a liquidus phase in the melt matrix, indicating elevated  $f_{H_2O}$  (von Engelhardt 1995). The shock stage IV sample from Seelbronn is a dark blue-grey melt fragment. In thin section, an agglutinated rim of lithic particles and a melt matrix devoid of phenocrysts can be observed. The core of this melt fragment exhibits abundant clinopyroxene phenocrysts as the only liquidus melt phase. This style of phenocryst crystallization is commonly interpreted as indicative of quenching under low  $f_{H_2O}$  conditions or very rapid quenching from very high temperatures (von Engelhardt et al. 1995; Whitehead et al. 2002; Osinski 2003).

## Popigai Crater

To characterize shock features in zircon from coherent impact melt rocks, we investigated two samples from the largest known Cenozoic impact structure, the Popigai crater in northern Siberia, which is 35.7 Ma old and 100 km in diameter (Masaitis 1994; Bottomley et al. 1997; Vishnevsky and Montanari 1999; Whitehead et al. 2002). The samples are from an outcrop in the crater (71°38'N, 11°12'E) and represent dark grey to black melt rock that incorporated various lithic clasts. Under the microscope, the samples exhibit hypo- and holocrystalline melt rock matrices with abundant hypersthene and labradorite phenocrysts and reaction coronas of hypersthene around quartz clasts. Monomineralic clasts occur, e.g., ballen quartz, quartz grains with several bands of decorated planar deformation features (PDFs), kink-banded, sometimes thermally decomposed biotite, checkerboard feldspar, and some without a distinct shock metamorphic overprint. Some polymineralic lithic clasts of shock stages I–III, e.g., gneiss fragments, were observed as well.

## Chicxulub Crater

The Chicxulub impact structure on the Yucatán Peninsula, Mexico, has a diameter of ~180 km (e.g., Hildebrand et al. 1995; Morgan et al. 1997, 2000; Vermeesch and Morgan 2004) and was formed 65 million years ago (e.g., Hildebrand et al. 1991; Swisher et al. 1992). The ICDP-Yaxcopoil-1 borehole (Yax-1) was drilled about 62 km to the south-southwest of the center of the Chicxulub impact structure (Urrutia-Fucugauchi et al. 2004), within the annular trough between the peak ring and the crater rim. It encountered about 100 m of suevitic, impact melt rock-bearing breccias (Dressler et al. 2003, 2004; Stöffler et al. 2004; Tuchscherer et al. 2004a; Kring et al. 2004). These units are underlain by sedimentary “megablocks” (Kenkmann et al. 2004), in which Yax-1 terminated. The megablocks are predominantly composed of brecciated dolomite, limestone, anhydrite and some impact induced dike breccias (Wittmann et al. 2004b). Because of the scarcity of clastic sedimentation in the sedimentary target sequence (López Ramos 1975), zircon was almost exclusively derived from crystalline target rocks of pan-African age (Krogh et al. 1993b). We analyzed 17 thin sections of samples from Yax-1 that comprise suevites, impact melt rocks, and dike breccias (Fig. 1).

## Experimentally Shocked Samples

Thin sections of non-metamict zircon that was experimentally shocked to 38, 40, 60 and 80 GPa at the Ernst Mach Institute in Germany were available for analysis. These samples were previously described by Leroux et al. (1999), Reimold et al. (2002), and Gucsik et al. (2004a, 2004b) (Figs. 2a and 2b).

## ANALYTICAL METHODS AND REFERENCE MATERIALS

The zircon grains were found by systematic scanning of 24 thin sections in high-contrast backscattered electron mode (BSE) under the scanning electron microscope. Some ZrSiO<sub>4</sub> grains were checked for their major element composition by energy dispersive spectroscopy (EDX) before wavelength dispersive (WDX) compositional mapping under the electron microprobe was performed to confirm the presence of ZrO<sub>2</sub> next to ZrSiO<sub>4</sub>. To collect qualitative structural information, microRaman spectroscopy was performed on a notch filter based Dilor LabRam spectrometer, with a He-Ne laser of 632.8 nm wavelength. The energy of 3 mW was transferred to the sample with a spot size of ~1 μm. Spectra were recorded by three-fold accumulation and collection times between 3 and 100 seconds, with a thermoelectrically cooled CCD detector operated with a 1800 grooves/mm grating in the frequency range between 200–1200 cm<sup>-1</sup>. The wave number accuracy is about 1 cm<sup>-1</sup>. Background reduction was achieved by Gauss-Lorenz fitting using the LabSpec v.2.08 software by Dilor SA and Université de Reims. Details on the deconvoluting procedure are given in Nasdala et al. (2001) and references therein. Additionally, we investigated three grain separates of shock stage III gneiss samples from Seelbronn and Zipplingen and the shock stage IV impact melt samples from Aumühle by optical microscopy and microRaman spectroscopy. The ZrSiO<sub>4</sub> grains are a residue from cyclic acid dissolution by application of HF, HCl, and H<sub>3</sub>BO<sub>3</sub> as described in Schmitt et al. (2005). Four of these ZrSiO<sub>4</sub> grains from the Zipplingen sample were subsequently mounted on a thin section for SEM analysis. As reference materials for Raman spectroscopy, a thin section of natural zircon from Australia and baddeleyite from the Phalborwa carbonatite taken from the collections of the Museum für Naturkunde were used.

## RESULTS

### Experimentally Shocked ZrSiO<sub>4</sub>

All measurements of the experimentally shocked zircon (Fig. 3) agree with previously published Raman spectra of reidite (Gucsik et al. 2004a, 2004b). Reidite is the only phase in the samples shocked to 40, 60, and 80 GPa and background intensities increase until 60 GPa before they decrease toward the level of the unshocked precursor in the 80 GPa sample (Fig. 3). We did not find relics of zircon coexisting with reidite in the sample shocked to 40 GPa, which have been described by other authors (Leroux et al. 1999; Gucsik et al. 2004a, 2004b). Scarce relics of zircon coexisting with reidite were found in the sample shocked to 38 GPa with very low intensities and broad half-widths (FWHM) of 10.6 and 13.4 cm<sup>-1</sup> from initial average values of 2–4 cm<sup>-1</sup> in the unshocked material, which indicates shock-induced

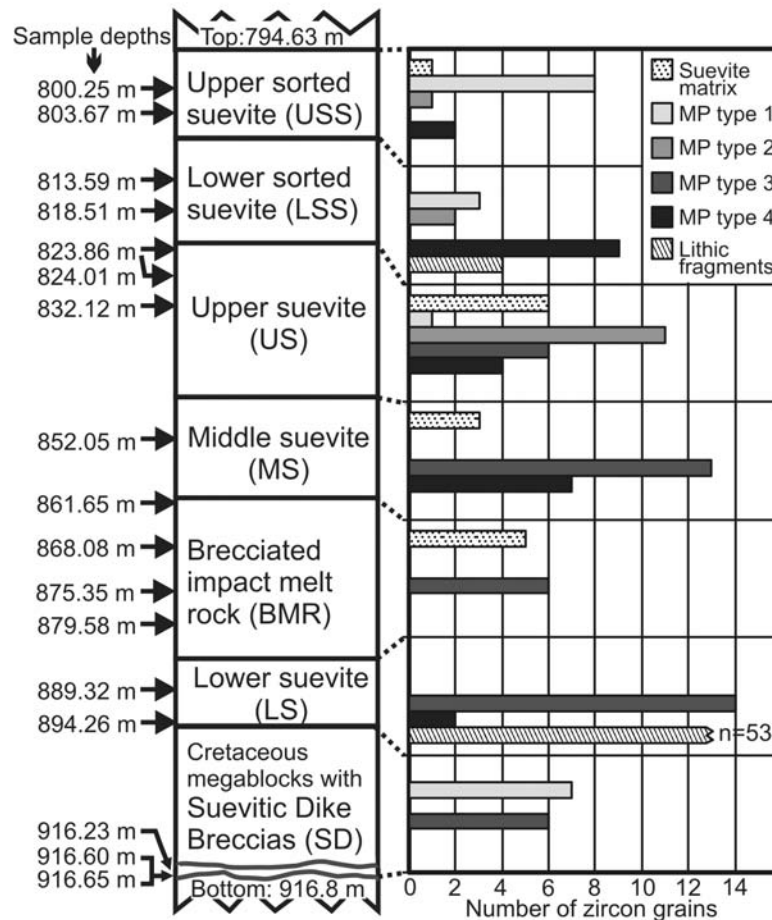


Fig. 1. A schematic profile of the analyzed section of Chicxulub drill core Yaxcopoil-1 and host materials of zircons as encountered in the respective units. Sample locations are indicated with their respective depths; unit nomenclature after Stöffler et al. (2004). Melt particles (MP) type 1 exhibit brownish green colors, amoeboid shapes, and frequently perlitic textures and are commonly lacking phenocrysts (Hecht et al. 2004; Tuchscherer et al. 2004b). MP type 2 contain abundant vesicles, have green to brown colors, and have crystallized some feldspar phenocrysts. Some exhibit shard morphologies with armored rims of accreted fine particles from the ejecta plume. MP type 3 have mostly white to brownish colors and generally exhibit abundant plagioclase and diopside phenocrysts in an altered melt matrix. MP type 4 are dark brown and contain finely disseminated iron oxides and variably abundant feldspar phenocrysts. The suevite matrix is composed of mineral fragments and melt particles and suffered variable degrees of hydrothermal overprint by calcite and hematite (Stöffler et al. 2004). Kring et al. (2004) and Dressler et al. (2004) discuss the possibility that the matrix had been in a melted state shortly after emplacement. The lithic fragment in a lower sorted suevite (LSS) sample is an amphibolite facies calc-silicate. Quartz and plagioclase exhibit decorated PDFs and biotite displays kink bands, indicating lower shock stage I conditions of shock pressures between 10 and 20 GPa (Stöffler 1971a; Stöffler and Langenhorst 1994; Grieve et al. 1996). The lithic fragment from the lower suevite (LS) sample is a dm-size granite. The granitic fabric is retained, although the mineral components suffered intense thermal overprint. Biotite is thermally decomposed, feldspar is mostly recrystallized and PDFs in quartz are decorated. This indicates upper shock stage I conditions of 20 to 35 GPa.

amorphization (Gucsik et al. 2004b). In contrast to other studies, we did not find indications of granularization or decomposition in the samples shocked to 60 and 80 GPa (Kusaba et al. 1985; Deutsch and Schärer 1990; Leroux et al. 1999).

## Ries Crater

### *Lithic Fragments of Shock Stage II–III*

The three thin sections of the Zipplingen and Seelbronn samples yielded  $ZrSiO_4$  grains (Fig. 4; Table 1), which show

intense undulous extinction under the optical microscope. Most grains are associated with recrystallized shock melts of plagioclase and biotite. Other host materials are cordierite, diaplectic quartz glass with coesite inclusions (Figs. 5a and 5b), sillimanite, titanite, and kink-banded biotite. Maskelynite as a host is only retained in the shock stage II sample from Aumühle.

All grains analyzed in the sample from Zipplingen, including those in the grain separate, indicate the presence of reidite together with zircon. Some  $ZrSiO_4$  grains in the Seelbronn and Aumühle samples indicate the sole presence of

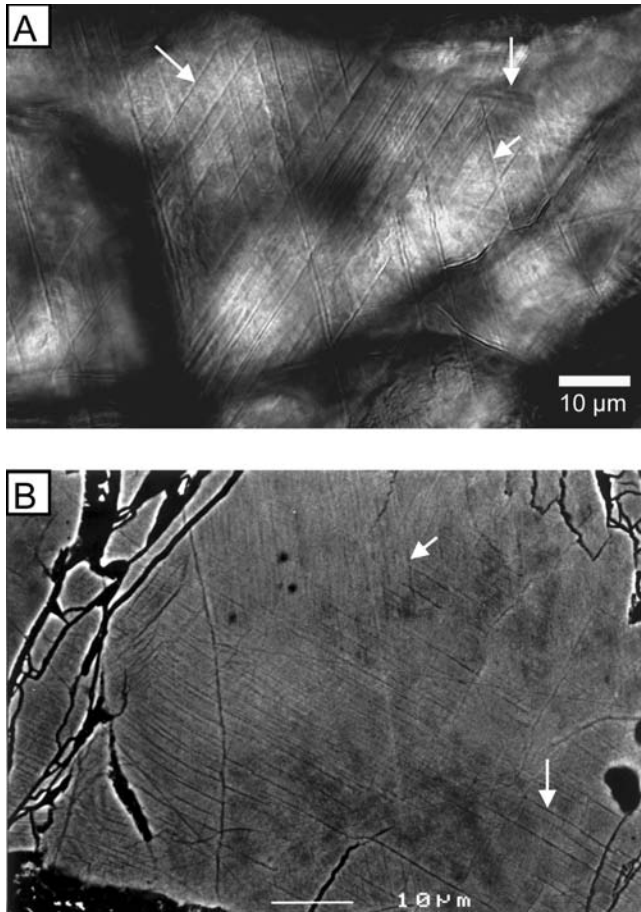


Fig. 2.  $ZrSiO_4$  experimentally shocked to 60 GPa that transformed to reidite. a) Plane-polarized light micrograph displays three bands of planar microstructures, as indicated by arrows. b) Scanning electron microscope (SEM), backscattered electron mode (BSE) image indicates two bands of planar microstructures.

zircon. Reidite-zircon grains exhibit zoning patterns in discrete domains and sub-parallel lamellae of sub- $\mu\text{m}$  thicknesses and spacings (Figs. 5b and 5c). Raman spectra show variable intensity ratios of the indicative  $\nu_3$  Raman bands of zircon that span a range of frequencies and full widths at half maximum (FWHM) (Figs. 5d and 6) that are in accordance with the amorphization trends of relic zircon domains in experimentally shocked  $ZrSiO_4$  (Gucsik et al. 2004b). Raman mapping of relic compositional zoning areas reveal the predominance of zircon in areas with a high degree of impurities, while reidite-zircon occurs in unzoned regions (Figs. 7a and 7c). A granular texture occurs only at an incipient stage at the rim of one grain (Fig. 5c) from the Zipplingen sample. Reidite was not found in this granular textured rim (Fig. 5d). No  $ZrO_2$  was indicated in SEM-EDX analyses and backscattered images or microRaman spectroscopic analyses.

Reflected light microscopy was applied to analyze the grain separate samples with regard to shock features. These observations were checked by SEM imaging of thin sections

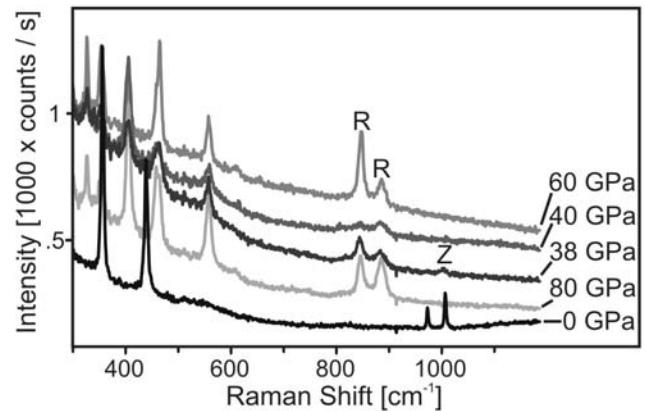


Fig. 3. Raman spectra of experimentally shocked  $ZrSiO_4$  specimen and unshocked zircon that were taken at identical measurement conditions. Indicative zircon band positions (Z) and those of reidite (R) are only coexisting in the sample shocked at 38 GPa.

of four of these grains. These SEM images revealed large voids and granular textures together with domains of smooth surfaces with planar microstructures (Fig. 7d). MicroRaman spectroscopy confirmed the presence of reidite in the grain separate samples (Table 1) and therefore verified the thin section analyses. Moreover, this is evidence for the resistance of reidite to acid treatment. However, the presence of granular textures and voids (Fig. 7d) indicates the dissolution of one component of the  $ZrSiO_4$  grains, most likely an amorphous phase.

#### Lithic Fragments of Shock Stage IV

A large percentage of  $ZrSiO_4$  grains in the two thin sections from Aumühle and Seelbronn (Fig. 4; Table 1) exhibit undulous extinction under the microscope. All grains are embedded in the melt matrices. Most of the granular textured zircon grains appear very porous with dark brown to black colors and are barely birefringent. However, about half of the granular textured grains from the more strongly devitrified sample from the Aumühle sample are polycrystalline with regular optical properties.

The fraction of grains that exhibit coronas of  $ZrO_2$  granules (Figs. 8a and 8b) are mostly associated with granular textured zircon, but intergrowths with fractured single grain zircon occur as well and one grain is completely decomposed to  $ZrO_2$  (Fig. 8c). All grains analyzed with decomposition coronas yield Raman spectra of baddeleyite (López et al. 2001). This is indicated by the most prominent and distinct Raman band of baddeleyite at  $\sim 474\text{ cm}^{-1}$  (Fig. 9). The indicative band of the tetragonal  $ZrO_2$  polymorph at  $\sim 270\text{ cm}^{-1}$  (López et al. 2001) was not found. Because the cubic high temperature polymorph of  $ZrO_2$  is reported to only display one Raman band at  $616\text{ cm}^{-1}$  that also occurs in the Raman spectrum of baddeleyite (López et al. 2001), this polymorph coexisting with baddeleyite can not be verified by Raman spectroscopy. Four of the grains

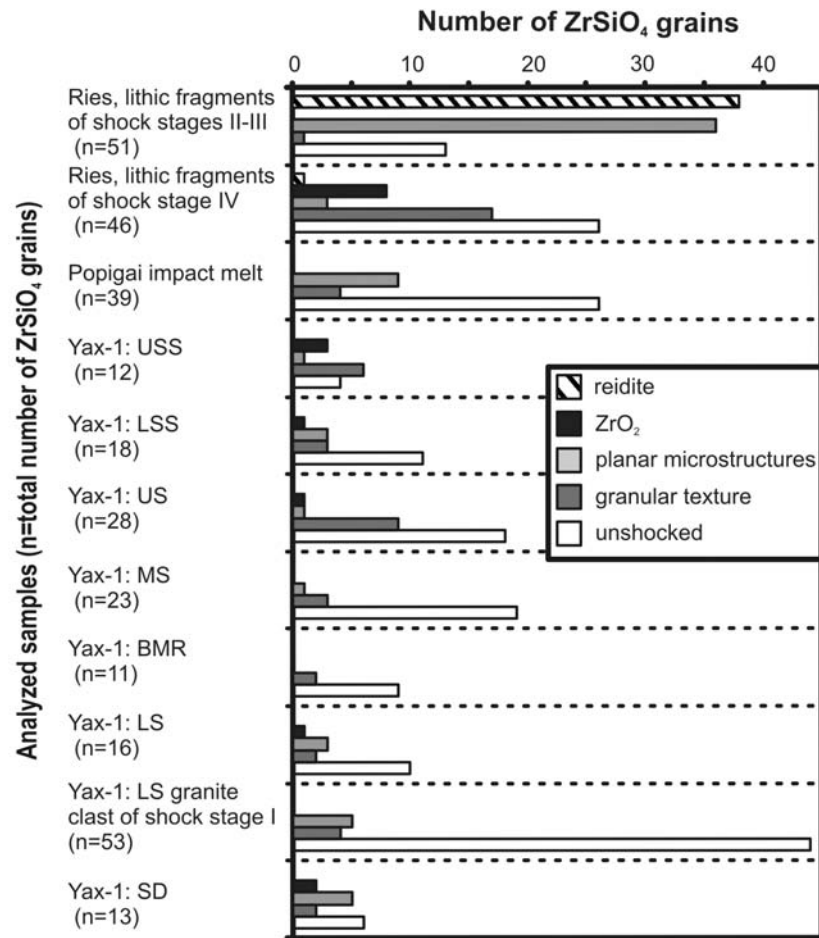


Fig. 4. Absolute abundance of shock-induced features in the ZrSiO<sub>4</sub> grains analyzed in thin section. Single grains may exhibit multiple shock features, e.g., reidite and planar microstructures or granular textures and ZrO<sub>2</sub>; therefore, abundances of shock features plus unshocked grains do not generally add up to the sum of analyzed grains. Abbreviations as introduced in Fig. 1.

Table 1. Statistical data for natural ZrSiO<sub>4</sub> grains. Thin section analyses unless noted otherwise.

Sample types	Number of grains	Min.–max. size (μm)	Median size (μm)	Planar micro-structures (%)	Granular textures (%)	Decomposed to ZrO <sub>2</sub> (%)	Reidite (%)	Total shock features (%)
Ries, lithic fragments of shock stages II–III	51	15–191	54	71	2	n.d.	75	75
Ries, lithic fragments of shock stages II–III, grain separates	16	45–341	121	19	25	n.d.	88	94
Ries, clasts in shock stage IV	46	18–90	44	7	37	17	2	43
Ries, clast in shock stage IV, grain separate	11	67–179	105	36	27	n.d.	n.d.	55
Popigai impact melt	39	19–131	43	23	10	n.d.	n.d.	33
Yax-1: USS <sup>a</sup>	12	8–115	25.5	8	50	25	n.d.	67
Yax-1: LSS <sup>a</sup>	18	8–52	20	17	17	6	n.d.	39
Yax-1: US <sup>a</sup>	28	10–102	20.5	4	32	4	n.d.	36
Yax-1: MS <sup>a</sup>	23	13–67	17	4	13	n.d.	n.d.	17
Yax-1: BMR <sup>a</sup>	11	12–70	20	n.d.	18	n.d.	n.d.	18
Yax-1: LS <sup>a</sup>	16	13–86	22	19	13	6	n.d.	38
Yax-1: LS <sup>a</sup> granite clast of shock stage I	53	15–110	39.5	9	8	n.d.	n.d.	17
Yax-1: SD <sup>a</sup>	13	14–183	36	38	15	15	n.d.	54
Yax-1 total	174	8–183	27	11	17	5	n.d.	30

<sup>a</sup>Unit abbreviations as introduced in Fig. 1.

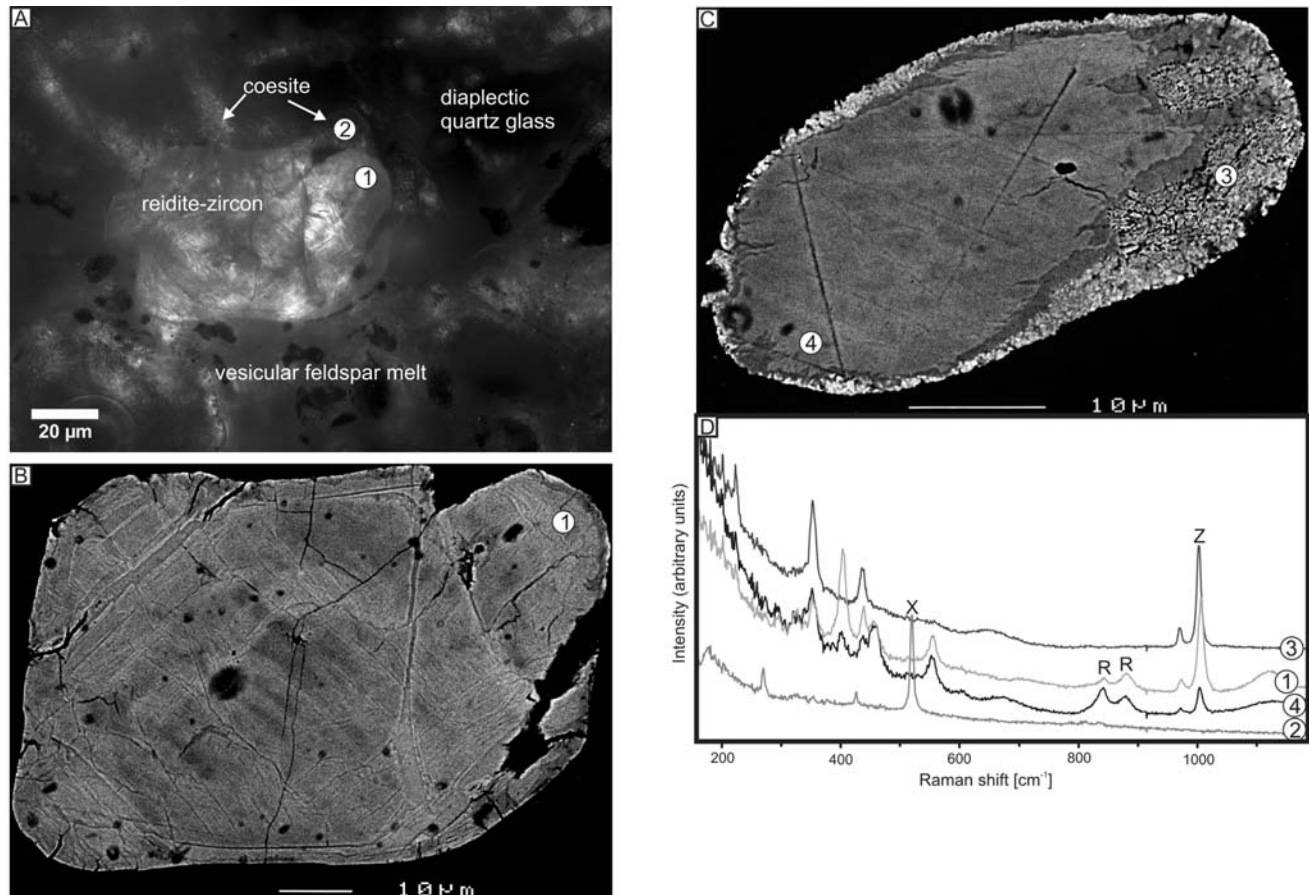


Fig. 5. Reidite from the Ries crater. a) and b) Reidite-zircon grain with complex zoning pattern and planar microstructures associated with coesite, diaplectic quartz glass, and vesicular feldspar melt in the shock stage III sample from Zipplingen (optical microscope, crossed polarizers and SEM-BSE image, respectively). c) Reidite-zircon grain associated with vesicular, recrystallized plagioclase melt in shock stage III sample from Zipplingen. Note the rim with a granular texture (SEM-BSE image). d) Raman spectra of domains indicated with labels in (a), (b), and (c): (1) reidite-zircon, respective band frequencies for reidite (R) are  $-842\text{ cm}^{-1}$  and  $880\text{ cm}^{-1}$  and for zircon (Z)  $-1006\text{ cm}^{-1}$ ; (2) coesite with the indicative peak frequency at  $518\text{ cm}^{-1}$  (X); (3) zircon (Z) spectrum of the granular rim with frequency of  $1001\text{ cm}^{-1}$ ; and (4) reidite-zircon spectrum of core with frequency of (Z) at  $1003\text{ cm}^{-1}$  and (R) at  $839\text{ cm}^{-1}$  and  $878\text{ cm}^{-1}$ .

with decomposition coronas yield spectra with the indicative band of the orthorhombic-II  $\text{ZrO}_2$  polymorph at  $661\text{ cm}^{-1}$  (Arashi et al. 1990; Haines et al. 1997) (Fig. 9).

One grain in the more rapidly quenched sample from Seelbronn exhibits a high density of planar microstructures and Raman spectra of coexisting reidite and zircon. Otherwise, planar microstructures occur as parallel bands of tiny bubbles in zircon with spacings below  $1\text{ }\mu\text{m}$ . Interestingly, the grain separate sample from Aumühle displays the exclusive presence of zircon while decomposed grains are missing altogether and planar microstructures seem to be accentuated (Table 1).

### Popigai Crater

Two-thirds of the  $\text{ZrSiO}_4$  grains in the two thin sections are embedded in the melt matrix and one-third are associated with lithic clasts that float in the melt matrix.  $\text{ZrSiO}_4$  grains

that are inclusions in kink-banded biotite, quartz with decorated PDFs, and quartz without shock features do not show impact-induced features. All  $\text{ZrSiO}_4$  grains that are intergrown with ballen quartz or polycrystalline feldspar (Figs. 10a and 10b) exhibit shock features. Two granular textured  $\text{ZrSiO}_4$  grains with dark brown colors occur in the melt matrix. One of these grains indicates incipient isotropization (Figs. 10c and 10d), while the other one displays regular optical properties of a polycrystalline texture. Another two granular-textured grains are inclusions in a cm-size gneiss fragment with annealed features of shock stage III. These  $\text{ZrSiO}_4$  grains have brown colors (Figs. 10e and 10f) and appear partially recrystallized. Decorated planar microstructures with spacings of  $1\text{--}4\text{ }\mu\text{m}$  and widths  $\ll 1\text{ }\mu\text{m}$  (Figs. 10a and 10b) occur in translucent to light brown grains that show dense fracture patterns. All  $\text{ZrSiO}_4$  grains display Raman spectra of zircon without indications of advanced metamictization (Fig. 11), reidite or  $\text{ZrO}_2$  (Table 1). The

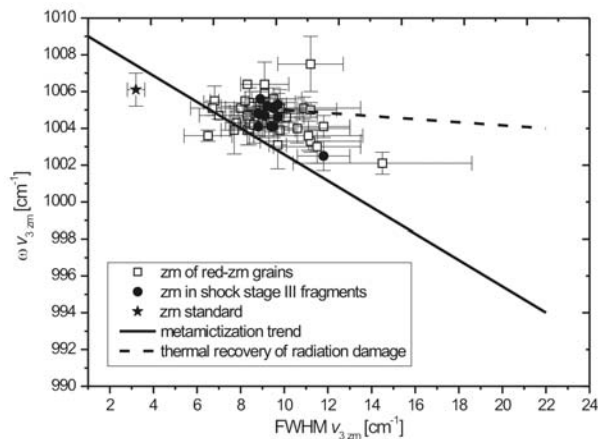


Fig. 6. Full width at half-maximum (FWHM) plotted versus frequency of Raman shift ( $\omega$ ) of the  $\nu_3$  anti-symmetric stretching mode of Si-O in zircon in the Raman spectrum of reidite-zircon and zircon grains from shock stages II–III and IV samples from the Ries crater, respectively. Error bars indicate standard deviation of a mean from multiple spectra of the same grain. For reference, means and standard deviation of 15 measurements of natural, unshocked zircon is plotted. The solid line indicates the trend of natural radiation damage of zircon after Nasdala et al. (2002) and Geisler and Pidgeon (2002). Trend of thermal recovery of radiation damaged zircon after Geisler and Pidgeon (2002).

variations in zircon  $\nu_3$  band FWHM and frequencies is smaller in comparison to the grains analyzed in the Ries and Chicxulub samples, indicating less amorphous zircon and therefore more pronounced thermal annealing.

### Chicxulub Crater

The 17 thin sections from drill core Yax-1 yielded  $\text{ZrSiO}_4$  grains that are mostly associated with melt particles. About one third of them occur in shock stage I crystalline rock fragments. Figure 1 displays the relative distribution of  $\text{ZrSiO}_4$  host particles in the units of Yax-1 and Fig. 12 shows the proportions of shocked  $\text{ZrSiO}_4$  grains in these hosts.

Grains that bear planar microstructures exhibit regular to reduced birefringence and clear to light brown colors. One fourth of them display two to three bands of sub- $\mu\text{m}$  wide planar features that intersect at various angles (Figs. 13a and 13b). The rest show bands of pores in one to two directions that are reminiscent of “decorated” PDFs (Figs. 13c and 13e).

$\text{ZrSiO}_4$  grains with granular textures were found in every unit from the analyzed section of Yax-1 (Fig. 1; Table 1). Two-thirds of these grains are of a dark brown color and exhibit strongly reduced birefringence and a high density of nm-size vesicles (Fig. 14a). One-third appears more strongly recrystallized to a polycrystalline texture (Figs. 14b and 14e). Only a fraction of the grains in one of the shock stage I crystalline basement fragments analyzed exhibit shock features (Table 1). These grains belong to the granite

fragment that experienced upper shock stage I pressures >20 GPa.

Generally, two styles of decomposed  $\text{ZrSiO}_4$  grains can be distinguished. First, the “quenched” type, which displays coronas of separate  $\text{ZrO}_2$  granules around a zircon core (Figs. 15a–d). This type is like the decomposed grains from the Ries samples (Figs. 8a–c). It occurs in two-thirds of the decomposed grains and all of them are associated with type 1 melt particles in the uppermost units of Yax-1. The other type occurs as vermicular intergrowths of  $\text{ZrO}_2$  with zircon near the rim in grains that are associated with type 1 and type 3 melt particles (Figs. 15e–g). This suggests incipient breakdown (Figs. 15e and 15f) and recovery (Fig. 15g), respectively.  $\text{ZrO}_2$  associated with granular textured zircon (Figs. 15a–d) was confirmed by Raman spectroscopy in about 13% of the granular textured zircon grains. However, SEM images and EDX-qualitative analyses indicate that  $\text{ZrO}_2$  may be present in far more granular textured grains as nm-size round entities with a high mass contrast.

Featureless  $\text{ZrSiO}_4$  grains in Yax-1 yield Raman spectra that range from those of well-crystallized zircon with Raman shifts of the  $\nu_3$  band of  $\sim 1005$ – $1008 \text{ cm}^{-1}$  and FWHM of  $3$ – $5 \text{ cm}^{-1}$  to rare examples of moderately disordered crystalline structures with frequencies  $< 1000 \text{ cm}^{-1}$  and FWHM of  $\sim 20 \text{ cm}^{-1}$  (Nasdala et al. 2004) (Fig. 16). No spectra of reidite or strongly metamict zircon were recorded. Raman spectra of zircon grains with planar microstructures are not distinguishable from those of the “unshocked” specimens (Fig. 16). Granular textured grains exhibit Raman characteristics that overall follow the trend of natural irradiation damage of Nasdala et al. (2002) and Geisler and Pidgeon (2002). Plots of FWHM versus Raman shift for the zircon components of  $\text{ZrO}_2$ -zircon intergrowths indicate large variations and a wide spread of frequencies compared to the other zircon spectra (Fig. 16). This suggests higher degrees of amorphization compared to all other shocked zircons analyzed. All Raman spectra of  $\text{ZrO}_2$  coexisting with zircon indicate the presence of baddeleyite (López et al. 2001). Two grains (one example in Figs. 15a and 15b) in the uppermost suevite units upper sorted suevite (USS) and lower sorted suevite (LSS) display Raman spectra with bands at  $661 \text{ cm}^{-1}$  that may indicate the presence of relics of the orthorhombic II polymorph of  $\text{ZrO}_2$ .

## DISCUSSION

### Planar Microstructures and Reidite

Planar microstructures in zircon develop along with the transition to reidite (Leroux et al. 1999; Reimold et al. 2002; Finch and Hanchar 2003). This transition occurs in a mixed phase regime of pure zircon and reidite between 20–52 GPa (Fiske et al. 1994) (Fig. 17) and results in an  $\sim 10\%$  decrease in volume (Reid and Ringwood 1969; Kusaba et al. 1985;



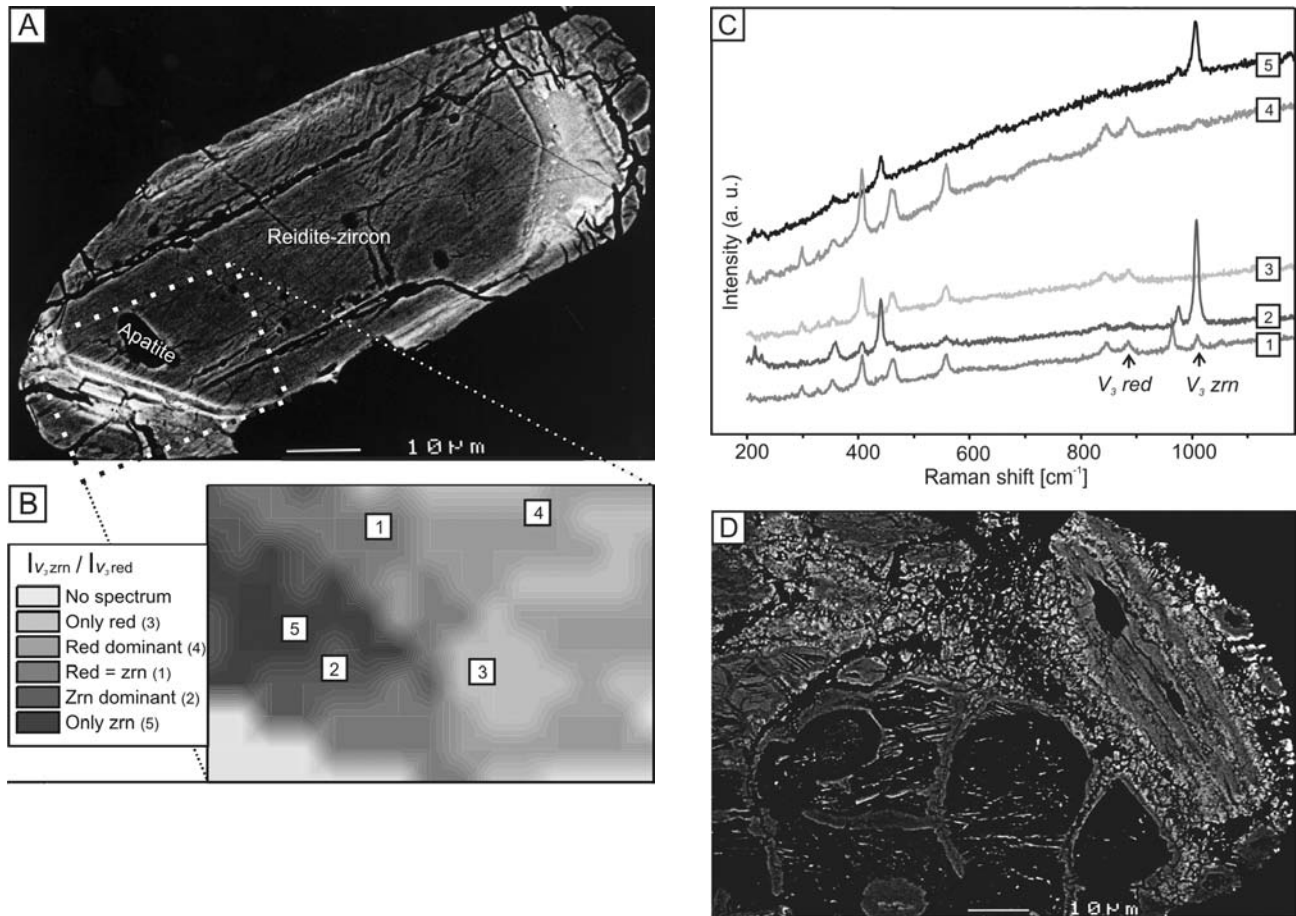


Fig. 7. a) Compositionally zoned zircon-reidite grain embedded in recrystallized, vesicular plagioclase melt of shock stage III sample from Seelbronn, Ries crater (SEM-BSE image). b) Raman mapping of reidite-zircon area indicated in (a). Ratio of the  $\nu_3$  bands of zircon (zrn) and reidite (red) at  $\sim 1006\text{ cm}^{-1}$  and  $\sim 880\text{ cm}^{-1}$ , respectively. c) Single Raman spectra of exemplary measurement spots (1–5) in (b). Note the presence of the indicative band of apatite at  $962\text{ cm}^{-1}$  in spectrum (1). d) Zircon-reidite grain from acid treated grain separate of the shock stage III fragment from Zipplingen (thin section SEM-BSE image).

Knittle and Williams 1993). Analyses of the experimentally shocked  $\text{ZrSiO}_4$  samples reveal that the 60 and 80 GPa samples exhibit the most pronounced development of optically recordable planar microstructures (Figs. 2a and 2b). Conspicuous “trails of bubbles” that frequently occur in zircon grains with regular optical properties from the samples of Yax-1 and Popigai likely represent “decorated” PDFs (Grieve et al. 1996; Kamo et al. 1996; Leroux and Doukhan 1996; Moser 1997) that were formed due to a thermally induced crystallization of diaplectic  $\text{ZrSiO}_4$  glass in these features. Paragenetic relations of these decorated PDFs from the Popigai and Yax-1 samples suggest post-shock thermal annealing in shock stage IV materials at temperatures of  $\sim 1200\text{ }^\circ\text{C}$  ( $T$ - $t$  paths [d–g] in Fig. 18). Because no decorated PDFs occur in the reidite-zircon grains from the Ries samples,  $1200\text{ }^\circ\text{C}$  is the best approximation for an upper limit for post-shock temperatures regarding the preservation of pristine PDF in zircon. The preservation of PDFs and reidite may thus be restricted to shock stages I–III of non-porous quartzo-

feldspathic rocks. Exceptions can occur in components of shock stage IV impact melts that experienced very rapid quenching as evidenced by the sample from Seelbronn (Ries crater) ( $T$ - $t$  path [c] in Fig. 18). We found that reidite occurs almost always in shock stages II–III fragments of the Aumühle, Seelbronn, and Zipplingen suevite deposits of the Ries crater. This petrologic context indicates formation conditions under equilibrium shock pressures of 35–50 GPa and post-shock temperatures of 300–1200  $^\circ\text{C}$  followed by rapid quenching ( $T$ - $t$  path [a] in Fig. 18). No back-transformation of reidite to zircon due to grain separation processes, acid leaching, and Raman or SEM analysis were noticeable in our analyses of zircon-reidite from the Ries crater.

The occurrence of reidite intergrown with zircon in naturally shocked  $\text{ZrSiO}_4$  is unlike the experimentally shocked zircons that indicate near complete conversion to the high-pressure polymorph at comparable shock pressure ranges. Because shock experiments represent a simplification

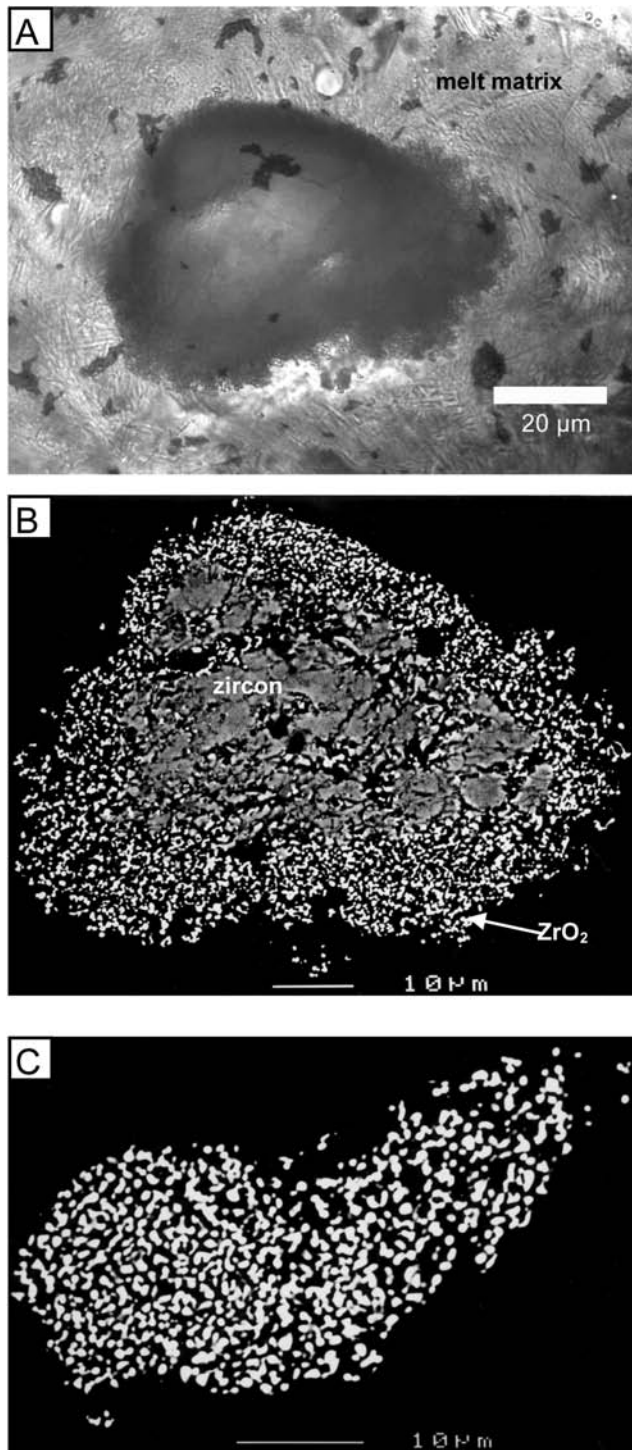


Fig. 8. a) and b) Partly decomposed, black zircon grain in glassy matrix with pyroxene phenocrysts of shock stage IV sample from Seelbronn, Ries crater. Optical microscope, plane-polarized light and SEM-BSE image, respectively. A core of granular textured zircon is retained while the rim region exhibits  $\mu\text{m}$ -size granules of  $\text{ZrO}_2$ . c) Decomposed zircon grain in shock stage IV sample from Seelbronn. The  $\text{ZrO}_2$  granules are enclosed in the glassy melt matrix (SEM-BSE image).

of natural shock events, certain limitations apply, most notably in the duration of the shock wave (e.g., Stöffler 1972; Grieve et al. 1996) and the development of post-shock temperatures. These may be significantly lower in shock experiments than in naturally shocked samples (DeCarli et al. 2002). Gucsik et al. (2004a, 2004b) interpreted the difference between natural occurrence of reidite-zircon and experimental evidence as being due to heterogeneous shock pressures in natural impactites. Therefore, these authors suggested lower shock pressures for their zircon-reidite sample than indicated by petrography. However, heterogeneities in shock are commonly induced by positive pressure and temperature excursions from the equilibrium shock conditions (Stöffler and Langenhorst 1994; Heider and Kenkmann 2003). For example, micrometer-size hotspots that can occur during the shock compression of porous solids (DeCarli et al. 2002) must be considered for zircon, which is prone to developing porosities from auto-irradiation. This could explain a temperature-induced partial back-transformation of reidite to the zircon structure at equilibrium post-shock temperature conditions that are insufficient to crystallize diaplectic quartz glass, which occurs at temperatures of  $\sim 1100^\circ\text{C}$  (Rehfeldt-Oskierski et al. 1986; Grieve et al. 1996). Another explanation for the inhomogeneous occurrence of reidite in shock stage III samples could be impurities (Figs. 7a–c), which were shown to hamper the transformation to reidite (van Westrenen et al. 2004). Additionally, pre-existing metamictization may inhibit the transformation to reidite during a shock event because the martensitic transformation process, as proposed by Kusaba et al. (1986), requires a pre-existing zircon lattice. A certain degree of metamictization may result in the failure to contain the shear strain during distortion of the lattice relics and consequently result in shock-induced amorphization. The physical expression of this process may lie in the substantial decrease of the elastic moduli of zircon with increasing radiation damage (van Westrenen et al. 2004, and references therein).

#### Decomposition of Zircon

At ambient pressures, pure zircon decomposes at  $1676^\circ\text{C}$  to a mixture of cristobalite and tetragonal  $\text{ZrO}_2$  (Butterman and Foster 1967).  $\text{ZrO}_2$  is known to occur in six different polymorphs of which only baddeleyite, the monoclinic low-temperature and low-pressure polymorph, and the orthorhombic II high-pressure polymorph are stable at ambient conditions (Arashi et al. 1990). All other polymorphs (tetragonal, cubic, hexagonal, and orthorhombic I) result from displacive transformations and consequently revert to baddeleyite at ambient pressure and temperature (Ohtaka et al. 1994; Haines et al. 1997). Because baddeleyite cannot be the primarily resultant polymorph of temperature and/or

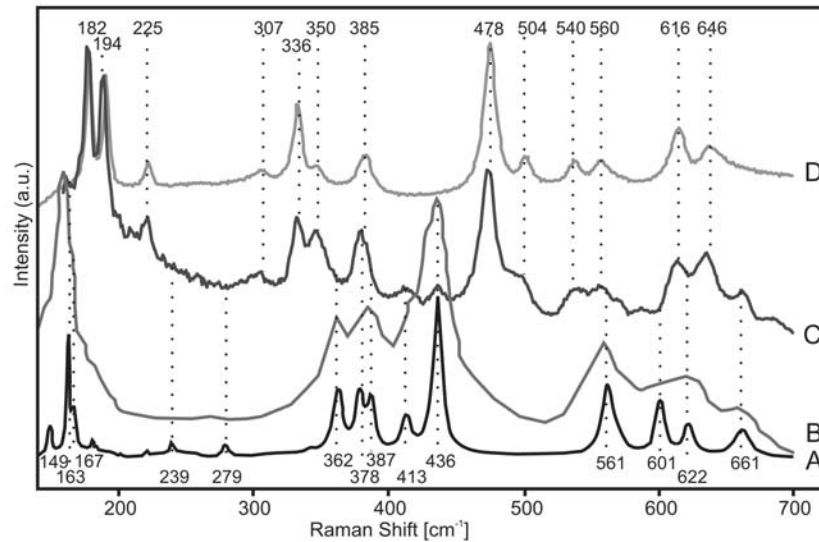


Fig. 9. Raman spectra of  $\text{ZrO}_2$ . Line A is a high-resolution orthorhombic II  $\text{ZrO}_2$  spectrum that is redrawn after Haines et al. (1997); line B is a low-resolution orthorhombic II  $\text{ZrO}_2$  spectrum, redrawn after Arashi et al. (1990); line C is from a partly decomposed grain of the shock stage IV sample from Aumühle, Ries crater, that indicates the presence of baddeleyite, zircon, and possibly orthorhombic II  $\text{ZrO}_2$ ; and line D is from natural monoclinic  $\text{ZrO}_2$  (baddeleyite) from Phalborwa. Note that the most prominent band of orthorhombic II  $\text{ZrO}_2$  at  $436\text{ cm}^{-1}$  also occurs in zircon. Dotted lines are visual guides; peak indication after López et al. (2001) on top refers to baddeleyite, on bottom after Haines et al. (1997) to orthorhombic II  $\text{ZrO}_2$ .

pressure induced decomposition of  $\text{ZrSiO}_4$  (Butterman and Foster 1967; Ohtaka et al. 1994), relics of other polymorphs are to be expected in decomposed  $\text{ZrSiO}_4$ . In the decomposed  $\text{ZrSiO}_4$  from the Ries and Chicxulub craters, we found zircon, baddeleyite and possible relics of the orthorhombic II polymorph of  $\text{ZrO}_2$ . This polymorph is stable above  $1000\text{ }^\circ\text{C}$  and  $>70\text{ GPa}$  and quenchable (Haines et al. 1997). We could not detect all the characteristic Raman bands of this polymorph. This problem was previously attributed to low spectral resolution and residual strain (Haines et al. 1997). Orthorhombic II  $\text{ZrO}_2$  was shown to form in shock experiments at pressures above  $80\text{--}90\text{ GPa}$  (Mashimo et al. 1983; Kusaba et al. 1985). Such possible relics of a pressure-induced decomposition were only detected in grains that are associated with rapidly quenched impact melt particles (Figs. 8a, 8b, 15a, and 15b). In contrast, grains that indicate reversion to zircon are mostly associated with melt particles that bear liquidus phase phenocrysts in Yax-1 (Figs. 15e–g).

### Granular Textured Zircon

The onset of formation of granular textures in  $\text{ZrSiO}_4$  was found in the Ries shock stage III samples. Although the grains barely exhibit granularization in thin section, the occurrence of grains with domains of reduced optical properties was revealed as shock induced amorphization in the grain separates of the same samples. The amorphous  $\text{ZrSiO}_4$  was dissolved during acid treatment (Fig. 7d), confirming previous findings of granular textures in zircon-reidite intergrowths in the distal ejecta of the Chesapeake Bay

impact after etching with acids and alkalis (Glass and Liu 2002).

Further formation conditions of granular textured  $\text{ZrSiO}_4$  can be deduced from the occurrence as inclusions in ballen quartz (Figs. 10e and 10f). Ballen quartz is characteristic for the devitrification of diaplectic quartz glass, which was shown to occur at temperatures  $>1100\text{--}1300\text{ }^\circ\text{C}$  in annealing experiments (e.g., Short 1970; Stöffler 1974b; Rehfeldt-Oskierski et al. 1986; Stöffler and Langenhorst 1994; Grieve et al. 1996).  $\text{ZrSiO}_4$  that occurs in diaplectic quartz glass does not exhibit granular textures but consists of zircon and reidite intergrowths (Figs. 5a, 5b, and 5d). This suggests that some granular textures form due to the reversion of reidite to zircon, which results in a lattice expansion by  $\sim 11\%$ .

We found that a recovery of optical properties accompanies a continuum of granular textures that ranges from grains with a high density of “microvesicles,” suggestive of degassing in a  $\text{ZrSiO}_4$  melt (Figs. 10d and 14a), to grains that recrystallized to  $\mu\text{m}$ -size euhedral crystallites (Figs. 14b–e). Raman spectroscopy indicates variations in crystallinity of the granular textured zircon grains that do not substantially differ from the “unshocked” grains (Figs. 11 and 16). Accounts of Raman spectra of “zircon glass” are scant and ambiguous in the literature. It can tentatively be assumed that diaplectic zircon glass should yield Raman spectra that resemble those of strongly metamict zircon (e.g., Nasdala et al. 2001, 2002, 2004; Geisler and Pidgeon 2002; Zhang et al. 2000a, 2004b). However, such spectra were not obtained in any measurements of this study. Also, additional Raman bands, as indicated by Gucsik et al. (2004b) from

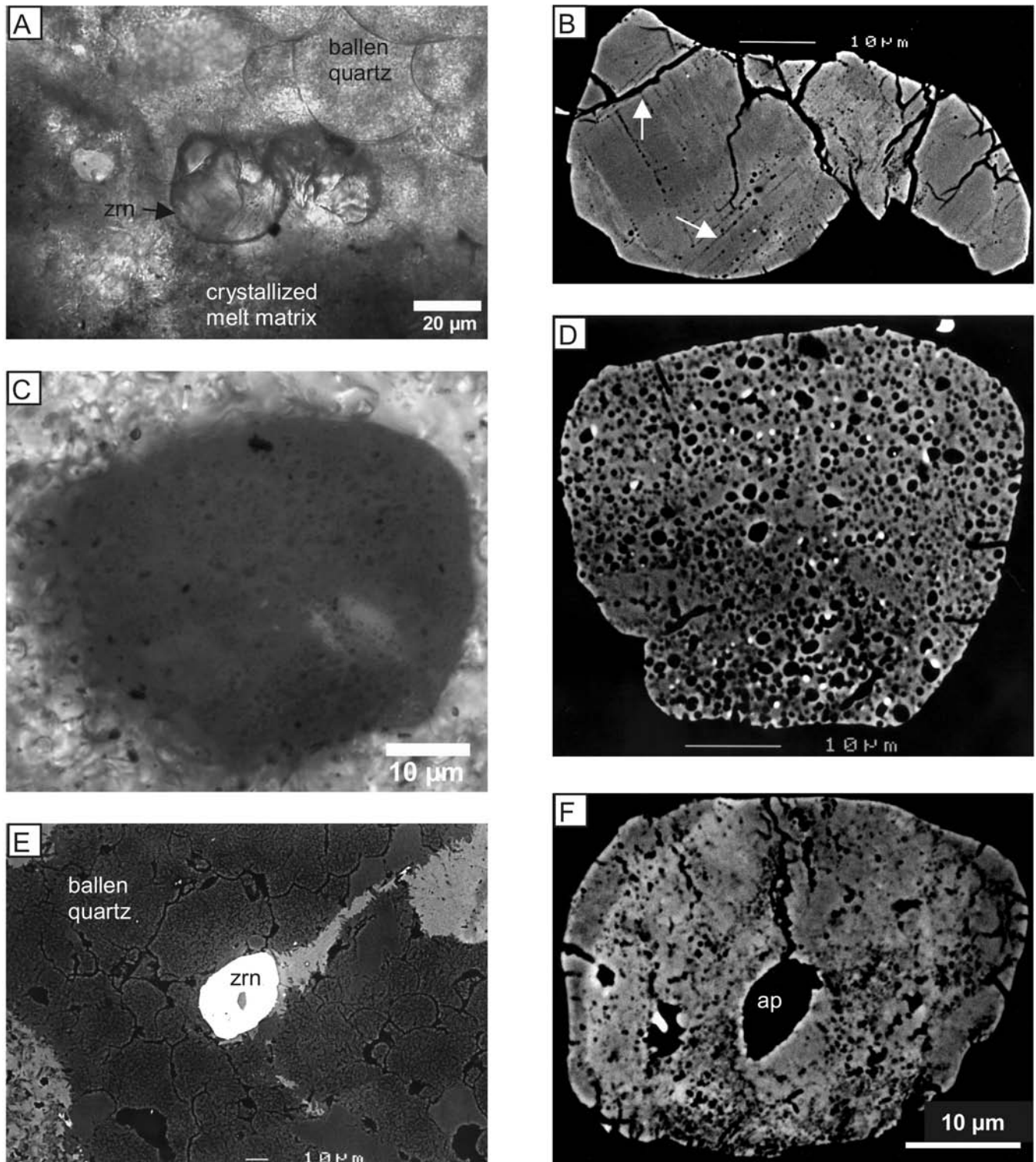


Fig. 10. Popigai impact melt rock samples. a) and b) A zircon grain with two sets of intersecting planar microstructures that is intergrown with ballen quartz and the melt matrix (optical microscope, plane-polarized light and SEM-BSE image, respectively). c) and d) Black, granular textured zircon grain embedded in the melt rock matrix (optical microscope, plane polarized light, and SEM-BSE image, respectively). Note that the granular texture exhibits abundant microvesicles and tiny inclusions of high mass contrast. e) and f) SEM-BSE images of zircon grain embedded in ballen quartz of annealed shock stage III gneiss fragment. The inclusion is apatite (ap).

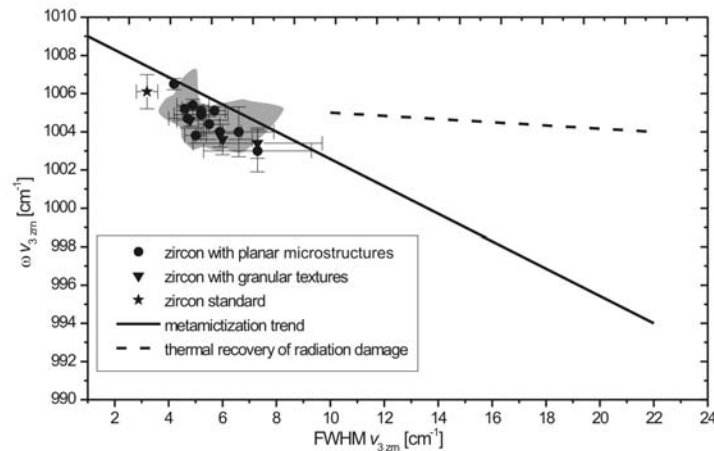


Fig. 11. Full width at half-maximum (FWHM) plotted versus Raman shift position of the  $\nu_3$  anti-symmetric stretching mode of Si-O ( $\omega \nu_3$ ) in the Raman spectra of zircon grains from the Popigai impact melt rock samples. Error bars indicate standard deviation of a mean from multiple spectra of the same grain. For reference, means and standard deviation of 15 measurements of natural, unshocked zircon is plotted. The shaded area represents measurements of the zircons without shock features. Trend of radiation damage of zircon after Nasdala et al. (2002) and Geisler and Pidgeon (2002). Note that according to this trend, pronounced metamictization is indicated for  $\text{FWHM} > 20$  and  $\omega \nu_3 < 1000$ . Thermal recovery trend after Geisler and Pidgeon (2002).

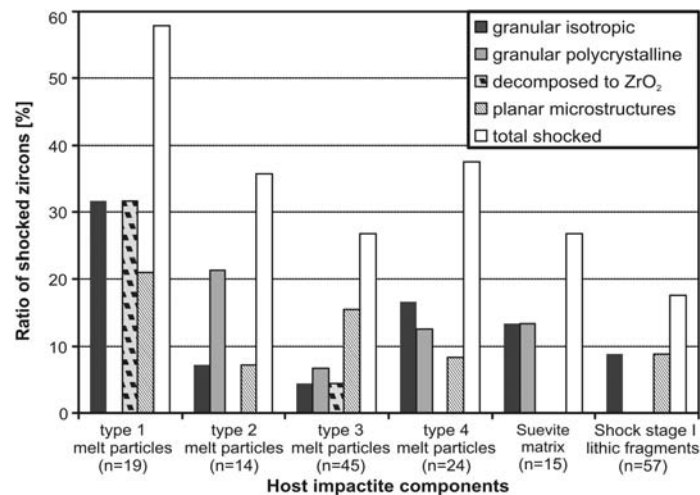


Fig. 12. The relative proportions of different shock effects in zircons of Yax-1 host components. Melt types after Hecht et al. (2004). All shocked grains in the lithic fragments of shock stage I occur in the fragment that experienced upper shock stage I conditions with an estimated shock pressure  $> 20$  GPa. Single grains can exhibit multiple shock features, therefore, ratios of all shock features do not generally add up to the ratio of total shocked grains.

experimentally shocked samples, or by Zhang et al. (2000b) from amorphous zircon coexisting with  $\text{SiO}_2$  and tetragonal  $\text{ZrO}_2$ , were not consistently identified. However, we found systematic background intensity variations in Raman spectra of the experimentally shocked samples (Fig. 3). This pattern could indicate an increase in coexisting amorphous material in the samples from 38–60 GPa, which approximately span the mixed phase regime (Fig. 17). In the high-pressure phase regime at 80 GPa, background intensity drops towards the level of the unshocked, non-metamict precursor zircon.

Distinct steps of thermal recovery of amorphous zircon are known from annealing experiments between  $\sim 1100$ –

1450 °C that result in distinct granular textures (Weber 1990; McLaren et al. 1994; Capitani et al. 2000; Zhang et al. 2000a; Ewing et al. 2003). Granular textured zircon with dark colors and reduced birefringence may therefore represent less intense thermal annealing at lower temperatures, while the polycrystalline type probably experienced more prolonged annealing at higher temperatures. Because diaplectic glasses can crystallize at far lower temperatures than “normal” glass (Dworak 1969; Rehfeldt-Oskierski et al. 1986; Stöffler and Langenhorst 1994), the thermal annealing of diaplectic zircon glass could occur at far lower temperatures than needed for the decomposition of zircon.

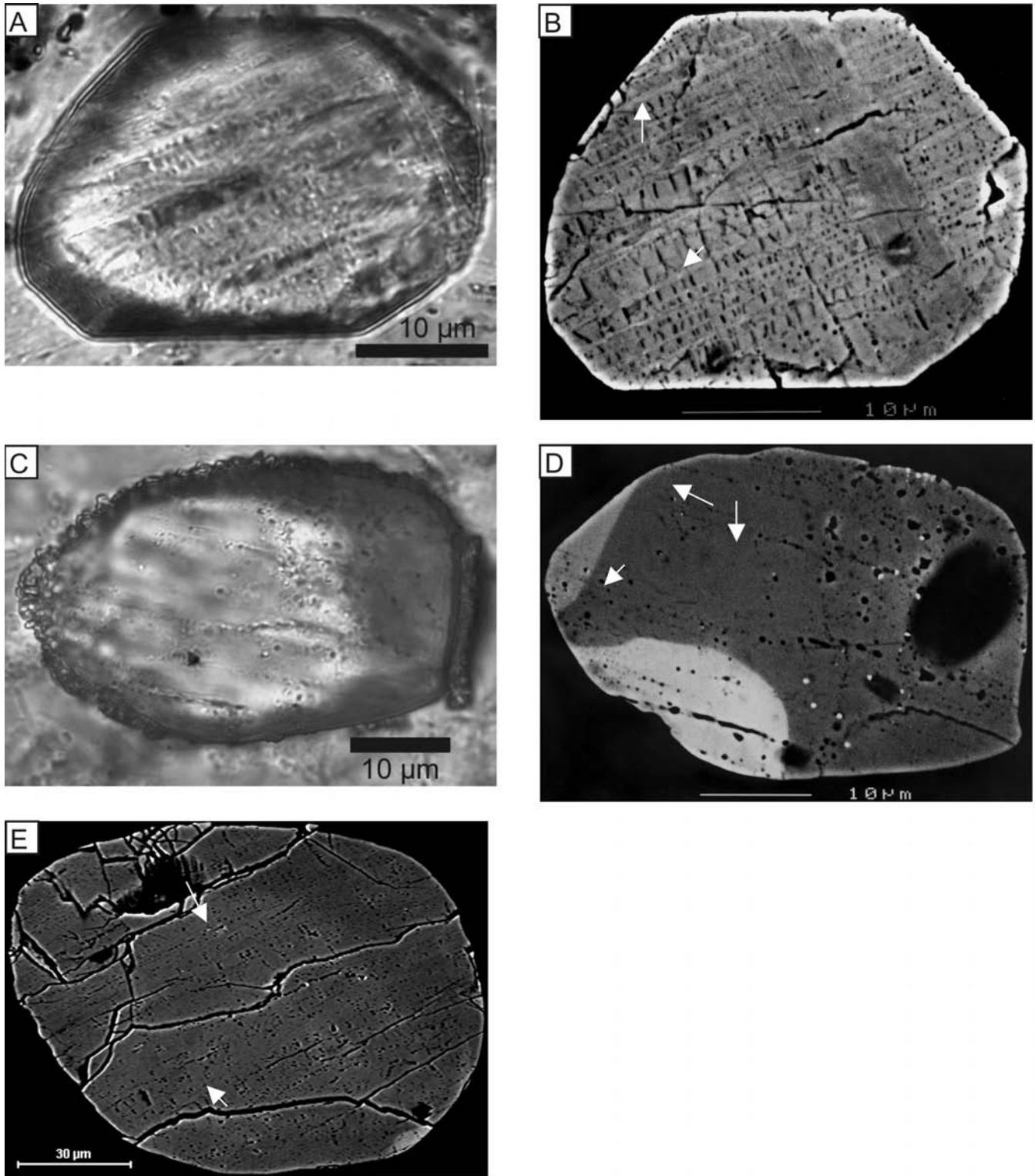


Fig. 13. a) and b) Euhedral zircon grain in type 2 melt rock host of SD sample at 916.65 m. Two bands of intersecting planar microstructures are present in the zircon grain (arrows) (optical microscope, plane-polarized light and SEM-BSE image, respectively). c) and d) Subhedral zircon grain in perlitic type 1 melt particle host in LSS sample at 818.51 m. One strongly and two additional weakly expressed parallel bands are displayed (arrows) (optical microscope, plane-polarized light and SEM-BSE image, respectively). e) Subhedral zircon grain with two sets of planar microstructures (arrows) in type 1 melt particle from SD sample at 916.60 m (SEM-BSE image).

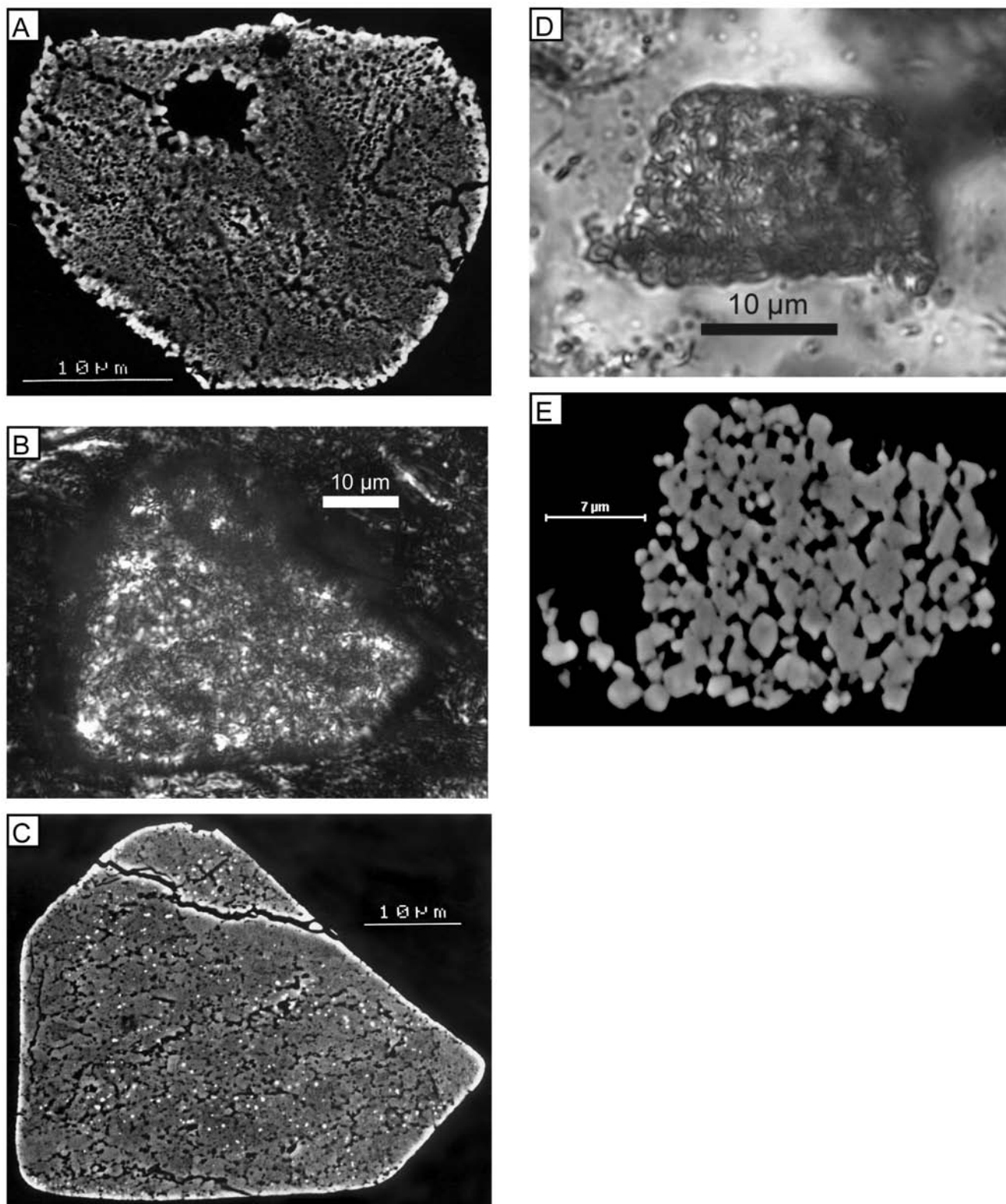


Fig. 14. a) Subhedral zircon grain with a granular texture that exhibits abundant microvesicles in the clastic matrix of US sample at 824.01 m (SEM-BSE image). b) and c) Polycrystalline, granular textured zircon grain of US sample at 824.01 m that is enclosed in a type 2 melt particle (optical microscope, crossed polarizers and SEM-BSE image, respectively). d) and e) Coarsely crystallized, composite zircon grain in blocky quartz of BMR sample at 875.35 m (optical microscope, crossed polarizers and SEM-BSE image, respectively).

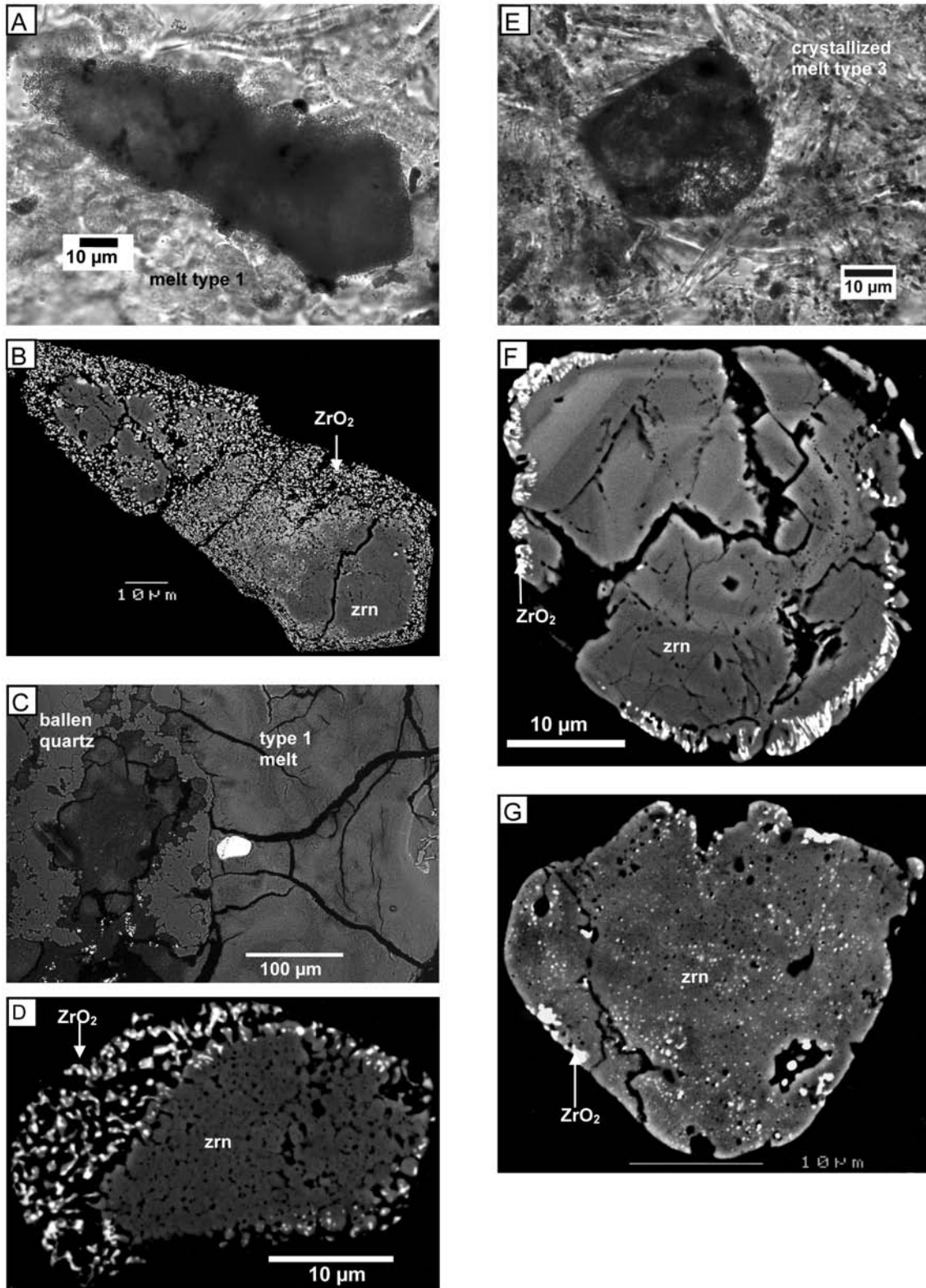


Fig. 15. a) and b) Decomposed zircon grain in USS sample at 800.25 m. Enclosed in a perlitic type 1 melt particle, it exhibits a granular texture and a rim of  $ZrO_2$  granules (plane-polarized light and SEM-BSE image, respectively). c) and d) Decomposed zircon grain in US sample at 823.86 m. Embedded in a type 1 melt particle, it has a granular texture and rim of granular to vermicular  $ZrO_2$ -zircon intergrowths (SEM-BSE images). e) and f) Zircon grain enclosed in a type 3 melt particle in LS sample at 889.32 m with a rim of zircon-baddeleyite intergrowths and compositionally zoned core (plane-polarized light and SEM-BSE image, respectively). g) Granular textured zircon grain in a type 3 melt particle of SD sample at 916.23 m with baddeleyite patches (SEM-BSE image).



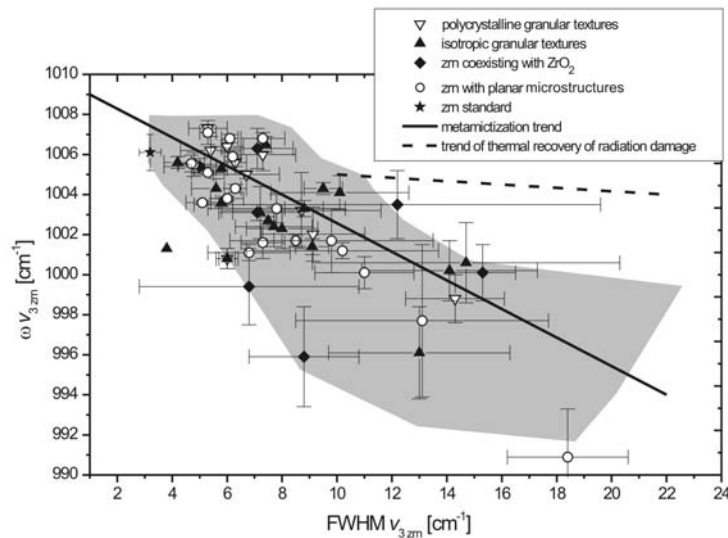


Fig. 16. Full width at half-maximum (FWHM) plotted versus Raman shift frequency ( $\omega$ ) of the  $\nu_3$  anti-symmetric stretching mode of Si-O in the Raman spectra of zircon grains in Yax-1 samples. Means of several measurements and standard deviations (error bars) are plotted. Shaded area represents measurements of Yax-1 zircons without shock features. Solid line marks trend of natural radiation damage of zircon after Nasdala et al. (2001) and Geisler and Pidgeon (2002). Dashed line represents thermal annealing trend of metamict zircon after Geisler and Pidgeon (2002).

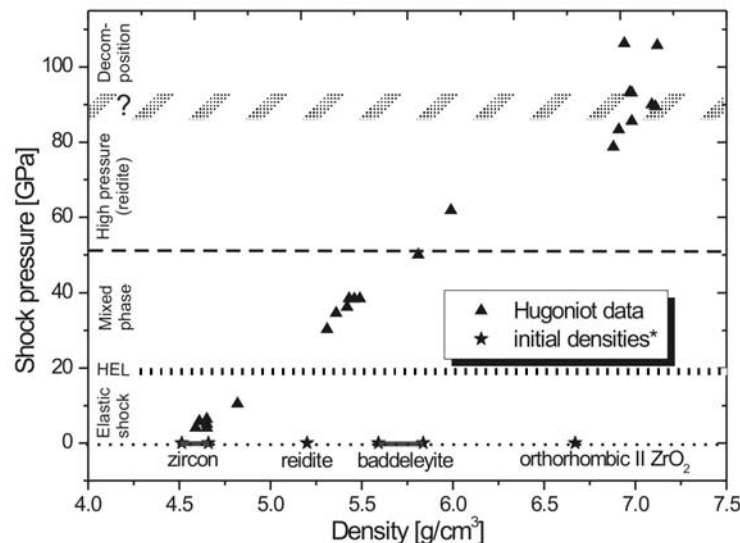


Fig. 17. Hugoniot data and ranges of initial densities for zircon and baddeleyite from Mashimo et al. (1983). Phase boundaries redrawn after Mashimo et al. (1983) and Fiske et al. (1994). Reidite density after Glass et al. (2002), density of orthorhombic II  $\text{ZrO}_2$  after Liu (1979).

### Implications for Yax-1

The full range of progressive stages of shock metamorphism was found to occur in crystalline basement clasts of all suevitic units in Yax-1 (Schmitt et al. 2003; Stöffler et al. 2004; Kring et al. 2004; Dressler et al. 2004; Tuchscherer et al. 2004a). However, all shock features in quartz and feldspar are annealed and melt components can be distinguished by variable degrees of devitrification before and during quenching. The principal results of this study indicate

that perlitic type 1 melt particles are indicative of the most rapid quenching in Yax-1 (Fig. 1). This melt particle type is the dominant host for zircons that exhibit decomposition to  $\text{ZrO}_2$ . Also, all granular textured zircon grains found in this host are of the isotropized type that experienced least annealing. Moreover, this melt particle type retained the highest ratio of shocked versus unshocked zircon grains (Fig. 12). As shock stage IV materials, such melt particles indicate shock pressures  $>60$  GPa and post-shock temperatures  $>1500$  °C (Stöffler 1971a) (Fig. 18). Their

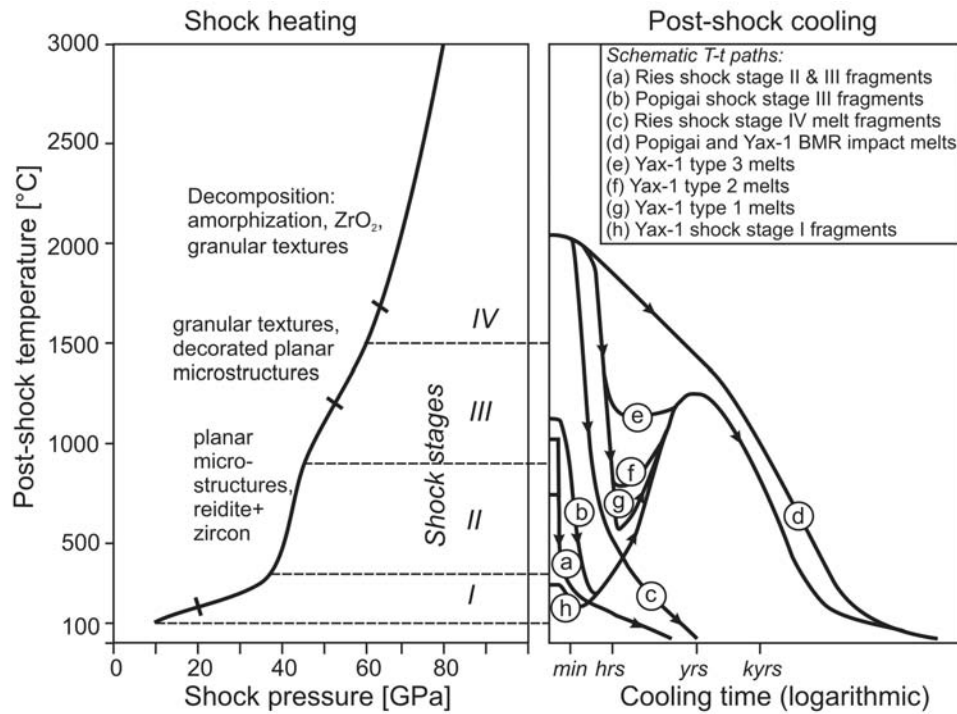


Fig. 18. Post-shock temperature as a function of shock pressure in naturally shocked, non-porous quartzo-feldspathic rocks (left) and respective shock stages after data from Stöffler (1971a). Stability ranges of shock features of  $ZrSiO_4$  are projected into the diagram. Projections of schematic post-shock cooling paths for the naturally shocked samples analyzed in this study are plotted in the right diagram. Impact melt particle types of Yax-1 after Hecht et al. (2004).

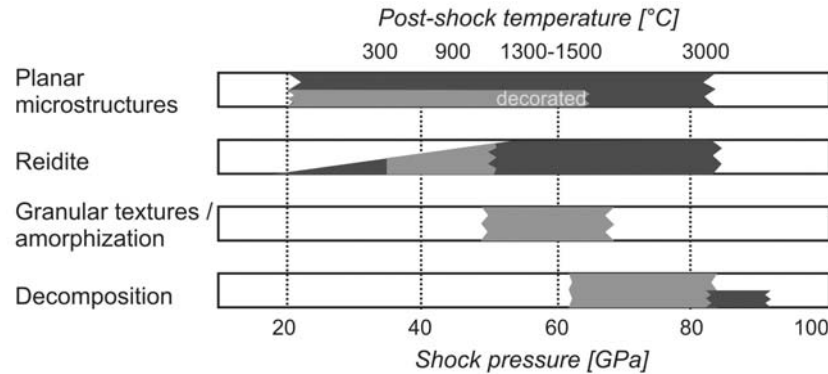


Fig. 19. A compilation of shock features of  $ZrSiO_4$ . Post-shock temperature estimates for non-porous quartzo-feldspathic rocks after Stöffler (1971a). Black shading indicates constraints from experimental evidence (Leroux et al. 1999; Mashimo et al. 1983; Fiske et al. 1994; Kusaba et al. 1985; this study). Grey shading indicates constraints from natural impactites.

cooling history allowed the crystallization of ballen quartz but the crystallization of liquidus phase phenocrysts was inhibited. This indicates rapid quenching below 600 °C from initial shock temperatures in excess of some 1500 °C, followed by thermal annealing to temperatures of about 1200 °C (Rehfeldt-Oskierski et al. 1986; Stöffler and Langenhorst 1994; von Engelhardt et al. 1995) (Fig. 18). Type 1 melt particles are restricted to the USS, LSS, the uppermost Upper Suevite (US), and the Suevitic Dike (SD) suevite units in Yax-1 (Fig. 1). Towards the BMR, decomposition textures

of zircon become annealed and granular textured grains exhibit gradual coarsening and recovery of optical properties. This indicates an annealing gradient in Yax-1 with the highest quenching rates in the USS and the SD from temperatures >1676 °C (Butterman and Foster 1967) to below the glass transition temperature of melt particles of ~680 °C before deposition (Arndt and Häberle 1973; von Engelhardt et al. 1995). Quenching was slowest in the BMR because the temperature at which precipitation of liquidus phase phenocrysts ceases (~600 °C) (von Engelhardt et al. 1995)

had only been reached after abundant crystallization of liquidus phase phenocrysts had occurred ( $T-t$  path [d] in Fig. 18). This possibly allowed resorption of components in the BMR and development of reaction coronas around lithic fragments, similar to the Popigai impact melt rocks (Vishnevsky and Montanari 1999; Whitehead et al. 2002). General post-shock temperatures in excess of 1200 °C for the whole sequence are indicated by the lack of reidite, which is in accordance with the observations related to annealed shock features in quartz (Rehfeldt-Oskierski et al. 1986; Stöffler and Langenhorst 1994; Schmitt et al. 2003) (Fig. 18).

## CONCLUSIONS

We combined our findings and experimental evidence for the occurrence of shock features in  $ZrSiO_4$  in a diagram, which depicts the progressive stages of shock metamorphism of zircon (Fig. 19). A comparison of experimentally shocked zircon with zircons of rapidly quenched impactites from the Ries crater indicates that the martensitic transformation to the high-pressure polymorph reidite may be hampered by impurities and pre-impact metamictization. Therefore, compared to shock experiments, the martensitic transformation is far less extensive in samples shocked to comparable shock-pressures at the Ries crater. Nonetheless, natural reidite-zircon intergrowths occur in shock stage II and III gneiss fragments of the Ries suevite together with diaplectic quartz glass, coesite, and impact diamonds. Reidite can also occur very rarely incorporated in rapidly quenched shock stage IV impact melts of the suevite. Reidite-zircon grains of shock stage III fragments from the Ries crater show the onset of shock-induced amorphization but do not exhibit decomposition to  $ZrO_2$ . Paragenetic relationships with ballen quartz imply that reidite decomposes to granular textured zircon at temperatures  $>1100$  °C. Granular textures in zircon do not occur in experimentally shocked zircon up to pressures of 80 GPa but were found as the most common impact-induced feature in the samples from the Chicxulub crater. We suggest that they represent the recovery from amorphized zircon in analogy to annealing textures of thermally recovered metamict zircon and reconverted zircon-reidite and reidite grains that were formed in a shock pressure range between 20 and  $>80$  GPa. The development of this feature appears mainly due to high temperature annealing. Planar microstructures occur in experimentally shocked zircon with increasing abundance up to shock pressures of 80 GPa and seem to be linked to the martensitic transformation to reidite.

Decomposed zircon is restricted to shock stage IV impact melt particles. The low-temperature and low-pressure  $ZrO_2$  polymorph baddeleyite is generally present in decomposed zircon, although it is not a stable high-temperature or high-pressure polymorph. We found possible relics of an orthorhombic II high-pressure polymorph of  $ZrO_2$  that is the only quenchable high pressure polymorph of  $ZrO_2$ . The

decomposition texture of zircon was not found in samples of impact melt rocks from the Popigai and Chicxulub craters that indicate extensive crystallization of phenocrysts. A systematic study of zircons in a continuous impactite deposit at the Chicxulub crater suggests annealing of decomposed zircon, PDFs and amorphous zircon. Shock features in zircon at Yax-1 reflect the cooling history of impact melt components until the cessation of phenocryst crystallization. This spans the time between formation of the impact melt until deposition and cooling below temperatures of  $\sim 600$ – $680$  °C.

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