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Mineralogical and geochemical aspects of impact craters

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ABSTRACT

The importance of impact cratering on terrestrial planets is obvious from the abundance of craters on their surfaces. On Earth, active geological processes rapidly obliterate the cratering record. To date only about 170 impact structures have been recognized on the Earth's surface. Mineralogical, petrographic, and geochemical criteria are used to identify the impact origin of such structures or related ejecta layers. The two most important criteria are the presence of shock metamorphic effects in mineral and rock inclusions in breccias and melt rocks, as well as the demonstration, by geochemical techniques, that these rocks contain a minor extraterrestrial component. There is a variety of macroscopic and microscopic shock metamorphic effects. The most important ones include the presence of planar deformation features in rock-forming minerals, high-pressure polymorphs (e.g. of coesite and stishovite from quartz, or diamond from graphite), diaplectic glass, and rock and mineral melts. These features have been studied by traditional methods involving the petrographic microscope, and more recently with a variety of instrumental techniques, including transmission electron microscopy, Raman spectroscopy, cathodoluminescence imaging and spectroscopy, and high-resolution X-ray computed tomography. Geochemical methods to detect an extraterrestrial component include measurements of the concentrations of siderophile elements, mainly of the platinum-group elements (PGEs), and, more recently, chromium and osmium isotopic studies. The latter two methods can provide confirmation that these elements are actually of meteoritic origin. The Cr isotopic method is also capable of providing information on the meteorite type. In impact studies there is now a trend towards the use of interdisciplinary and multi-technique approaches to solve open questions.

KEYWORDS: impact structures, craters, shock metamorphism, planar deformation features, high pressure polymorphs, geochemistry of extraterrestrial material

Introduction and history of impact cratering

TODAY, impact cratering is recognized as a dominant (if not the most important) surface-modifying process in the planetary system. During the last few decades, planetary scientists and astronomers have demonstrated that our moon, Mercury, Venus, Mars, the asteroids and the moons of the outer gas planets are all covered (some surfaces to saturation) with meteorite impact craters. However, only recently has this observation become accepted among astronomers and geologists, because up to the first third of the 20th century, it was commonly accepted that all lunar craters are of volcanic origin (and at that time, the presence of craters on planetary bodies other than the moon had not yet been established). Their origin had been discussed since 1610, when Galileo Galilei discovered the presence of craters on the moon. Geologists paid no attention to the moon for the following centuries, so that the discussion of lunar craters was left to the astronomers. One of the earliest researchers to speculate about the origin of lunar craters was Robert Hooke in 1665, who came up with two alternatives. First, he dropped solid objects into a mixture of clay and water and found that these experiments resulted in crater-like features. However, he rejected the possibility that the lunar craters could have formed by such 'impact' processes, because it was not clear from "whence those bodies should come", as the interplanetary

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space was, at that time, considered to be empty. After all, Hooke performed his experiments 135 years before the first asteroid, Ceres, was discovered by Piazzi in Palermo. Thus, he preferred a second hypothesis, in which, from experiments with 'boiled alabaster', he concluded that the lunar craters formed by some kind of gas – rejecting a perfectly correct explanation because the 'boundary conditions' were missing.

The 18th century was dominated by the volcanic theory, as expressed by, e.g. Herschel, Schröter, and Beer and Mädler. In 1787, the astronomer William Herschel (1738–1822), the discoverer of Uranus, claimed to have observed a volcanic eruption on the Moon. Conversely, the slightly eccentric German astronomer Franz von Paula Gruithuisen (1774–1852) was a strong advocate of the impact hypothesis, but his position was not taken too seriously, as a few years earlier he had announced that through his telescope he had seen populated cities on the Moon, with cows grazing on lunar meadows, and a star-shaped temple.

In the 19th century, not much progress was made. In the early 1870s, two important books on the moon were published, both of which were titled *The Moon*. The more influential one was by Nasmyth and Carpenter (1874), in which they recreated lunar features in plaster casts after visual observations and photographed these models under low-angle illumination, resulting in spectacular and somewhat exaggerated lunar landscapes. Nasmyth and Carpenter were firm believers in the volcanic theory for the formation of lunar craters, and cleverly explained even the formation of central peaks. In contrast, the author of the other book, Proctor (1873), rejected any resemblance of lunar features with terrestrial analogues and seriously advocated the impact theory for the formation of lunar craters. At the end of the 19th century, in 1892, Groove Karl Gilbert, chief geologist of the US Geological Survey, concluded – partly based on experiments made in his hotel room during a lecture tour – that the formation of lunar craters can be best explained by the impact theory. In contrast, he rejected the hypothesis that Meteor Crater in Arizona was formed by impact. This is odd because fragments of iron meteorites had actually been found around this crater.

Real progress was only made in the first decades of the 20th century, when the mining engineer Daniel Moreau Barringer (1860–1929) studied the 'Coon Butte' or 'Crater Mountain' structure (as the 'Meteor Crater' was then called) in central Arizona. Despite the opinion of several leading geologists (including Gilbert) that this structure was of volcanic origin, and that the presence of the meteorite fragments was only a coincidence, Barringer was convinced that this was an impact crater. His work laid the foundations for a wider acceptance of the existence of impact craters on Earth. Around that time several astronomers and physicists also provided the theoretical framework for our understanding of the formation of impact craters. Until then researchers thought that bolides hitting the surface at angles different from vertical would create elliptical craters, in obvious contradiction to what is observed on the moon, and also that the diameter of a bolide would be one third to half of the crater diameter. In fact, even Barringer was of that opinion, which was the reason for his commercial interest in Meteor Crater – he anticipated finding an iron meteorite (full of precious metals!) several hundred meters in diameter below the crater floor. Finally, theoretical studies around the 1920s demonstrated that due to the enormous velocity with which large meteorites (asteroids, comets) hit planetary surfaces, only very small bodies are necessary to crate significantly larger craters, that in terms of physics, impact crater formation is similar to the formation of an explosion crater, and that resulting craters are almost always circular. For example, an object of only ~30–40 m in diameter was responsible for the formation of the 1.2 km diameter Meteor Crater. However, in terms of lunar crater studies, this just meant that the impact hypothesis was discussed as a possible alternative to the still-dominant volcanic theory. As late as 1965, just four years before the first samples were brought back from the moon, astronomers and geologists from 'vulcanist' and 'impact theorist' camps still held major debates and heated discussions. Further details on the history of impact crater studies can be found in the books by Hoyt (1987) and Mark (1987), and the review papers by Schultz (1998) and Koeberl (2001*a*).

The idea that an extraterrestrial object might have influenced the geological and biological evolution of the Earth was not even seriously considered. This might explain the mixture of disbelief, rejection and ridicule with which the suggestion was greeted that an asteroid or comet impact wiped out the dinosaurs and other species at the end of the Cretaceous (Alvarez *et al*., 1980).

It was the debate that followed this suggestion, which, over the past 20 years, finally led to a more general realization that impact cratering is an important process on the Earth as well, and not only on the other planetary bodies of the solar system. In a historical survey of the debates related to the cause of the mass extinctions at Cretaceous-Tertiary (K-T) boundary, Glen (1994) found that "those scientists who were very narrowly focused in their studies... were less likely to embrace any part of the impact hypothesis" and that "resistance to the [impact] hypothesis seemed inverse to familiarity with impacting studies." For the last few decades, planetary scientists, astronomers, and meteoriticists, who work with the products of impact cratering, have grown to accept impact cratering as a normal geological phenomenon, whereas "another group, the paleontologists, is confounded by what appears to be an *ad hoc* theory about a non-existent phenomenon" (Raup, in Glen, 1994, p. 147). Details on K-T boundary research can be found, for example, in a series of conference proceedings (Silver and Schultz, 1982; Sharpton and Ward, 1990; Ryder *et al*., 1996; Koeberl and MacLeod, 2002), but see also references in Smit (1999).

Mineralogy and geochemistry have been essential in providing the crucial evidence (in the form of shocked minerals and geochemical signatures of extraterrestrial contamination) that finally established impact cratering as a natural geological process on Earth. In the present review, I summarize the evidence, from mineralogical, geochemical and related techniques, concerning impact cratering.

Impact craters: general considerations, formation and recognition

Impact cratering is a high-energy event that occurs at more or less irregular intervals (although over long periods of time, an average cratering rate can be established). Part of the problem regarding recognition of the remnants of impact events is the fact that terrestrial processes (weathering, plate tectonics, etc.) either cover or erase the surface expression of impact structures on Earth. Many impact structures have been covered by younger (i.e. post-impact) sediments and are not visible on the surface. Others have been destroyed by erosion. In some cases, the ejecta have been found far from any possible impact structure. The study of these ejecta led, in turn, to the discovery of some impact craters (see below).

An aspect of impact cratering that may be underestimated is the influence of impacts on the geological and biological evolution of our own planet. Considering the flux of asteroids and comets as inferred from, for example, the lunar cratering record, we know that numerous subsurface or partly eroded impact craters of various sizes remain to be discovered on the Earth. Astronomers have a fairly good understanding of the rate with which asteroids and comets strike the earth (e.g. Shoemaker *et al*., 1990). For example, Earth-crossing asteroids with diameters $\geqslant 1$ km collide with the earth at a frequency of about four impacts per million years (Shoemaker *et al*., 1990), and each such impact forms a crater $\geqslant 10$ km in diameter. Impactors ~2 km in diameter collide with the Earth about once or twice every million years. Impacts of earth-orbit crossing asteroids dominate the formation of craters on Earth that are <30 km in diameter, while comet impacts probably form the majority of craters that are >50 km in diameter (Shoemaker *et al*., 1990). Even the impact of relatively small extraterrestrial bodies can have disastrous consequences for our civilization. There is a 1 in 10,000 chance that a large asteroid or comet 2 km in diameter (corresponding to a crater of ~25–50 km in diameter) may collide with the Earth during the next century, severely disrupting the ecosphere and annihilating a large percentage of the Earth's population (Chapman and Morrison, 1994; Lewis, 1997). A better understanding of impact structures and their formation is interesting not only for earth and planetary scientists, but also for society in general. The impact in 1994 of fragments of Comet Shoemaker-Levy 9 on Jupiter provided a demonstration that impact processes in the solar system are not as rare as one might have thought.

Therefore, before discussing the detailed mineralogical and geochemical characteristics of impact craters, it seems pertinent to give a short overview of their formation, criteria for recognition, and their general geology. From the morphological point of view, we need to distinguish between an impact 'crater', i.e. the feature that results from the impact, and an impact 'structure', which is what we observe today, i.e. long after formation and modification of the crater. On Earth we know two distinctly different morphological forms: 'simple' craters (small bowl-shaped craters) with diameters of up to

$\leqslant$2 to 4 km, and 'complex' craters, which are larger and have diameters of $\geqslant$2 to 4 km (the exact changeover diameter between simple and complex crater depends on the composition of the target). Complex craters are characterized by a peak or peak ring that consists of rocks that are uplifted from greater depth and which would not have been exposed on the surface without the impact. The stratigraphic uplift amounts to ~0.1 of the crater diameter (e.g. Melosh 1989). Craters of both types have an outer rim and are filled by a mixture of fallback ejecta and material slumped in from the walls and crater rim during the early phases of formation. Such crater infill may include brecciated and/or fractured rocks, and impact melt rocks. Fresh simple craters have an apparent depth (measured from the crater rim to present-day crater floor) that is about one third of the crater diameter, whereas the value for complex craters is closer to one sixth. On Earth all small craters (0.5–10 km diameter) are relatively young, because erosional processes obliterate them within a few million years, causing a severe deficit of such small craters. Details on crater morphology are given in Melosh (1989).

The formation of a crater by hypervelocity impact is – not only in geological terms – a very rapid process that is customarily divided into three stages: (1) contact/compression; (2) excavation; and (3) post-impact crater modification. For more detailed discussions of the physical principles of impact crater formation, the interested reader is referred to the literature (e.g. Melosh, 1989, and references therein). Here I can give only a brief overview. The most important aspect of impact cratering concerns the release of large amounts of kinetic energy (equal to $\frac{1}{2}mv^2$, m = mass, v = velocity) when an extraterrestrial body hits the surface of the Earth with cosmic velocities (ranging from ~11 to 72 km/s). The physical processes that govern the formation of an impact crater are the result of the extremely large amounts of energy that are liberated almost instantaneously when the projectile hits the ground. For example, a meteorite with a diameter of 250 m has a kinetic energy that is roughly equivalent to ~1000 megatons of TNT, which would lead to the formation of a crater ~5 km in diameter. There is a difference between the behaviour of a stony impactor and an iron one. Due to the difference in mechanical strength, smaller iron meteorites can reach the ground intact, in contrast to stony meteorites, which may undergo catastrophic disintegration in the atmosphere. The impact energy can be compared to that of 'normal' terrestrial processes, such as volcanic eruptions or earthquakes. During a small impact event, which may lead to craters of 5–10 km in diameter, about 10^{24-25} ergs (10^{17-18} J) are released, comparable to ~6×10^{23} ergs (6×10^{16} J) that were released over several months during the 1980 eruption of Mount St. Helens (see French, 1998). In the case of an impact, the kinetic energy is concentrated more or less at a point on the Earth's surface, leading to an enormous local energy increase.

The formation of an impact crater can be summarized as follows: First, a relatively small extraterrestrial body, travelling at a velocity of several tens of kilometers per second, hits the surface; this marks the beginning of the contact and compression stage. Almost immediately, a small amount of material is ejected from the impact site during a process called jetting with velocities that can approach about one half of the impact velocity. The jetted material is strongly contaminated with projectile material. When the projectile hits the surface, a shock wave propagates hemispherically into the ground. Because the pressures in the shock waves are so high, the release of the pressure (decompression) results in almost instantaneous melting and vaporization of the projectile – and of large amounts of target rocks. Results of the interaction of the shock wave with matter can be observed in various forms of shocked minerals and rocks, all of which originate during the contact (or compression) stage, which only lasts up to a few seconds even for large impacts. After the passage of the shock wave, the high pressure is released by a so-called rarefaction wave (also called release wave), which follows the shock front. The rarefaction wave is a pressure wave, not a shock wave, and travels at the speed of sound in the shocked material. The rarefaction wave leads to the creation of a mass flow that opens up the crater, marking the beginning of the excavation phase. Important changes in the rocks and minerals occur upon decompression, when the material follows a release adiabat in a pressure versus specific volume diagram. Excess heat appears in the decompressed material, which may result in phase changes (e.g. melting or vaporization).

The actual crater is excavated during this stage. Complex interactions between the shock wave(s) and the target, as well as the release wave(s), lead to an excavation flow. In the upper layers of the target, material moves mainly upwards and out, whereas in lower levels material moves mainly down and outwards, which results in a bowl-shaped depression, the 'transient cavity'. This cavity grows in size as long as the shock and release waves are energetic enough to excavate material from the impact location. At this point a note of caution is necessary. For a crater ~200 km in diameter, the depth of the transient cavity can easily reach 60 km. However, only about one third of this is excavation, the rest is simply material that is pushed down. Thus, even the largest craters known on Earth have not resulted in excavation of mantle material, and impact-induced volcanism has been called "a geological myth" by Melosh (2001). Afterwards, gravity and rock-mechanical effects lead to a collapse of the steep and unstable rims of the transient cavity, widening and filling of the crater. Compared to the contact stage, the excavation stage takes longer, but still only up to a minute or two even in large craters >200 km in diameter. Details on the physics and mechanics of the formation of impact craters can be found in the book by Melosh (1989).

Important witnesses for the characteristics of the impact process are the affected rocks. As mentioned above, crater structures are filled with melted, shocked and brecciated rocks. Some of these are *in situ*, but others will have been transported, in some cases considerable distances from the source crater. The latter are called ejecta. Some of that material can fall back directly into the crater, and most of the ejecta end up close to the crater (<5 crater radii; these are called 'proximal' ejecta), but a small fraction may travel much greater distances and are then called 'distal' ejecta. The recent reviews by Montanari and Koeberl (2000) and Koeberl (2001*b*) contain more detailed information on impact ejecta.

This brings us to the topic of how to recognize an impact crater. On the Moon and other planetary bodies that lack an appreciable atmosphere, impact craters can commonly be recognized from morphological characteristics, but on Earth complications arise as a consequence of the obliteration, deformation, or burial of impact craters. This problem made it necessary to develop diagnostic criteria for the identification and confirmation of impact structures on Earth (see also French, 1998). The most important of these characteristics are: (1) crater morphology; (2) geophysical anomalies; (3) evidence for shock metamorphism; and (4) the presence of meteorites or geochemical evidence for traces of the meteoritic projectile. Morphological and geophysical observations are important in providing supplementary (or initial) information. Geological structures with a circular outline in locations with no other obvious mechanism for producing near-circular features may be of impact origin and at least deserve further attention. Geophysical methods are also useful in identifying promising structures for further studies, especially in the case of subsurface features. In complex craters the central uplift usually consists of dense basement rocks and usually contains severely shocked material. This uplift is often more resistant to erosion than the rest of the crater, and thus, in old eroded structures the central uplift may be the only remnant of the crater that can be identified. Geophysical characteristics of impact craters include gravity, magnetic properties, reflection and refraction seismics, electrical resistivity, and others (see Grieve and Pilkington, 1996, for a review).

Of the criteria mentioned above, only the presence of diagnostic shock metamorphic effects and, in some cases, the discovery of meteorites, or traces thereof, are generally accepted to provide unambiguous evidence for an impact origin. Shock deformation can be expressed in macroscopic form (shatter cones) or in microscopic form (see below). The same two criteria apply to distal impact ejecta layers and allow us to confirm that material found in such layers originated in an impact event at a possibly still unknown location. So far about 170 impact structures have been identified on Earth based on these criteria.

Impactites (breccias, melt rocks)

For the nomenclature of impactites there are some well-established and widely accepted (although not internationally standardized) classification criteria (e.g. Stöffler *et al*., 1979; Stöffler and Grieve, 1994*a*,*b*; French, 1998). Some authors prefer a terminology that is specific to the particular crater they are studying, but such local terms make it very difficult to compare rock units from different impact structures. A possible shortcoming of the general impactite terminology may be the lack of genetic information, for example, with regard to the possibility that more than one type of suevitic or fragmental impact breccia may have been deposited within the crater, perhaps by different processes, such as atmospheric fall-out, or base surge deposition.

Nevertheless, I follow Stöffler and Grieve (1994*b*) and French (1998) to define the most important impact formations (see also Montanari and Koeberl, 2000, for a more detailed discussion). An 'impactite' is a collective term for all rocks affected by (an) impact(s) resulting from collision(s) of planetary bodies. The classification scheme for impactites uses criteria that combine: (1) lithological components, texture, and degree of shock metamorphism; and (2) mode of occurrence (in- or outside the crater). In terms of location, we distinguish between parautochthonous rocks beneath and allochthonous (or allogenic) rocks that fill the crater (crater-fill units, e.g. breccias and melt rocks) and also occur as ejecta around the crater. French (1998) distinguishes four locations in and around an impact structure, which are, with their associated rock units: (1) sub-crater (parautochthonous rocks, cross-cutting allogenic units, pseudotachylite); (2) crater interior (allogenic crater-fill deposits: lithic [fragmental] breccias, suevitic breccias, impact melt breccias); (3) crater rim region (proximal ejecta deposits); and (4) distal ejecta. Figure 1 shows schematically the distribution of the most important impact-related rocks in a hypothetical impact crater.

Parautochthonous rocks may include target rocks that were subjected to shock metamorphism but remained in place, as well as impactites (e.g. monomict fragmental impact breccias that remained *in situ*, but were internally brecciated, and where breccia clasts were subjected to small-scale movements or rotation). Another breccia type, 'pseudotachylite', a friction melt, has been reported from sub-crater basement, in the form of small veins and dykes hardly ever exceeding a few cm in width. Only in very large impact structures (e.g. Sudbury, Canada, or Vredefort, South Africa) have large amounts of such breccia been observed. Pseudotachylite needs to be distinguished from other dyke breccias in crater floor locations (including impact melt breccia, fragmental, and suevitic breccia injections, or clastic breccias, such as cataclasites, or even pre- or post-impact tectonically-produced pseudotachylites; see Reimold, 1995, 1998).

The crater fill contains a variety of breccia types. 'Fragmental impact breccia' is a "monomict or polymict impact breccia with clastic matrix containing shocked and unshocked mineral and lithic clasts, but lacking cogenetic impact melt particles" (Stöffler and Grieve, 1994*b*). These rocks have also been termed "lithic breccia" (French, 1998). 'Impact melt breccia' was defined by Stöffler and Grieve (1994*b*) as an "impact melt rock containing lithic and mineral clasts displaying variable degrees of shock metamorphism in a crystalline, semihyaline or hyaline matrix (crystalline or glassy impact melt breccias)" (with an 'impact melt rock' being a "crystalline, semihyaline or hyaline rock solidified from impact melt"). Suevite (or suevitic breccia) is defined as a "polymict breccia with clastic matrix containing lithic and mineral clasts in various stages of shock metamorphism including cogenetic impact melt particles which are in a glassy or crystallized state". Figure 2 shows a suevite from the Ries crater in Germany. The distribution of the rock types is a function of their formation and the order in which they formed. For example, lithic breccias can occur not

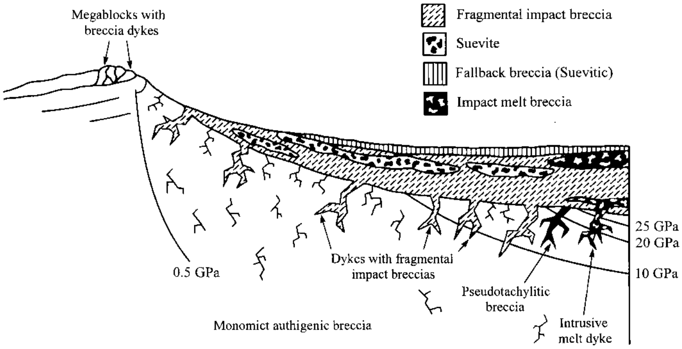

FIG. 1. Schematic cross-section through half of a hypothetical impact crater, showing the distribution of most of the important impact-derived rock formations.

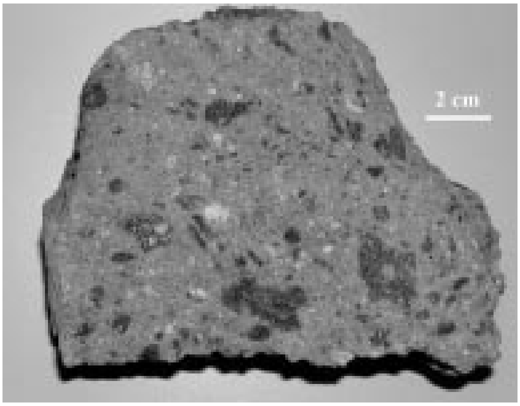

FIG. 2. Suevitic (polymict glass-bearing) impact breccia from the Ries crater, southern Germany. The dark frothy inclusions are impact glass.

only inside, but also outside a crater. For the identification of meteorite impact structures, suevites and impact melt breccias (or impact melt rocks) are the most commonly studied units. It is easy to distinguish between the two impact formations, as suevites are polymict breccias that contain inclusions of melt rock (or impact glass), i.e. they are clast-dominated ('melt fragment breccias'), and impact melt breccias have a melt matrix with a variable amount of (often shocked) rock fragment inclusions (they are matrix-dominated breccias that also have been termed 'melt-matrix breccias'). Whether these various breccia types are indeed present and/or preserved in a crater depends on factors including the size of the crater, the composition, and the porosity of the target area, and the level of erosion.

The rocks in the crater rim zone are usually subjected only to relatively low shock pressures (commonly <2 GPa), leading mostly to fracturing and brecciation, and often do not show shock-characteristic deformation. Even at craters of several kilometers in diameter, crater rim rocks that are *in situ* rarely show evidence for shock deformation. In well-preserved impact structures the area immediately outside the crater rim is covered by a sequence of different impactite deposits (e.g. French, 1998), which often allow the identification of these structures as being of impact origin. Distal ejecta can be recognized as such only if they include either shocked minerals or rock fragments, and/or meteoritic components (see Koeberl, 2001*b*, for a review).

Tektites and microtektites are natural glasses that form an important group of distal ejecta. Mainly as a result of chemical studies, it is now commonly accepted that tektites are the product of melting and quenching of terrestrial rocks during hypervelocity impact on the Earth. The chemistry of tektites is in many respects identical to the composition of upper crustal material. Tektites are currently known to occur in four 'strewn fields' of Cenozoic age on the surface of the Earth. These can be defined as geographically extended areas over which tektite material is found. They are called the North American, Central European (moldavite), Ivory Coast, and Australasian strewn fields. Tektites found within each strewn field have the same age and similar petrological, physical, and chemical properties. Relatively reliable links between craters and tektite strewn fields have been established between the Bosumtwi (Ghana), the Ries (Germany), and the Chesapeake Bay (USA) craters and the Ivory Coast, Central European, and North American fields, respectively. The source crater of the Australasian strewn field has not yet been identified. Tektites have been the subject of much study, but their discussion is beyond the scope of the present review. For details on tektites see the reviews by, e.g. Koeberl (1994), Montanari and Koeberl (2000), and Koeberl (2001*b*).

Shock metamorphism

In nature, shock metamorphic effects are uniquely characteristic of shock levels associated with hypervelocity impact. The response of materials to shock has been the subject of study over much of the second half of the 20th century, in part stimulated by military research. Controlled shock-wave experiments, which allow the collection of shocked samples for further studies, using various techniques, have led to a good understanding of the conditions for the formation of shock metamorphic products and a pressure-temperature calibration of the effects of shock pressures up to ~100 GPa (see e.g. French and Short, 1968; Stöffler, 1972, 1974; Stöffler and Langenhorst, 1994; Huffman and Reimold, 1996; Langenhorst and Deutsch, 1998; and references therein). Shock metamorphic effects are best studied in the various breccia types that are found within and around the crater structure (see above). During impact, shock pressures of $\geqslant 100$ GPa and temperatures $\geqslant 3000$°C are produced in large volumes of target rock. These conditions are significantly different from those of endogenic metamorphism of crustal rocks, with maximum temperatures of ~1200°C and pressures usually of <2 GPa (Fig. 3). Shock compression is not a thermodynamically reversible process, and most of the structural and phase changes in minerals and rocks are uniquely characteristic of the high pressures (5–>50 GPa) and extreme strain rates (10^6–10^8 s^{-1}) associated with impact. The products of static compression, as well as those of volcanic or tectonic processes, differ from those of shock metamorphism, because of lower peak pressures and strain rates that are different by many orders of magnitude. The descriptions in this chapter follow in part the review by Montanari and Koeberl (2000).

A wide variety of shock metamorphic effects has been identified, with the most common ones listed in Table 1. The best diagnostic indicators for shock metamorphism are features that can be studied easily using the polarizing microscope. They include planar microdeformation features, optical mosaicism, changes in refractive index, birefringence, and optical axis angle, isotropization (e.g. formation of diaplectic glasses), and phase changes (high pressure phases; melting). Kink bands (mainly in micas) have also been described as a result of shock metamorphism, but can also be the result of normal tectonic deformation.

Shatter cones

These features have often been described as the only good macroscopic indicator of impact-generated deformation, and a variety of structures have been proposed to be of impact origin on the basis of shatter-cone occurrences. Shatter cones form in a variety of target rocks, including crystalline igneous and metamorphic rocks, sandstones, shales and carbonates, but they are best developed in fine-grained rocks, such as limestone. In general, shatter cones are cones with regular thin grooves (striae) that radiate from the top (the apex) of a cone. An example is shown in Fig. 4. They can range in size from <1 cm to >1 m. Shatter cones occur mostly in the central uplift and in outer and lower parts of a crater and may be preserved even if a structure is deeply eroded. Unfortunately, conclusive criteria for the recognition of 'true' shatter cones have not yet been defined, and it is easy to confuse them with concussion features, pressure-solution features (cone-in-cone structure), or abraded or otherwise striated features. The formation mechanism of shatter cones is poorly understood. It seems that although the shatter cones themselves form at fairly low shock pressures, localized melting on shatter cone surfaces requires locally higher pressures and/or temperatures. The apices of shatter cones have also been used, after graphical

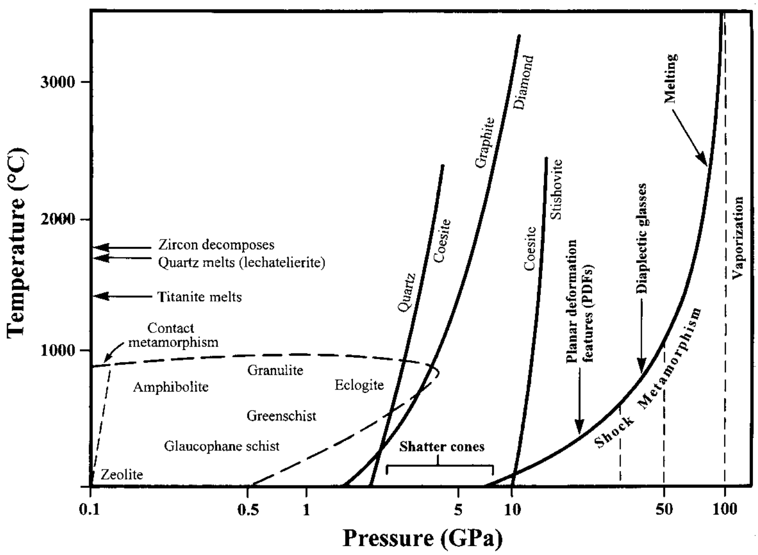

FIG. 3. Comparison of the conditions for endogenic metamorphism and shock metamorphism in a pressure-temperature plot. Also indicated are the onset pressures of various irreversible structural changes in the rocks due to shock metamorphism. The curve on the right shows the relation between pressure and post-shock temperature for shock metamorphism of granitic rocks (after French, 1998, and Montanari and Koeberl, 2000).

TABLE 1. Characteristics of shock deformation features in rocks and minerals.

Pressure (GPa)	Features	Target characteristics	Feature characteristics
2–45	Shatter cones	Best developed in homogeneous fine-grained, massive rocks.	Conical fracture surfaces with subordinate striations radiating from a focal point.
5–45	Planar fractures and Planar deformation features (PDFs)	Greatest abundance in crystalline rocks; found in many rock-forming minerals; e.g. quartz, feldspar, olivine and zircon.	PDFs: Sets of extremely straight, sharply-defined parallel lamellae; may occur in multiple sets with specific crystallographic orientations.
30–40	Diaplectic glass	Most important in quartz and feldspar (e.g. maskelynite from plagioclase).	Isotropization through solid-state transformation under preservation of crystal habit as well as primary defects and sometimes planar features. Index of refraction lower than in corresponding crystal but higher than in fusion glass.
15–50	High-pressure polymorphs	Quartz polymorphs most common: coesite, stishovite; but also ringwoodite from olivine, and others.	Recognizable by crystal parameters, confirmed usually with XRD or NMR; abundance influenced by post-shock temperature and shock duration; stishovite is temperature-labile.
>15	Impact diamonds	From carbon (graphite) present in target rocks; rare.	Cubic (hexagonal?) form; usually very small but occasionally up to mm size; inherits graphite crystal shape.
45→70	Mineral melts	Rock-forming minerals (e.g. lechatelierite from quartz).	Impact melts are either glassy (fusion glasses) or crystalline; of macroscopically homogeneous, but microscopically often heterogeneous composition.

XRD = X-ray diffraction; NMR= nuclear magnetic resonance; PDF = planar deformation features
Table after Montanari and Koeberl (2000)

restoration to their original horizontal preimpact position, to reconstruct the source of the shock wave (e.g. see French, 1998, pp. 38–40), but this method has yielded conflicting results due to multiple orientations of shatter cones within one rock. Nevertheless, shatter cones can serve as potential macroscopic shock indicators.

Mosaicism

This shock-characteristic feature has been observed in a number of rock-forming minerals and appears as an irregular mottled optical extinction pattern, which is distinctly different from the undulatory extinction that, for example, occurs in tectonically deformed quartz. Mosaicism can be measured in the optical microscope by determining the scatter of optical axes in different regions of crystals showing

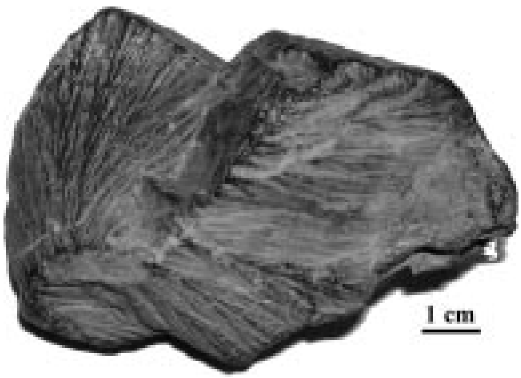

FIG. 4. Shatter cone in fine-grained carbonate rock from the Haughton impact structure, Devon Island, Canada. At least two cones are visible in this view.

mosaicism. Mosaicism can be semiquantitatively defined by X-ray diffraction study of the asterism of single crystal grains, where it shows up as a characteristic increase (with increasing shock pressure) of the width of individual lattice diffraction spots in diffraction patterns. Highly-shocked quartz crystals show a diffraction pattern that becomes similar to a powder pattern, because of shock-induced polycrystallinity. Many shocked quartz grains that show planar microstructures also show mosaicism. In addition, it should be noted that the crystal lattice of shocked quartz shows expansion above shock pressures of 25 GPa, leading to an expansion of the cell volume by $\leqslant 3\%$ (Langenhorst, 1994).

Planar microstructures

These are the most characteristic expressions of shock metamorphism and occur as planar fractures (PFs) and planar deformation features (PDFs). The characteristics of these two features for quartz are summarized in Table 2. As mentioned above, the presence of PDFs in rock-forming minerals (e.g. quartz, feldspar or olivine) provides diagnostic evidence for shock deformation, and, thus, for the impact origin of a geological structure or ejecta layer (see e.g. French and Short, 1968; Stöffler, 1972, 1974; Stöffler and Langenhorst, 1994; Huffman and Reimold, 1996; Grieve *et al*., 1996; French, 1998; Montanari and Koeberl, 2000). Planar fractures, in contrast to irregular, non-planar fractures, are thin fissures, spaced ~20 µm or more apart, which are parallel to rational crystallographic planes with low Miller indices, such as (0001) or {101} in quartz (e.g. Engelhardt and Bertsch, 1969). To the inexperienced observer, it is not always easy to distinguish 'true' PDFs from other lamellar features (fractures, fluid inclusion trails).

The most important characteristics of PDFs are that they are extremely narrow, closely and regularly spaced, completely straight, parallel, extend through the whole grain, and usually show more than one set per grain. This way they can be distinguished from features that are produced at lower strain rates, such as the tectonically formed Böhm lamellae, which are not completely straight, occur only in one set, usually consist of bands that are >10 µm wide, and are spaced at distances of >10 µm. It was demonstrated from Transmission Electron Microscopy (TEM) studies (see e.g. Goltrant *et al*., 1991) that PDFs consist of amorphous silica, i.e. they are planes of amorphous quartz that extend throughout the quartz crystal. This allows them to be preferentially etched, for example by hydrofluoric acid, emphasizing the planar deformation features (a proper etching method has been described by Gratz *et al*., 1996). The PDFs occur in planes that correspond to specific rational crystallographic orientations. In quartz, the (0001) or *c* (basal), {103} or ω, and {102} or π orientations are the most common ones (for details, see Stöffler and Langenhorst, 1994; Grieve *et al*., 1996; French *et al*., 1998). With increasing shock pressure, the distances between the planes decrease, and the PDFs become more closely spaced and more

TABLE 2. Characteristics of planar fractures and planar deformation features in quartz.

Nomenclature	1. Planar fractures (PFs) 2. Planar deformation features (PDF) 2.1 Non-decorated PDFs 2.2 Decorated
Crystallographic orientation	1. PFs: poles usually parallel to (0001) and $\{10\bar{1}1\}$ 2. PDFs: poles usually parallel to $\{10\bar{1}3\}$, $\{10\bar{1}2\}$, $\{10\bar{1}1\}$, (0001), $\{11\bar{2}2\}$, $\{11\bar{2}1\}$, $\{10\bar{1}0\}$, $\{11\bar{2}0\}$, $\{21\bar{3}1\}$, $\{51\bar{6}1\}$, etc.
Properties at scale of optical microscopy	Multiple sets of PFs or PDFs (up to 15 orientations) per grain; straight and parallel to each other Thickness of PDFs: 1–3 µm Regular spacing: >15 µm (PFs), 2–10 µm (PDFs)
Properties of PDFs at TEM scale	Two types of primary lamellae are observed: 1. Amorphous lamellae with a thickness of ~30 nm (at pressures <25 GPa) and ~200 nm (at pressure >25 GPa) 2. Brazil twin lamellae parallel to (0001)

Modified after Stöffler and Langenhorst (1994) and Montanari and Koeberl (2000) homogeneously distributed over the grain, until at ~$\geqslant$35 GPa the grains show complete isotropization. Depending on the peak pressure, PDFs are observed in ~2 to 10 orientations per grain. Figure 5 shows two examples of multiple sets of PDFs in quartz from an impact structure. To confirm the presence of PDFs, it is necessary to measure their crystallographic orientations by using either a universal stage (Emmons, 1943) or a spindle stage (Medenbach, 1985), or to characterize them by TEM (see e.g. Goltrant *et al*., 1991; Leroux *et al*., 1994).

Because PDFs are well developed in quartz (Stöffler and Langenhorst, 1994), and because their crystallographic orientations are easy to measure in this mineral, most studies report only shock features in quartz. However, other rock-forming minerals, as well as accessory minerals, such as zircon (e.g. Bohor *et al*., 1993; Leroux *et al*., 1999), develop PDFs as well (see also Stöffler, 1972, 1974). The relative frequencies of the crystallographic orientations of PDFs can be used to calibrate shock pressure regimes. Such studies can be done by measuring the angles between the *c* axis and a set of PDFs in individual quartz grains in a thin-section with a universal stage (see Montanari and Koeberl, 2000, chapter 6, for techniques). Figure 6 shows an example of a histogram of PDF orientations in quartz grains from suevitic breccia from the Bosumtwi impact structure, Ghana.

Bulk optical and other properties

It has been shown that there is a decrease of the density of shocked quartz with increasing shock pressure (e.g. Stöffler and Langenhorst, 1994). At shock pressures up to ~25 GPa, only a slight decrease is noticeable, followed by a significant drop in density between 25 and 35 GPa, depending on the direction of the shock wave relative to the *c* axis of the quartz crystal, and the pre-shock temperature (Fig. 7). Optical properties, such as the birefringence of quartz and the refractive index, also show an inverse relationship with shock pressure in the 25 to 35 GPa range. At 35 GPa, isotropization (formation of diaplectic quartz glass – see below) occurs (Fig. 8). The data also indicate that with increasing shock pressure the birefringence ($n_\omega - n_\varepsilon$) decreases.

Diaplectic glass

This isotropic phase preserves the crystal habit, original crystal defects, and, in some cases, planar features, and forms at shock pressures in excess of ~35 GPa (Table 1) without melting by solid-state transformation. Diaplectic glass has a refractive index that is slightly lower, and a density that is slightly higher, than that of synthetic quartz glass. At pressures that exceed ~50 GPa, lechatelierite, a 'normal' mineral melt, forms by fusion of quartz.

High-pressure polymorphs

Phase transitions to high-pressure polymorphs are a result of a solid state transformation process. Common minerals that form metastable high-pressure phases include (density in g/cm^3 is given in parentheses): stishovite (4.23 g/cm^3) and coesite (2.93 g/cm^3) from quartz (2.65 g/cm^3);

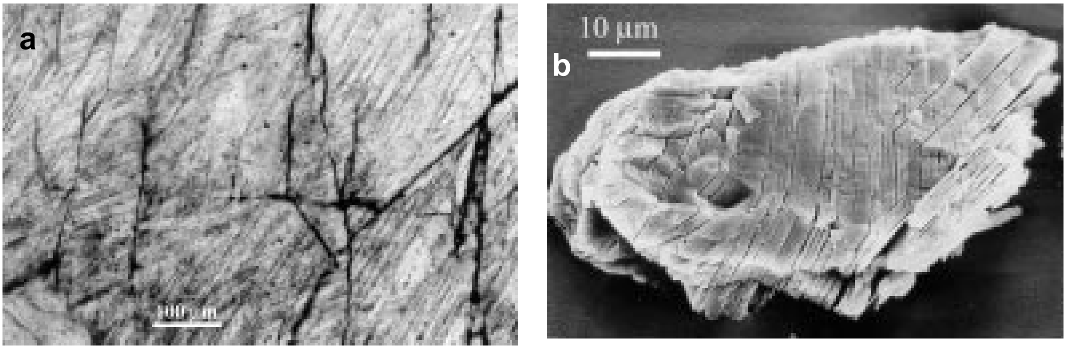

FIG. 5. Planar deformation features (PDFs) in quartz. (*a*) Typical appearance of PDFs in thin-section; three sets of PDFs in a quartz grain from a granitic breccia from the Woodleigh impact structure, Australia; crossed polarizers. (*b*) Secondary electron image of an acid-etched quartz grain from the K-T boundary layer at DSDP site 596, showing three sets of PDFs, clearly indicating that they are planes that penetrate the whole grain (image courtesy B.F. Bohor).

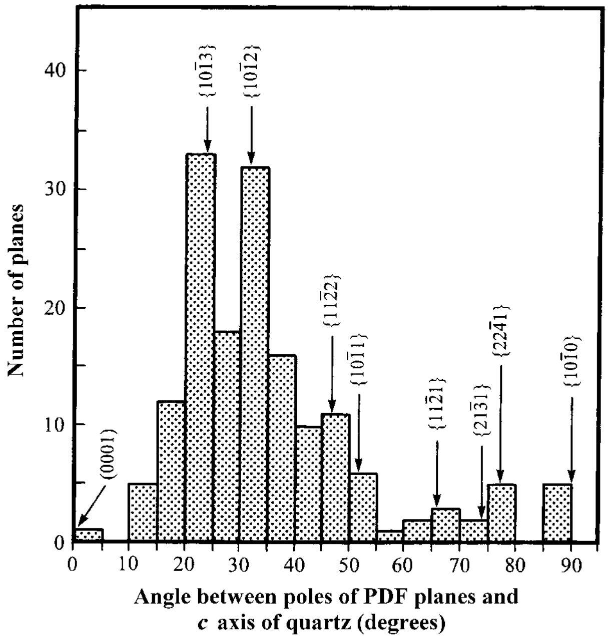

FIG. 6. Crystallographic orientations of planar deformation features (PDFs) in quartz grains from suevite inclusions, Bosumtwi impact structure, Ghana. Only data for quartz grains with two or more sets of PDFs per grain are plotted. Statistics: 162 planes in 68 grains were measured. Data from Boamah and Koeberl (in prep.).

jadeite (3.24 g/cm^3) from plagioclase (2.63–2.76 g/cm^3), and majorite (3.67 g/cm^3) from pyroxene (3.20–3.52 g/cm^3) (see e.g. Stöffler, 1972, for details). Stishovite forms at lower shock pressures than coesite, probably because stishovite forms directly during shock compression, whereas

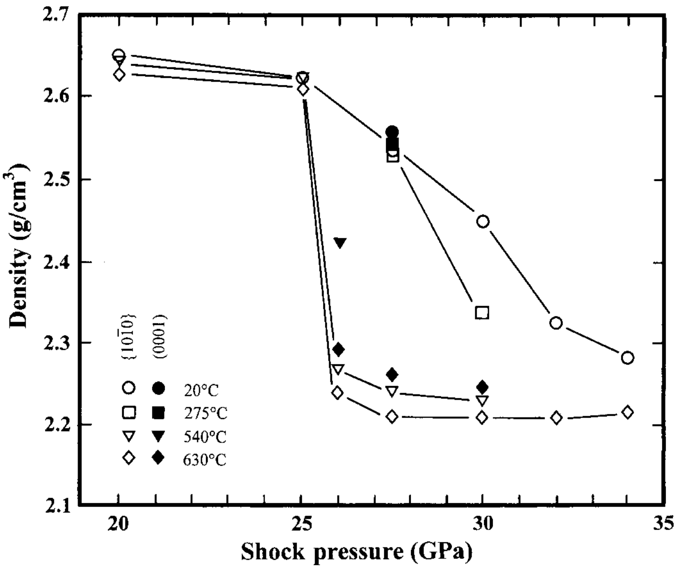

FIG. 7. Relationship between density of shocked quartz and shock pressure relative to the pre-shock temperature of the quartz, from shock experiments described by Stöffler and Langenhorst (1994).

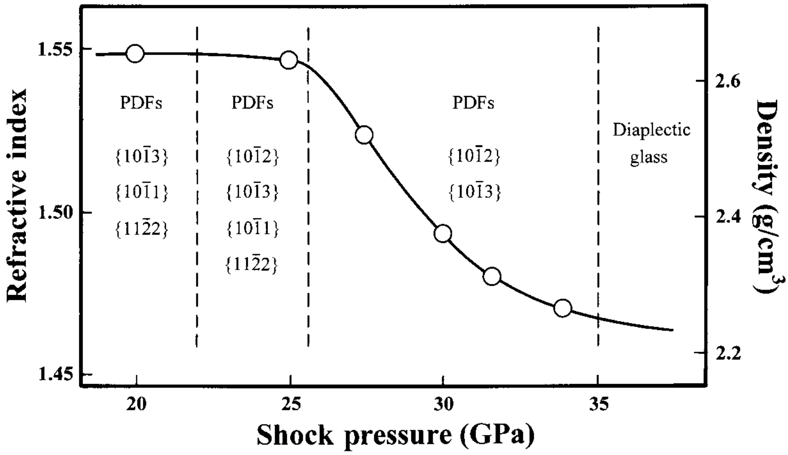

FIG. 8. Schematic relation between refractive index and density of quartz and shock pressure. Thus, the refractive index, together with the determination of the crystallographic orientations of PDFs in the quartz grains, provides information on the shock pressure (after Stöffler and Langenhorst, 1994).

coesite crystallizes during pressure release. The first time that coesite and stishovite were found in nature was in impactites, and stishovite has so far not been found in any other natural rocks. In contrast, there are rare occurrences of coesite in metamorphic rocks of ultra-high-pressure origin or in kimberlites, but it is easy to distinguish these coesites from those in impactites because they occur in significantly different mineral assemblages (see also Grieve *et al.*, 1996; Glass and Wu, 1993).

Another interesting high-pressure phase is diamond that forms from carbon in graphite- or coal-bearing target rocks (e.g. Gilmour, 1998). For example, the impact diamonds at the Popigai impact structure in Siberia commonly preserve the crystal habit of their precursor material, which is mostly hexagonal graphite within gneiss. Diamond occurs here in the form of polycrystalline aggregates with sizes of 20 µm to ~10 mm, with individual diamond microcrystals being on the order of 1 µm or less (e.g. Koeberl *et al.*, 1997). Impact-derived diamonds have also been found to be intergrown with silicon carbide (SiC) in suevites from the Ries crater in Germany (Hough *et al.*, 1995), and at the K/T boundary.

Mineral and rock melts

The passage of shock waves through rocks generates temperatures far beyond those reached even in volcanic eruptions, and at pressures exceeding ~60 GPa, rocks undergo complete (bulk) melting. The high temperatures are demonstrated by the presence of inclusions of high-temperature minerals, such as lechatelierite, which is the monomineralic quartz melt and forms from pure quartz at temperatures >1700°C, or baddeleyite, which is the thermal decomposition product of zircon, forming at a temperature of ~1900°C. Lechatelierite is not found in any other natural rock, except in fulgurites, which form by fusion of soil or sand when lightning hits the ground. Lechatelierite does not occur in any volcanic igneous rocks. Depending on the initial temperature, the location within the crater, the composition of the melt, and the speed of cooling, impact melts result in either impact glasses (if they cool quickly), or in fine-grained impact melt rocks (if they cool slowly). As mentioned above, suevitic breccias contain inclusions of glass fragments or melt clasts, whereas impact melt rocks contain clasts of shocked minerals or lithic clasts. Recently, carbonate melts have been identified (e.g. Osinski and Spray, 2001).

Because the glass undergoes slow devitrification, impact glasses are more common at young impact craters than at old impact structures. Very fine-grained recrystallization textures are often characteristic of devitrified impact glasses. Impact glasses have chemical and isotopic compositions that are very similar to those of individual target rocks or mixtures of several rock types. For example, it is possible to use the rare earth element (*REE*) distribution patterns, or the isotopic compositions, which are identical to those of the (often sedimentary or metasedimentary) target rocks, to distinguish the impact melt rocks from intrusive or volcanic rocks (e.g. Blum and Chamberlain, 1992; Blum *et al*., 1993). Impact glasses also have much lower water contents (0.001 – 0.05 wt.%) than volcanic or other natural glasses (e.g. Beran and Koeberl, 1997).

Impact melt rocks are true igneous rocks that have formed by cooling and crystallization of high-temperature silicate melts. Even though they often have textures and mineral compositions that are similar to those of volcanic igneous rocks, evidence for an impact origin can be obtained from evidence for shock metamorphism (e.g. PDFs in rock-forming minerals; lechatelierite). Geochemical studies may also provide evidence for an impact origin of a melt rock. For example, the isotopic composition is different for volcanic rocks and locally melted crustal rocks (e.g. Chaussidon and Koeberl, 1995), or the presence of a meteoritic component in such rocks can be established by geochemical analyses (see below). One important aspect of impact melts and glasses is that they often are the most suitable material for the dating of an impact structure (see the reviews by Deutsch and Schärer, 1994; Montanari and Koeberl, 2000).

Hydrothermal minerals in impact structures

These minerals are not related to shock metamorphism, but are the result of impact-generated hydrothermal systems. A recent review by Naumov (2002), based on studies of the hydrothermal mineralization in large Russian impact structures and literature data for other craters, found that the dominant hydrothermal assemblages at all craters are clay minerals (smectites, chlorites and mixed-layered smectite-chlorites), various zeolites, calcite, and pyrite; in addition, cristobalite, quartz, opal, anhydrite, gypsum, prehnite, epidote, andradite, actinolite and albite occur locally. At the Puchezh-Katunki structure (diameter 80 km), the abundant hydrothermal mineralization within the central uplift area shows distinct vertical distribution due to post-impact thermal gradients, whereas at Kara and Popigai (65 and 100 km in diameter, respectively), the hydrothermal alteration affects mainly the crater-fill impact melt rocks. In general, the hydrothermal mineralogy in impact craters is determined by the composition of the target rocks and the composition, temperature, Eh and pH of the available solutions.

Geochemistry of impactites: meteoritic components

One of the most important driving forces for impact research in the past decades has been the study of rocks from the Cretaceous-Tertiary (K-T) boundary. Alvarez *et al*. (1980) found that the concentrations of the rare platinum group elements (PGEs; Ru, Rh, Pd, Os, Ir, and Pt) and of other siderophile elements (e.g. Co, Ni) in the thin clay layer that marks the K-T boundary are considerably enriched compared to those found in normal crustal rocks. These significant enrichments (up to four orders of magnitude) and the characteristic inter-element ratios were interpreted by Alvarez *et al*. (1980) to be the result of a large asteroid or comet impact, which also caused extreme environmental stress. Shortly thereafter, Bohor *et al*. (1984) discovered the presence of shocked minerals in K-T boundary rocks and thus confirmed the connection to an impact event. This was probably the most spectacular application of geochemistry to verify the impact origin of a rock unit. The K-T boundary case involved distal ejecta, but the same method can be applied to breccias or melt rocks. During impact, a small amount of the finely dispersed meteoritic melt (droplets) or vapour is mixed with a much larger quantity of target rock vapour and melt, and this mixture later forms impact melt rocks, melt breccias, or impact glass. In most cases, the contribution of meteoritic matter to these impactite lithologies is very small (commonly <<1%), leading to only slight chemical changes in the resulting impactites.

As discussed by, for example, Koeberl (1998), the detection of such small amounts of meteoritic matter within the normal upper crustal compositional signature of the target rocks is extremely difficult. Only elements that have high abundances in meteorites, but low ones in terrestrial crustal rocks are useful – as were the siderophile platinum-group elements in the case of the K-T boundary layer. It is also necessary to take into account that different meteorite groups and types have different compositions. Elevated siderophile element contents in impact melts, compared to target rock abundances, can be indicative of the presence of either a chondritic or an iron meteoritic component. Achondritic projectiles (stony meteorites that underwent magmatic differentiation) are much more difficult to discern, because they have significantly lower abundances of the key siderophile elements. It is also necessary to sample all possible target rocks to determine the so-called indigenous component (i.e. the contribution to the siderophile element content of the impact melt rocks from the target).

Meteoritic components have been identified for just over 40 impact structures (see Koeberl, 1998, for a list), out of the more than 170 impact structures that have so far been identified on Earth. This number reflects mostly the extent to which these structures have been studied in detail, as only a few of these impact structures were first identified by finding a meteoritic component (the majority has been confirmed by the identification of shock metamorphic effects). Iridium is most often determined as a proxy for all PGEs, because it can be measured with the best detection limit of all PGEs, by neutron activation analysis (which was, for a long time, the only more or less routine method for Ir measurements at sub-ppb abundance levels in small samples). The use of PGE abundances and ratios avoids some of the ambiguities that result if only moderately siderophile elements, such as Cr, Co or Ni are used to try and demonstrate the presence of a meteoritic component (see Koeberl, 1998, for a discussion).

Recent studies of impact glasses from some small craters for which the meteorite has been partly preserved (e.g. Meteor Crater, Wabar, Wolf Creek, Henbury) have indicated that the siderophile elements are significantly and variably fractionated in their interelement ratios compared to the initial ratios in the impacting meteorite. Mittlefehldt *et al*. (1992) proposed that the siderophile element fractionations may have occurred during the early phases of the impact, while the projectile was undergoing decompression and before mixing with the target materials, as the data did not fit simple vapour fractionation. This observation complicates any attempts to directly infer projectile types of small craters from siderophile element ratios in impactites. And, indeed, the element ratios at, for example, Aouelloul or Brent do not readily conform to those of any known meteorite types, but can be interpreted in various ways. Pierazzo *et al*. (1997) calculated that there is a correlation between the amount of melt and vapour with increasing impact velocity, which may be the most important factor controlling the incorporation of a meteoritic component (the amount of which is known to vary widely between craters of similar size, and also within impact breccias and melt rocks from a single crater). Such an energy scaling relationship would not, however, explain observed fractionations within a single crater. A variety of fractionation effects have also been documented for distal ejecta at various localities around the world. For example, high PGE abundances were discovered in impact ejecta from the Acraman structure in Australia, but show deviations from chondritic patterns due to low-temperature hydrothermal alteration (e.g. Gostin *et al*., 1989; *cf*. also Colodner *et al*., 1992).

Since the late 1970s, several studies tried to determine the type or class of meteorite for the impactor from analyses of impact melt rock or glass (e.g. Morgan *et al*., 1975; Palme *et al*., 1978, 1981; Palme, 1982), usually on the basis of PGE abundances and interelement ratios. However, these attempts were not always successful, as it is difficult to distinguish among different chondrite types. Part of the problem stems from the lack of PGE data for a statistically significant number of meteorites. This situation has now improved somewhat as a result of recent efforts by McDonald *et al*. (2001) and McDonald (2002). Other problems may arise if the target rocks have high abundances of siderophile elements or if the siderophile element concentrations in the impactites are very low. In such cases, the use of the osmium and chromium isotopic systems can help to establish the presence of a meteoritic component in impact melt rocks and breccias.

The Os isotopic system

The isotope ^{187}Os (one of seven stable isotopes of Os) forms by β^--decay of ^{187}Re (half-life of 42.3±1.3 Ga). Meteorites have contents of Os that are several orders of magnitude higher than terrestrial crustal rocks. Their Re abundances are lower than the Os abundances, resulting in Re/Os ratios less than or equal to 0.1, whereas the Re/Os ratio of terrestrial crustal rocks (at much lower Re and Os abundances) is usually no less than 10. As for conventional isotope systems, the abundance of the radiogenic isotope (^{187}Os) is normalized to the abundance of a non-radiogenic isotope (^{188}Os). As a result of the high Re and low Os concentrations in old crustal rocks, their ^{187}Os/^{188}Os ratio increases rapidly with time (average upper crustal ^{187}Os/^{188}Os = 1−1.2). In contrast, meteorites have low ^{187}Os/^{188}Os ratios of ~0.11−0.18, and, as osmium is much more abundant in meteorites than Re, only small changes in the meteoritic ^{187}Os/^{188}Os ratio occur with time. The first successful application of this isotope system to impact-related materials was the measurement of the Os isotopic composition of K-T boundary clays (Luck and Turekian, 1983), but an attempt to measure the Os isotopic composition of impactites was problematic due to the low Os abundances in these rocks (Fehn *et al.*, 1986). The introduction of the negative thermal ionization mass spectrometry (NTIMS) technique (e.g. Creaser *et al.*, 1991) finally allowed the measurement of Os isotopic ratios in samples of a few grams mass containing sub-ppb amounts of Os. The first successful application of this method dealt with tektites and impact glasses from the Bosumtwi impact structure in Ghana (Koeberl and Shirey, 1993).

Because of the relatively high meteoritic Os abundances, the addition of even a small amount of meteoritic matter to the crustal target rocks leads to a significant change of the Os isotopic signature of the resulting impactites (Fig. 9). Addition of achondritic meteoritic matter requires much higher percentages of meteoritic addition due to the much lower PGE abundances in achondrites compared to chondritic and iron meteorites. A complication is that the present day $^{187}Os/^{188}Os$ ratio of mantle rocks is about 0.13, which is similar to meteoritic values, although PGE abundances in typical mantle rocks are at least two orders of magnitude lower than those in (chondritic and iron) meteorites. Due to these differences in abundance, however, the mantle contribution needs to be about one hundred times larger than a meteoritic component, and the presence of such a significant mantle component would be easily discernable from petrographic studies of the clast population in breccias, and/or from geochemical data (especially Sr and Nd isotopes) of melt rocks. Compared to data obtained from PGE elemental abundances and ratios, the Os isotope method is superior with respect to detection limit and selectivity, as discussed in detail (with several case histories) by Koeberl and Shirey (1997). The method allowed the confirmation of meteoritic components at several impact structures (e.g. Koeberl *et al.*, 1996), and has also been used to confirm the impact origin of craters (e.g. Koeberl *et al.*, 1994). A disadvantage is that the Os isotopic method does not allow the determination of the projectile type.

The Cr isotopic system

Chromium isotopic data can not only provide evidence for the presence of an extraterrestrial component in impactites, but also help to determine the meteorite type. The method is based on the determination of the relative abundances of ^{53}Cr, which is the daughter product of the extinct radionuclide ^{53}Mn (half life = 3.7 Ma). The ^{53}Cr relative abundances are measured as the deviations of the $^{53}Cr/^{52}Cr$ ratio (expressed in ε units; 1 ε is 1 part in 10^4) in a sample relative to the standard terrestrial $^{53}Cr/^{52}Cr$ ratio by high-precision thermal ioniza-

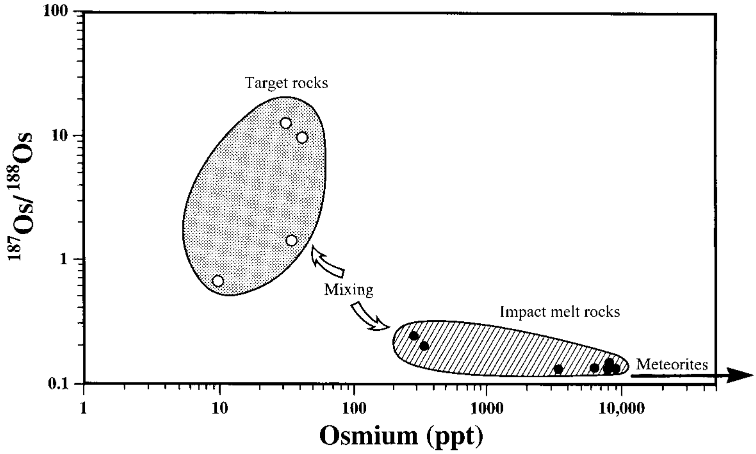

FIG. 9. Plot of Os isotope ratio *vs*. Os abundance for samples from the Morokweng impact structure, South Africa. The target rocks are characterized by low Os abundances and high $^{187}Os/^{188}Os$ ratios, whereas the opposite is true for the impact melt rocks, which clearly show the presence of a meteoritic component. After Koeberl *et al.* (2002*a*).

tion mass spectrometry. Terrestrial rocks do not show any variation in the $^{53}Cr/^{52}Cr$ ratio, because homogenization of the Earth was completed long after all primordial ^{53}Mn had decayed. In contrast, most meteorite groups analysed so far (Shukolyukov and Lugmair, 1998, 2000), such as carbonaceous, ordinary and enstatite chondrites, primitive achondrites, and other differentiated meteorites (including the SNC meteorites, which originated from Mars) show a variable excess of ^{53}Cr relative to terrestrial samples. The range for meteorites is about +0.1 to +1.3 ε, depending on the meteorite type, except for carbonaceous chondrites, which show an apparent deficit in ^{53}Cr of about −0.4 ε. These variations in Cr isotopic composition reflect heterogeneous ^{53}Mn distributions in the early solar system and early Mn/Cr fractionation in the solar nebula and in meteorite parent bodies (Lugmair and Shukolyukov, 1998). The negative ε value for carbonaceous chondrites is an artifact of using the $^{54}Cr/^{52}Cr$ ratio of the fractionation correction (Lugmair and Shukolyukov, 1998), because these meteorites carry a pre-solar ^{54}Cr component (Shukolyukov *et al*., 2000). The actual, un-normalized $^{53}Cr/^{52}Cr$ ratio is similar to that of other undifferentiated meteorites, and the apparent ^{53}Cr deficit in the carbonaceous chondrites is actually due to an excess of ^{54}Cr. However, the presence of ^{54}Cr excesses in bulk carbonaceous chondrites allows one to distinguish clearly these meteorites from the other meteorite classes.

Shukolyukov and Lugmair (1998) have used the Cr isotopic method on samples from the K-T boundary in Denmark and Spain and interpreted the data to be consistent with a carbonaceous chondritic impactor. More recently, Shukolyukov *et al*. (2000) also found evidence of a carbonaceous chondritic signal for samples from some of the Archaean spherule layers in the Barberton Mountain Land, South Africa. The origin of these spherule layers (e.g. Lowe *et al*., 1989; Kyte *et al*., 1992) has been controversial (e.g. Koeberl and Reimold, 1995), because some samples contained significantly higher PGE abundances than are found in meteorites – a clear sign of secondary processes. Shukolyukov and Lugmair (2000) reported on analyses of impact melt rocks from the East Clearwater (Canada), Lappajärvi (Finland), and Rochechouart (France) impact structures. In all three cases, the impactors were found to have had ordinary chondritic composition. In the case of East Clearwater, the new PGE data of McDonald (2002) are in agreement with this interpretation.

The Cr isotopic method thus, has the advantage over both the use of Os isotopes or PGE abundance ratios of being selective not only regarding the Cr source (terrestrial *vs*. extraterrestrial), but also regarding the meteorite type. However, the complicated and time-consuming analytical procedure is problematic. Also, a significant proportion of the Cr in an impactite, compared to the abundance in the target, has to be of extraterrestrial origin. As discussed in detail by Koeberl *et al*. (2002*a*), the detection limit of this method is a function of the Cr content in the (terrestrial) target rocks that were involved in the formation of the impact breccias or melt rocks. For example, if the average Cr concentration in the target is ~185 ppm (i.e. the average Cr concentration in the bulk continental crust), only an extraterrestrial component of >1.2% can be detected. In contrast, the Os isotopic method can detect ~10 times less abundant meteoritic components. Thus, while being more selective than the Os isotopic method, the Cr isotopic method is less sensitive.

Discussion – new developments

Mineralogical and geochemical studies have become essential in impact crater research. The confirmation of the impact origin of doubtful or new structures hinges on such studies, after geological and geophysical data have paved the way. Our understanding of shock metamorphic effects has increased significantly over the past decades, although it seems that caution needs to be applied when comparing experimentally obtained shock calibrations with natural phenomena (DeCarli *et al*., 2002). Nevertheless, the most important techniques that are used to obtain the evidence necessary to confirm the impact origin of rocks have not changed much – the time-honoured method of PDF orientation measurements by universal stage on an optical microscope is still considered the most crucial one. In fact, this technique is in trouble – in the past the universal stage was much used in petrography whereas today, most, if not all, microscope manufacturers have ceased to build these devices, and only a few people know how to use them. Unfortunately, no replacement method is in sight. The spindle stage is about as uncommon an instrument, it is less precise, more time consuming, and requires single grains, instead of the more practical thin-sections required for universal stage work. The TEM allows us to confirm unambiguously the presence of *bona fide* PDFs, but it is very expensive and time consuming, starting with the painstaking process of ion-beam thinning of sections.

There are a few techniques that are now beginning to be used for impactite studies, and time will tell whether or not they will become useful for more routine analyses. The problem with new methods is that often there is no database to assess the usefulness of the method in comparison with other techniques. There are several examples in the literature in which a new (and untested) method is used to confirm the impact origin of an unknown structure, without systematic work having been done on material from known impact structures or on experimentally shock-deformed samples. Another problem with new or unusual techniques, using uncommon or expensive equipment, is that in many cases only one or a few pilot studies are done, and no routine or systematic work follows. An example is magic-angle spinning nuclear magnetic resonance (MAS NMR), which is a very sensitive and reproducible shock pressure barometer for shocked quartz and feldspar. The width of the ^{29}Si NMR resonance peak of quartz correlates strongly and reproducibly with shock pressure between 7.5 and 22 GPa (Cygan *et al*., 1990, 1992). Unfortunately no follow-up studies or routine applications have been reported, even though this method is also very useful in detecting small amounts of high-pressure silica polymorphs (e.g. Yang *et al*., 1986). An open problem is the determination of the shock stage of carbonates, and preliminary investigations have explored the possible use of MAS NMR (Skala and Rohovec, 1998) and X-ray diffraction (e.g. Skala *et al*., 2002), but no unambiguous and reproducible shock barometric method has yet been published.

Some recent work has also been done using XANES and EXAFS from synchrotron radiation X-rays for the determination of the Fe and Al coordination numbers and Fe oxidation state of tektites and impact glasses (e.g. Giuli *et al*., 2000, 2001), indicating that these glasses formed at low pressures, but these studies require large accelerator facilities and are still at the exploration phase. Attempts have also been made to use catholuminescence (CL) imaging and spectroscopy in systematic studies of shocked quartz (Boggs *et al*., 2001) and zircon (Gucsik *et al*., 2002), with the latter study also employing micro-Raman spectroscopy to determine phase transitions and long- and short-range order of experimentally-shocked zircon. Compared to NMR or synchrotron work, CL and Raman equipment is readily available and sample preparation is easy; thus, there is a good chance that once the necessary databases are established, these methods may find routine applications in shock mineralogy and petrography. Raman spectroscopy is also a powerful technique for the study of impact-related carbon phases (e.g. El Goresy *et al*., 2001; Gilmour *et al*., 2002).

Another technique that has just recently been applied for the first time to the study of impactites is high-resolution X-ray computed tomography (HRXCT). Koeberl *et al*. (2002*b*) used this method to image the interior of suevites from the Bosumtwi and Ries craters to determine the three-dimensional distribution of clasts within the matrix of the suevites, to test this technique with respect to its suitability for the recognition of different clast types of different densities, and to determine textural characteristics of the tektite. Their results show that HRXCT allows the easy discrimination of the relatively frothy inclusions of glassy melt in the suevites, as they are darker than the matrix in the raw X-ray scans and can be traced through the whole sample (Fig. 10). Colour or grey-scale applications allow the distinction of at least four different clast types based on density differences. This method allows the determination of the 3D-distribution of the various clast populations in the impact breccia by image processing techniques, and to quantify their relative abundances, but, due to the highly specialized equipment necessary, it remains to be seen if this technique will attain routine use.

In terms of geochemistry, the most interesting new developments concern the use of a variety of isotope systems that only now, with the development of new analytical methods and instrumentation, are becoming accessible. These include the Cr and Os isotope systems (see previous section), as well as the Pt isotope system (e.g. Morgan *et al*., 2002), ion probe analyses of the stable isotope composition of distal ejecta (e.g. Chaussidon and Koeberl, 1995), and refinements in the Sr and Nd isotope techniques to analyse microtektites and clinopyroxene-bearing spherules from the two closely spaced Late Eocene impactoclastic layers to determine their source rocks (Whitehead *et al*., 2000). It is also interesting to note that Farley *et al.* (1998) found much-enhanced levels of ^{3}He coinciding with the two late Eocene impactoclastic

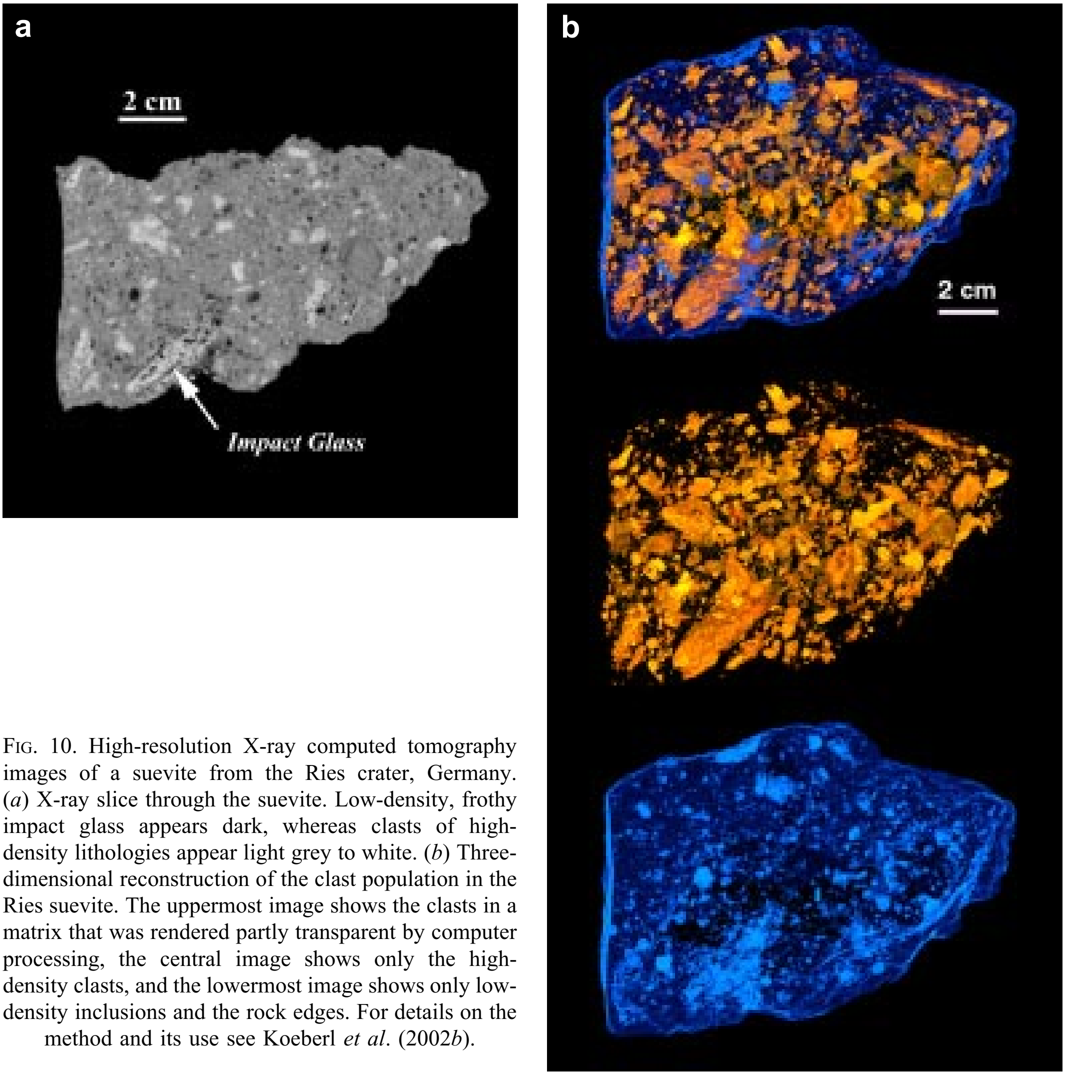

FIG. 10. High-resolution X-ray computed tomography images of a suevite from the Ries crater, Germany. (*a*) X-ray slice through the suevite. Low-density, frothy impact glass appears dark, whereas clasts of high-density lithologies appear light grey to white. (*b*) Three-dimensional reconstruction of the clast population in the Ries suevite. The uppermost image shows the clasts in a matrix that was rendered partly transparent by computer processing, the central image shows only the high-density clasts, and the lowermost image shows only low-density inclusions and the rock edges. For details on the method and its use see Koeberl *et al*. (2002*b*).

layers. This isotope is a proxy for the influx of extraterrestrial dust, and the data are interpreted to indicate enhanced comet activity in the inner solar system during the late Eocene, probably resulting in a higher impact rate than usual.

Some of the most interesting and important research will involve multidisciplinary and multi-technique approaches, as conventional studies may have reached a dead end. Some of the topics that may require a concerted effort include the occurrences of unusual spherule layers from Archaean and Precambrian rocks, mainly in Australia and South Africa. There is good evidence to conclude that these layers are the result of impact events, but none of these spherules is associated with shocked minerals, which has been suggested to be the result of impact with an oceanic target (Simonson *et al*., 1998). Some of these spherule layers show enrichments in the platinum-group elements and evidence for extraterrestrial chromium, but it is not clear why impact events in the Archaean would predominantly produce large volumes of spherules and no shocked minerals, in contrast to post-Archaean impact deposits. The question of how to identify Archaean impact deposits is becoming increasingly important (Simonson and Harnik, 2000).

Another interesting topic concerns the Permian-Triassic (P-Tr) boundary, which is associated with the largest mass extinction known in Earth history. Following the association of the K-T boundary mass extinction with a large impact event, it has been speculated that other major mass extinctions might also be related to impact events. So far the evidence in favour of such a proposal is controversial and data for the P-Tr boundary are incomplete. Some minor siderophile element anomalies were found in some P-Tr rocks, but they do not seem to have an extraterrestrial origin. Similarly controversial are reports regarding shocked quartz and other possible impact markers at the P-Tr boundary. Geochronological data indicate that the P-Tr boundary event was a very short event (e.g. Erwin *et al*., 2002; Rampino *et al*., 2002). Nevertheless, new methods will be necessary to reveal what really happened at the end of the Permian – meteorite impact or another short-time, high-energy event.

Conclusions

Mineralogical and geochemical methods have been used for many decades in the study of terrestrial meteorite impact craters. A clear step-change in the history of impact-related studies came with the realization that the K-T boundary bears unambiguous evidence for a large-scale catastrophic impact event (related to the formation of the 200 km diameter Chicxulub impact structure, Mexico). Analyses of the K-T ejecta layers led to improved detection sensitivities for impact markers, allowing identification of smaller events and the study of their effects. Distal impact ejecta layers can be used to study a possible relationship between biotic changes and impact events, because it is possible to study such a relationship in the same outcrops, whereas correlation with radiometric ages of a distant impact structure is always associated with larger errors. Investigations of impact markers yield important information regarding the physical and chemical conditions of their formation, such as temperature, pressure, oxygen fugacity and composition of the atmosphere. These data are necessary to understand the mechanisms of interaction of impact events with the environment and should ultimately lead to a better appreciation of the importance of impact events in the geological and biological evolution of the Earth. New geochemical techniques, such as the use of the Cr and Os isotopic systems, or analyses of comet-dust-derived ^{3}He in sediments, have helped to confirm or better explain several important impact events. Recent improvements in analytical methods and techniques will certainly continue to influence our understanding of the interaction between cosmic bodies and the Earth.

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