

Diamonds



Tiffany diamond, 287.42 ct, canary, from Kimberley, South Africa. PHOTO COURTESY OF TIFFANY & CO. ARCHIVES

George E. Harlow and Rondi M. Davies¹

Active research on diamond, a carbon mineral with superlative properties, extends into many realms of natural and material sciences. Extreme hardness and transparency make diamond a valuable gem and a high-pressure research tool, as well as a superabrasive. Natural formation at high pressure and resistance to weathering make diamonds our most informative messengers from Earth's mantle. A review of diamond's character and forms leads into the topics of the articles in this issue of *Elements*.

KEYWORDS: diamond, gem, high pressure, mantle, carbon

Diamond, the ultrahard cubic form of carbon, is a mineral requiring a long string of superlatives to describe its properties, its technological and commercial importance, and its roots into human culture and our physical world. Diamond is the hardest known substance, a strategic mineral critical to the market in superabrasives—over 800 million carats (160 metric tons) and about US\$10⁹ annually (Olson 2002), just for abrasive. Diamond, the king of gems, is at the heart of the most lucrative part of the gem industry, with an unmatched combination of brilliance, fire, hardness, and value (~US\$2 × 10¹⁰ annually for stones alone; Olson 2003). Natural diamonds are probably the oldest and deepest-sourced objects we will ever touch, and provide direct information about the mantle. The superlative character of diamond—linking technology, commerce, glamour, natural science, and material science—provides great impetus for ever-advancing scientific investigation. Consequently, when asked if diamond might serve as an inaugural topic for *Elements*, the answer had to be “yes.”

One of us has plowed the furrows of diamond subjects while creating a well-travelled exhibition entitled *The Nature of Diamonds*, accompanied by a book with the same name (Harlow 1998), while the other has cut her teeth studying inclusions in diamonds. Thus, we are both certified diamond junkies who find irresistible the attraction of diamond crystals, science, and personalities. And the activity relating to diamonds is abundant. Diamond is probably one of the only minerals on which several journals focus: *Diamond and Related Materials*, *Industrial Diamond Review*, *Industrie Diamanten Rundschau*, *New York Diamonds*. So, we had to restrain ourselves to invite only seven investigators or research groups to write articles on advancements in diamond-related science, with a geoscience connection of course, for this issue of *Elements*. The topics presented, however, do provide a view into the diversity and wealth of research on, and interest in, the densest form of element six.

Red chromian pyrope and green chromian diopside inclusions in a diamond octahedron from the Mir pipe, Sakha Republic, Russia (each about 0.2 mm across).

COURTESY UIGGM, SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES, NOVOSIBIRSK. PHOTO: GEORGE HARLOW

Diamond is a beautiful substance in many ways. Its simple but elegant crystal structure (FIG. 1), in which each carbon atom is bonded to four other atoms in a tetrahedral arrangement, yields a strong rigid framework. Combining this structural arrangement, which coincides with the hybrid sp^3 orbitals of carbon, with the unmatched strength of the C–C bond, explains most of diamond's properties, many of which are presented in TABLE 1.

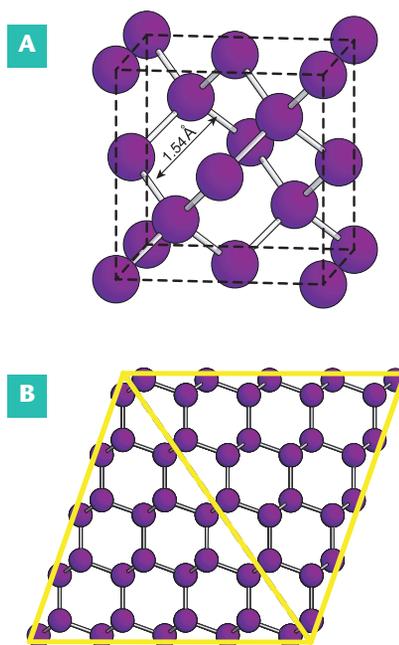


FIGURE 1 Ball and stick models of the diamond structure showing (A) the unit cell with the C–C distance indicated and (B) a projection with the boundaries of an octahedron, the archetypal “diamond” shape.

¹ American Museum of Natural History, New York, NY 10024-5192, USA
E-mail: gharlow@amnh.org; rdavies@amnh.org

TABLE 1

DIAMONDS: VITAL STATISTICS

Composition	C (carbon)
Crystallographic class	Cubic – hexoctahedral (highest of symmetries)
Space group	<i>Fd3m</i> $a = 3.57 \text{ \AA}$ (cell edge)
Common crystal forms (and indices)	Octahedron {111}, cube {100}, dodecahedron {110}, rounded variations due to etching
Twins	Spinel-law common, yielding the flat triangular “macle”
Hardness	10 on Mohs’ scale, 56–115 Knoop hardness number (GPa), 10,000 Brook’s indenter scale, octahedral face hardest, cube face softest
Moduli	Bulk modulus: ~500 GPa; Young’s modulus: ~1050 GPa
Cleavage	Excellent parallel to octahedron face {111}
Density	3.51 g cm ⁻³ (or specific gravity = 3.51)
Luster	Adamantine (the definition for this kind of luster)
Colors	Colorless, yellow, blue, green, and many others
Refractive index	2.4175 (in the yellow light of a sodium lamp)
Dispersion	Large (0.0437 – the difference in index at G and B Fraunhofer wavelengths), leading to rainbow colors on refraction
Optical transmission	Transparent over a broad range of the electromagnetic spectrum; an excellent material for optical windows
Thermal conductivity	Superb, 5 to 25 watts centimeter ⁻¹ °C ⁻¹ (at 300K); 4 times greater than copper; an excellent thermal conductor
Electrical conductivity	0 to ~100 ohm cm ⁻¹ (resistivity at 300K); an insulator

The rigid bonding leads to great hardness, incompressibility, and extraordinary thermal conductivity. Diamonds are called “ice” because of their ability to conduct heat so well; they feel icy cold because they rob heat from your diamond-touched lip. The uniform covalent bonding causes a large band gap, 5.5 eV, and makes diamond an electrical insulator and transparent over a broad portion of the electromagnetic spectrum. The dense packing of electrons yields a high refractive index (the ratio of light’s velocity in a vacuum to that in the material) of 2.42, quite remarkable for a material with such a low average atomic number. The list goes on, and the significance of these extraordinary properties will become evident in the articles in this issue of *Elements*.

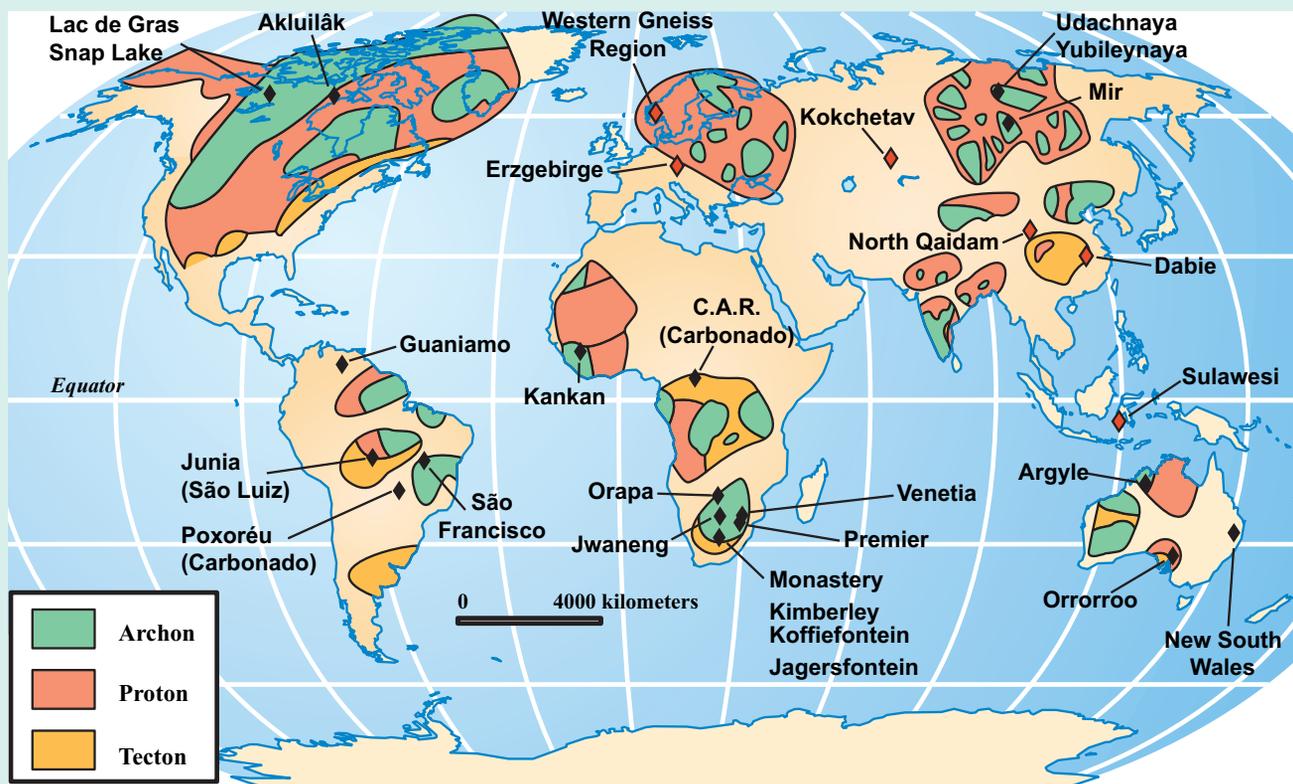
The high density of diamond (3.51 g cm⁻³) as compared to that of graphite (2.20 g cm⁻³), the other common polymorph of carbon, is a clear indication that diamond is a high-pressure mineral, formed mostly in Earth’s interior. Thus, diamond is a key indicator and recorder of events deep within our planet, in part because its extreme strength

and refractory nature permits it to survive exhumation to Earth’s surface and subsequent weathering (another aspect is the extraordinary volcanic style of kimberlites and lamproites, which act as express elevators to raise diamonds quickly from depth, but that is a different story). Moreover, inclusions captured in a diamond growing in the mantle are protected by its adamantite embrace, so diamonds have become our “space missions” to inner Earth, providing our most important samples for understanding the chemistry of the deep mantle. By extracting inclusions (yes, diamonds get busted, burned, and ground away) and analyzing them, researchers have discovered the association of diamond with peridotite and eclogite assemblages from the roots of ancient cratons. More recently, transition-zone and lower-mantle signature minerals have been identified. The contribution by Stachel, Brey, and Harris reviews the status of these, the deepest samples of Earth that we have at our finger tips. Diamonds, while essentially pure carbon, allow us to investigate their carbon source through isotopic analysis of C and the minor contained N. Cartigny presents the available isotopic data and shows how diamonds reveal the hallmarks of primitive Earth, recycled crustal sources, and crystallization processes.

Two lesser known and understood varieties of diamond are, first, natural polycrystalline diamond—carbonado and framesite—and, second, microdiamonds discovered over the last 20 years associated with metamorphic rocks. Heaney, Vicenzi, and De review the characteristics of carbonado and framesite and help unravel some of the mystery around these enigmatic materials. As a high-pressure mineral, diamond is an important indicator for recognizing portions of Earth’s crust that have been buried to ultrahigh-pressure (UHP) conditions (for crustal rocks, that is) and, more remarkably, returned to the surface with diamonds intact. Search for UHP terranes by recognizing diamond or coesite (a high-pressure form of SiO₂) has become an exciting direction in metamorphic petrology, with important implications for how the Earth works. However, only recently have studies focused on the small UHP diamonds themselves. Ogasawara reviews the UHP occurrences of diamond and the ideas behind the processes by which they are formed before focusing on the Kokchetav Massif, Kazakhstan, where the most varied and abundant microdiamonds have been found.

One of the most remarkable diamond discoveries in the last decades is that of the nanometer-sized diamonds in meteorites. Meteoritic diamonds are hardly new, since they were described in the Canyon Diablo iron meteorite in 1891 (Foote 1891). These were later interpreted as the conversion of graphite to diamond by shock metamorphism upon the meteorite’s impact with Earth. On the other hand, diamonds in the Nova Urei (Ringwood 1960; Carter et al. 1964) and Kenna (Berkley et al. 1976) ureilites formed by shock on the meteorite parent body. Searching for the most primitive materials and reservoirs of noble gases in primitive meteorites, such as carbonaceous chondrites, led Ed Anders and colleagues to seek the last moieties in meteorites that could not be dissolved by aggressive acid or base—diamond, graphite, and silicon carbide. Huss reviews the results of research on these “nanodiamonds” and their possible origin in supernovae prior to the formation of our solar system (we really get goose bumps thinking about the possibility that the carbon in our bodies arrived on Earth as diamond and later will be recycled by subduction, in a while of course, to make more diamond).

Diamond science owes much to the fact that it is the most desired of gemstones. Its great value has led to some very secretive research on how to carry out an alchemy reminiscent of turning lead into gold—turning brown diamonds colorless, and more. Pure diamond is colorless carbon, so



World map showing diamond sources cited in this issue. Colored areas demark “Archons”—cratons older than 2.5 Ga, “Protons”—cratons 1.6-2.5 Ga, and “Tectons”—0.8-1.6 Ga, important in prospecting for mantle-derived diamonds (see Stachel et al., this

issue). Black diamond symbols are used for mantle-derived sources and red diamonds for ultrahigh-pressure (UHP) metamorphic sources. (ADAPTED FROM LEVINSON 1998)

color is the product of trace amounts of another element, such as N or B, or defects, or some combination of these. Treatments have been developed to remove color or enhance color, and Shigley provides this story and describes the challenge to the gem industry. After all, people value the color nature has bestowed on a diamond far more than colors produced in the lab, so the industry must strive to maintain confidence by developing methods to distinguish the natural from the enhanced.

Our modern technological society owes much to the prowess of diamond as an abrasive and superhard material. In geoscience, the diamond anvil cell (DAC) has permitted experimentation at pressures above 100 GPa to better understand the interiors of planets and the basic properties

of matter. And, if only diamonds were large and common enough, we might all have watches with faces that could not be scratched, computers with diamond guts to extract the heat from much smaller and denser electronic microdevices, and DACs on our lab bench. Hemley, Chen, and Yan describe advances in growing diamonds by chemical vapor deposition (CVD), so that such possibilities, and more, are not just a dream.

These are just a few windows into the exciting science spanned by diamond research. We hope you will appreciate how much more this extraordinary mineral is than merely corresponding to 10 on the Mohs scale of hardness or being the featured bauble in an engagement ring. ■

REFERENCES

Berkley JL, Brown HG, Keil K, Carter NL, Mercier J-CC, Huss G (1976) The Kenna ureilite - an ultramafic rock with evidence for igneous, metamorphic, and shock origin. *Geochimica et Cosmochimica Acta* 40: 1429-1437

Carter NL, Kennedy, GC (1964) Origin of diamonds in the Canyon Diablo and Novo Urei meteorites. *Journal of Geophysical Research* 69: 2403-2421

Footo AE (1891) A new locality for meteoric iron with a preliminary notice of the discovery of diamonds in the iron. *American Journal of Science* 42: 413-417

Harlow GE (1998) *The Nature of Diamonds*. Cambridge University Press, Cambridge, 278 pp

Levinson, AA (1998) Diamond sources and their discovery. In: Harlow GE (ed) *The nature of diamonds*, Cambridge University Press, Cambridge, pp 72-104

Olson DW (2002) *Diamonds, Industrial*. US Geological Survey Minerals Yearbook (<http://minerals.usgs.gov/minerals/pubs/commodity/diamond/diamomyb02.pdf>)

Olson DW (2003) *Gemstones*. US Geological Survey Minerals Yearbook (<http://minerals.usgs.gov/minerals/pubs/commodity/gemstones/gemstmyb03.pdf>) and based on US representing ~ 60% of the world market (Harlow 1998).

Ringwood AE (1960) The Novo Urei meteorite. *Geochimica et Cosmochimica Acta* 20: 1-2 ■

Glossary for Diamond Science

Solid carbon in nature

Diamond – is the cubic form of carbon in which every carbon atom bonds with four other carbon atoms in a rigid tetrahedral framework. Its high density (3.51 g/cm³) requires high pressure for thermodynamic stability (see Fig. 1 in Cartigny, this issue, which shows diamond stability in relationship to the conditions interpreted to exist, on average, below old continents and young ocean floor).

Graphite – is the hexagonal form in which each carbon atom bonds with three others to form sheets weakly connected by residual (Van der Waals) forces.

Lonsdaleite – is a diamond-like structure with hexagonal symmetry and appears to be metastable.

Amorphous carbon – is non-crystalline carbon as found in soot. Buckey-balls or buckminsterfullerenes are an organized but non-crystalline (in the traditional sense) form.

Earth structure and mantle rocks

Lithosphere – the relatively rigid shallow solid Earth, consisting of the crust and the non-convecting portion of the mantle immediately beneath.

Asthenosphere – the relatively weak, convecting portion of Earth's upper mantle, with low seismic velocities and located essentially between the lithosphere and the transition zone.

Transition zone – a layer in the mantle from ~410 to 660 km depth, where olivine converts to wadsleyite and ringwoodite (see below). Below the transition zone, silicate perovskite plus ferro-periclase replace ringwoodite.

Pyrolite – coined by A.E. Ringwood for a model composition of Earth's primitive or "fertile" mantle, originally consisting of 1 part basalt (e.g., as from the mid-ocean ridge—MORB) and up to 4 parts anhydrous peridotite. There are many versions depending on whether the composition is used to model the seismological or melting properties of the upper mantle. (The term "fertile" and related words are a hot-bed of meanings and interpretations too rich to go into here beyond the simple sense of permitting the described rock to produce a melt of desired composition on adiabatic decompression).

Eclogite – a rock consisting of roughly equal parts green omphacitic *clinopyroxene* [nominally CaNa(Mg,Fe)AlSi₄O₁₂] and orange *garnet* [(Ca,Fe,Mg)₃Al₂Si₃O₁₂]. It is essentially the high-pressure metamorphic equivalent of basalt, the major constituent of the ocean floor.

Peridotite – is the principal rock in Earth's mantle. It is dominated by olivine (the gem variety is peridot), and is often subdivided into types containing *spinel* [(MgFe)(Al,Cr)₂O₄], indicating a shallower origin, or *garnet* [red and rich in *pyrope* (Mg₃Al₂Si₃O₁₂)], indicating deeper origin. The other important constituents are orthopyroxene and clinopyroxene.

Harzburgite – a peridotite essentially free (<5%) of clinopyroxene and thus depleted in elements like Na, Ca, and Al relative to pyrolite; it is interpreted to be the residue after extraction of a melt fraction.

Lherzolite – a peridotite with 2–10% clinopyroxene, considered to be representative of primitive or fertile mantle, since no melt has been extracted from it.

Wehrlite – a type of peridotite in which clinopyroxene is more abundant than orthopyroxene; it is thus thought to be overly "fertile," perhaps because it has been enriched by the addition of fluid or melt.

Minerals of the mantle

Olivine, wadsleyite, and ringwoodite – are (Mg,Fe)₂SiO₄ phases. Olivine is the orthosilicate α -form stable in rocks from Earth's surface to a depth of ~410 km where wadsleyite (the β -form) a denser di-silicate is stable, and at ~520 km ringwoodite (the γ -form with spinel structure) becomes stable (see Stachel et al.).

Pyroxene – a rock-forming, chain-silicate, mineral family with formula $MSiO_3$ – where M is usually a divalent metal or metals and Si is in tetrahedral coordination with oxygen.

Clinopyroxenes – have monoclinic symmetry and are generally rich in Ca + Mg + Fe and/or Na + Al.

Orthopyroxenes – are orthorhombic and have a formula close to (Mg,Fe)SiO₃.

Garnet – a rock-forming, orthosilicate, mineral family with formula $M^{2+}_3N^{3+}_2Si_3O_{12}$; M can be Ca, Mg, or Fe²⁺ and N is generally Al, Cr, or Fe³⁺

Majorite – is a form (polymorph) of silicate garnet in which Si resides in the 6-coordinated site (e.g., symbolized as ⁶Si) as well as the tetrahedral site: Mg₃⁶(MgSi)⁴Si₃O₁₂.

Ferropericlase – (or *magnesiowüstite*) is (Mg,Fe)O and significant in the deep mantle as a dense phase formed as a reaction product with MgSiO₃-perovskite in the reaction Mg₂SiO₄ = MgSiO₃ + MgO. IMA suggests ferroan periclase.

Perovskites – a structure type with potentially diverse compositions and with the same formula as pyroxene but different coordination: ¹²M⁶XO₃. Perovskite itself is CaTiO₃ and is stable at low pressures, but silicate perovskites, MgSiO₃ and CaSiO₃, are the main minerals of the lower mantle.

Isotope ratios and notations

Delta notation – isotope ratios are often reported in "delta notation", which gives the deviation of the measured ratio from the standard ratio in parts per thousand [$\delta^{13}C = ((^{13}C/^{12}C)_{meas}/(^{13}C/^{12}C)_{std}) - 1 \times 1000$] The standard for C is PDB, a fossil belemnite, for which the notation is sometimes presented as $\delta^{13}C_{PDB}$. In the case of oxygen, the formulation is based on ¹⁸O/¹⁶O with the standard being Standard Mean Ocean Water (SMOW); for sulfur it is ³⁴S/³²S with standard Canyon Diablo Troilite (CDT or a synthetic equivalent VCDT).

Noble Gases

³He/⁴He ratios – are used to measure the relative contributions from mantle and crustal sources in the production of a rock. Since ³He is primordial in origin but most ⁴He is radiogenic, low ³He/⁴He ratios suggest a strong input from the crust, where radionuclides are concentrated.