Graphitic carbon deposited from hydrothermal fluids occurs globally, in rocks from all depths in Earth’s crust and ranging in age from Precambrian to Tertiary. The varieties of deposits include graphitic cones and “artichokes” filling rock pores, explosively injected veins, graphitic pegmatites with platinum-bearing ores, and isochemical—“iso-isotopic” reactions of calcite + quartz to form graphite + wollastonite. In many deposits, carbon’s structure attains well-ordered, nearly perfect graphite crystallinity. The carbon isotope composition of hydrothermal graphitic material ranges widely, from that of biogenic organic debris to that of biogenic carbonate minerals, and overlaps the isotopic composition of mantle carbon as measured in diamonds.

**KEYWORDS:** graphite, hydrothermal ore deposits, carbon isotopes

**INTRODUCTION**

Among geochemists and petrologists, graphite has a reputation as a refractory mineral. As heating during metamorphism drives off its volatile H, O, and N, carbonaceous organic matter is converted to well-crystallized graphite. Graphite persists as a stable mineral to the highest temperatures of the granulate facies and the highest pressures of the coesite-eclogite facies (Buseck and Beyssac 2014 this issue). Graphite remains stable into the upper mantle where it is replaced by diamond. Refractory in the factory as well, graphite is used in crucibles and molds for casting molten metals. Chemically inert, one-carbon-atom-thick graphene sheets persist indefinitely under Earth’s oxidizing atmosphere (Lazzeri and Barreiro 2014 this issue). Resistant to oxidation and insoluble in water, it may be surprising to learn that graphite is found in deposits with the attributes of classic hydrothermal ore deposits. Mobilization and transportation of carbon, in fact, pose no insurmountable obstacles to hydrothermal deposition. Carbon is mobilized as CO$_2$ and CH$_4$ by heating carbonate and organic-rich sediments during metamorphism. Hydrous fluids containing CO$_2$ and CH$_4$, or HCO$_3$ and CO$_3^{2-}$, have substantial capacity to carry carbon. And as shown by the deposits described below, precipitation of graphitic carbon from such fluids is widespread in a variety of crustal environments.

The purpose of this article is to illustrate the diversity of graphitic carbon’s depositional environments and mechanisms in hydrothermal deposits of Earth’s crust, emphasizing unusual or recently described occurrences that may not be widely known. The descriptions of occurrences, below, begin with examples at the smallest of scales—grain boundaries and fluid inclusions—and proceed to outcrop scale. The organization is meant to provide a convincing set of examples validating the hypothesis that hydrothermal deposition of graphitic carbon is prevalent in Earth’s crust. Whether the origin of a deposit is described as hydrothermal, fluid-deposited, precipitated from carbonaceous vapor, or wall rock alteration and replacement, these appellations all emphasize the similarities shared between hydrothermal graphitic carbon and icons of crustal fluid–rock interaction, such as skarns, gold–quartz veins, and the black or white smokers of mid-ocean ridges.

Hydrothermal graphitic carbon records the presence of carbon-bearing, aqueous fluids along grain boundaries in rocks, in fluid inclusions, and in fissures. Alteration and replacement halos of secondary graphite in the wall rocks of vein deposits document the precipitation of graphite during the dissolution of the host rocks by fluids. Graphitic carbon is deposited from fluids in unmetamorphosed and metamorphosed sediments and in volcanic and plutonic rocks. Its occurrences extend downwards through the brittle–ductile transition into the lower crust and the upper mantle, as shown by its presence in upper mantle xenoliths.

The length scales of graphite deposition extend from micrometers to kilometers: from grain boundaries to altered plutons. Hydrothermal graphitic carbon deposits are distributed throughout geologic time, from the Precambrian to the Tertiary.

Hydrothermal ore deposits are studied using mineral–fluid phase equilibria, fluid inclusion microanalysis, stable isotope geochemistry, mapping of mineral distributions, and petrographic description of mineral textures. Investigations of graphitic carbon deposits share these tools, with emphasis on microscopic laser Raman spectroscopy for measuring graphite crystallinity and carbon isotope geochemistry for identifying carbon sources. Reflected, polarized-light microscopy is an informative technique for understanding graphite crystallization mechanisms. The strong reflection pleochroism of well-crystallized graphite makes it possible to identify single graphite crystals and their approximate crystallographic orientations in complex mineral intergrowths.

Recently published studies on crustal hydrothermal fluids (Yardley and Bodnar 2014), graphite and carbonaceous aqueous fluids (Huizenga and Touret 2012), carbon isotope geochemistry (Luque et al. 2012), and vein graphite (Luque et al. 2014), along with their lists of cited references, provide more detailed information.
VARIETIES OF GRAPHITE DEPOSITS

In crustal rocks, graphitic carbon occurs along grain boundaries, coating mineral grains and filling pores between grains (Frost et al. 1989). These occurrences, occupying as they do interstices between preexisting mineral grains, may be of secondary origin, precipitated from hydrothermal fluids, but, alternatively, they may record indigenous carbonaceous material remaining after heating biogenic organic matter. Establishing a hydrothermal or an indigenous origin for graphitic carbon at the submillimeter scale is difficult (Table 1 in Bernard and Papineau 2014 this issue). In an encyclopedic study of graphitic carbon on mineral grain boundaries in Paleoproterozoic and Archean rocks, Papineau et al. (2010a, b) found evidence of precipitation of graphite from hydrothermal fluids but also indications of in situ graphitization of residual biogenic organic matter. These studies demonstrate the ambiguity of limited data and the necessity to utilize all relevant chemical and physical examination methods in order to objectively test competing hypotheses of graphite formation.

Textures and microstructures characteristic of vapor deposition under laboratory conditions have been observed in grain-boundary graphitic carbon of crustal rocks. Graphene, a planar sheet of graphite structure one carbon atom thick, is strong, but it can be twisted, buckled, and stacked, forming nanostructures with the shapes of tubes, cones, onions, horns, and whiskers (Lazzi and Barreiro 2014). Carbon nanostructures serve as templates supporting the growth over geologic time periods of micrometer-sized structures visible using electron microscopy. Of the many shapes synthesized experimentally, only cones, tubes, and “artichokes” have been found in terrestrial rocks (Fig. 1). These graphitic structures do not have exactly the same d-spacing and Raman spectra as well-crystallized macroscopic graphite (Jaszczak et al. 2003, 2007). Nevertheless, their occurrence in nature provides compelling evidence of mechanisms of interaction between carbon-bearing fluids and the rocks they infiltrate. Invisible in hand specimen, unnoticed in thin section, graphene-based graphitic structures may be ubiquitous on grain boundaries of metamorphic rocks infiltrated by carbon-bearing fluids.

Daughter crystals of graphitic carbon in fluid inclusions in minerals provide observational evidence of graphite precipitation from fluids in crustal rocks (Fig. 2; cf Cesare 1995). The presence of graphite daughter crystals in fluid inclusions has been confirmed by microscopic laser Raman spectroscopy (Long et al. 2013).

A remarkable occurrence of graphitic carbon and microdiamonds has been found in fluid inclusions hosted by metamorphic garnets in late Jurassic metasedimentary rocks exposed at Lago di Cignana, western Alps, Italy. Discussion of a unique occurrence of diamond in an article on hydrothermal graphitic carbon is justified because the diamond crystals are coated by a thin layer of imperfectly crystalline graphitic carbon. If anyone doubts the precipitation of a refractory mineral like graphite from aqueous solutions, then let them consider precipitation of diamond in fluid inclusions. The fluid inclusions are hosted by manganiferous garnets derived from the metamorphism of marine manganiferous nodules and crusts. Manganiferous nodules and crusts on the seafloor are known to harbor microorganisms replete with carbonaceous tissue. Although the host rocks of the fluid inclusions are observed to be free of carbon, emphasizing a possible external source of the fluids, the presence of halos of ferric iron–enriched garnets surrounding diamond-bearing fluid inclusions suggests that carbon may have been “bleached” by oxidizing fluids. The marine sediments reached metamorphic temperatures of 600°C and pressures of 32 kbars during Eocene subduction of the African tectonic plate beneath the Eurasian plate, forming the Alpine mountain chain. Diamond and carbonaceous matter coppedrecipitated with magnesite, dolomite, and less abundant silicates and carbonates from
alkaline aqueous solutions in fluid inclusions. The aqueous solutions contain the ionic species SO$_4^{2-}$, HCO$_3^-$, CO$_2$, and Si(OH)$_4$. The molecular species CO$_2$ and CH$_4$ have not been detected in the fluid inclusions (Frezzotti et al. 2011, 2014).

Graphitic carbon precipitated from fluids in a postmagmatic environment of ultramafic and mafic rocks has been found in the Archean Stillwater (Montana, USA) and Proterozoic Bushveld (Republic of South Africa) layered intrusions. In both intrusions, pyroxenitic pegmatites crosscut primary igneous layering and are located near platinum ore bodies. Deposition of graphitic carbon was accompanied by postmagmatic hydrous silicates as well as sulfides, arsenides, and platinum-group minerals. Bushveld graphitic carbon has $\delta^{13}$C values of $-16.4$ to $-20.3\%$ and Stillwater $-14.7$ to $-16.3\%$ (Wilson et al. 1995). The hydrous silicates amphibole and biotite contain up to 0.3 wt% chlorine and graphitic carbon contains up to 1.9 wt% chlorine in the Bushveld occurrence (Ballhaus and Stumpfl 1985). Chlorapatite replaces calcic pyroxene in the presence of graphitic carbon in the Stillwater intrusion (Volborth and Housley 1984). The igneous minerals plagioclase and pyroxene are replaced by carbon, and pyroxene is serpentinized. Carbon depositional structures include crustiform layers and both tangential- and radial-textured spherulites (FIGS. 3, 4).

The Borrowdale graphitic carbon deposit in the English Lake District is a vein deposit that displays evidence of an origin by precipitation from aqueous fluids. Graphite–chlorite ore is localized along conjugate normal faults crosscutting Ordovician andesitic volcanic rocks and diorites. The host volcanic rocks, up to 5000 m thick, are unmetamorphosed and rest upon 5000 m of unmetamor-

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A thin, laterally extensive occurrence of graphitic carbon at Malaspina, Corsica, defines a reaction zone separating Mesozoic marine marble from serpentinite. The rocks were metamorphosed during Eocene subduction of the African plate beneath the Eurasian plate. The marble consists of calcite, quartz, small amounts of disordered graphitic carbon, metamorphic garnet, and phengitic mica. The reaction zone has the assemblage quartz, wollastonite, grossularite, diopside, graphite, and pectolite, along with apatite and titanite. Serpentinite is composed of serpentine, Cr-bearing magnetite, clinopyroxene, and uvarovite-rich garnet. The local presence of aragonite, the high-pressure form of calcite, included within garnet in the reaction zone suggests metamorphic pressures greater than 9 kbars.
during reaction zone formation. Raman spectroscopy of the marble’s disordered graphitic carbon gives a metamorphic temperature of approximately 430°C (Malvoisin et al. 2012). The crystallinity of carbonaceous material in the marble resembles that of weakly metamorphosed, disordered graphitic carbon, whereas graphite of the reaction zone is highly ordered structurally. A sampling traverse a few centimeters long from unreacted marble into the reaction zone shows the abrupt disappearance of calcite and the appearance of wollastonite, accompanied by the elimination of carbonaceous matter and the appearance of well-crystallized graphite. The reaction zone is approximately “isochemical” as well as “iso-isotopic” with respect to marble, because its bulk carbon content, 2 to 3 wt%, and the δ\(^{13}\)C value of graphite in the reaction zone, -5 to 0‰, are approximately equal to those of calcite in the marble (Galvez et al. 2013a, b).

**CHARACTERISTICS OF HYDROTHERMAL DEPOSITS OF GRAPHITIC CARBON**

The foregoing examples illustrate a number of characteristics shared between more typical hydrothermal deposits, such as gold–quartz veins, and deposits of graphitic carbon. Graphitic carbon veins are found at the intersections of faults and dikes, along pluton–wall rock contacts, and in shear zones, all of which are structures that focus fluid flow. Wall rock alteration and replacement by graphitic carbon is prevalent either in halos surrounding veins or disseminated throughout granitoids undergoing infiltration by aqueous fluids. Crustiform, layered graphitic carbon, each layer distinguished by different grain sizes and crystallographic orientations, records successive precipitation events under changing depositional conditions.

Hydrothermal graphitic carbon deposits have, in addition, unique features. Microscopic growth forms of graphitic carbon deposited on grain boundaries resemble the nanostructural features observed in laboratory studies of vapor deposition. In centimeter- to meter-scale vein deposits, the atomic structure of hydrothermal carbon attains the crystalline perfection of graphite sensu stricto, and is, in many cases, incommensurate with the poor crystallinity of wall rock carbon.

Commercial deposits of chemically pure, highly crystalline vein graphite have been exploited in Precambrian terranes of high metamorphic grade, such as in Sri Lanka (Binu-Lal et al. 2003) and Dillon, Montana, USA (Duke et al. 1990). The deposits described above demonstrate that high-grade metamorphism is not required either preceding or accompanying hydrothermal graphite precipitation. Borrowdale deposition took place in unmetamorphosed rocks within a few kilometers of Earth’s surface at temperatures of 400 to 500°C and pressures of 1 to 2 kilobars (Ortega et al. 2010).

Hydrothermal graphitic carbon is found under highly variable geological conditions, from 9 kb at Malaspina to 1 kb at Borrowdale, and from 700°C in Sri Lanka to 400°C in Borrowdale. Grain-boundary graphite may be ubiquitous in metamorphic rocks. Graphitic carbon spherulites (Fig. 3c) are of low volume but pervasively replace feldspar in granitoid rocks over hundreds of square kilometers in New Hampshire, USA (Duke and Rumble 1986).

**SOURCES, TRANSPORT, AND PRECIPITATION OF HYDROTHERMAL GRAPHITE**

Crustal sources of water and carbon-bearing species include volatiles exsolved from crystallizing magmas and fluids released from metamorphic rocks by thermally driven reactions among silicate, hydrous, and carbonate minerals. At shallow crustal levels, water is released from sediments by the collapse of rock pores due to the weight of overlying strata. More deeply buried rocks produce water by geothermal heating of hydrous minerals. Carbon dioxide is freed from heated limestone by decarbonation reactions between calcite and silicate minerals. Methane is produced by heating organic debris from dead organisms. Despite the insolubility of graphitic carbon in water, its effective solubility is sufficiently high under crustal conditions that large quantities of carbon can be transported as molecular CO\(_2\) and CH\(_4\) or ionic HCO\(_3^-\) and CO\(_3^{2-}\).
That graphitic carbon precipitates readily from hydrothermal fluids should not be surprising in light of calculated graphite stability in C–O–H phase diagrams (Fig. 6). The saturation surface of graphite in equilibrium with fluid is convex towards the fluid phase as plotted on an isothermal–isobaric phase diagram of the system C–O–H. Aqueous solutions with different ratios of CO₂ to CH₄ dominate most of the fluid-only stability field. The curvature of the saturation surface, in itself, is sufficient to guarantee the existence of conditions favoring graphite precipitation. Mixing fluids with different CO₂/CH₄ ratios across the convex saturation boundary will result in oversaturated solutions. Precipitation of graphite from mixed fluids is expected, provided there are no kinetic inhibitions. But when the impacts of changing temperature and pressure are considered, graphite precipitation is even more strongly favored. A decrease in temperature or an increase in pressure expands the saturation boundary at the expense of fluid; in this case, previously unsaturated fluid finds itself oversaturated and thus prepared to precipitate graphite. Examining Figure 6 reveals alternative mechanisms for graphite precipitation. Consider a hydrous fluid with minor amounts of CO₂ and CH₄ infiltrating a rock with anhydrous minerals (Duke and Rumble 1986). Hydration reactions between fluid and minerals will drive the composition of residual fluid directly away from the coordinate labeled “H₂O” and towards graphite’s saturation surface. These conditions led to the retrograde association of secondary graphite with hydrous silicates widely observed in plutonic rocks in New Hampshire, USA.

But many graphite deposits found in nature cannot be explained by phase relations in the C–O–H system alone. Graphite occurring with chlorapatite and Cl-bearing hydrous silicates in the Bushveld and Stillwater layered intrusions mandates a chlorinated fluid (Ballhaus and Stumpf 1985; Mathez et al. 1989). Sulfide minerals coprecipitated with graphite in the Bushveld, the Stillwater, and other deposits record the presence of sulfur-bearing species in solution. Graphitic carbon and diamond precipitated from an aqueous solution of the ionic species SO₄²⁻, HCO₃⁻, and CO₂²⁻ with no detectable CO₂ or CH₄ are inconsistent with a fluid consisting solely of molecular species (Frezzotti et al. 2011, 2014). Hydrothermal fluids restricted to the system C–O–H are not capable of causing coprecipitation of other minerals, such as tourmaline (Fig. 3A, D), with graphite, nor would they be effective in dissolving and replacing silicate minerals in the wall rocks of graphite veins (Fig. 5). Chloride-bearing solutions, however, are capable of carrying the boron needed for tourmaline. Such solutions would enhance the solubility of silicate minerals in wall rocks. The presence of chloride-bearing brines, in solution or immiscible with carbonaceous aqueous fluids, provides a mechanism for coupling graphitic with non-carbonaceous mineralization.

**CARBON ISOTOPE GEOCHEMISTRY**

The carbon isotope values (defined previously) of hydrothermal graphite deposits span the entire range commonly observed in crustal rocks, from the values of thermally degraded organic matter to those of carbonate sediments. The values for hydrothermal graphite deposits overlap mantle values at δ¹³C_VPDB = −5‰, as recorded by diamonds (Shirey et al. 2013). Borrowdale has δ¹³C_VPDB as low as −29 to −35‰, similar to that of organic debris (Barrenechea et al. 2009). Malaspina graphite matches the calcite it replaces at δ¹³C_VPDB = 0‰ (Galvez et al. 2013b). Bushveld and Stillwater graphites carry intermediate values (Wilson et al. 1995). These examples suggest that the carbon source is the primary control on the δ¹³C values of hydrothermal graphite, with fluid mixing from different sources accounting for intermediate values. The magnitude of fractionation effects between graphite and fluids of different CO₂/CH₄ ratios is as much as 10‰ (Figure 5 in Duke and Rumble 1986); this effect is potentially significant but, nevertheless, is small in relation to the entire range of variation in δ¹³C values seen in hydrothermal deposits. The refractory character of graphite with respect to carbon isotopic exchange is well illustrated by millimeter-scale analytical traverses across graphite crystals. A Precambrian, granulite facies graphite grain records a 4‰ change in δ¹³C,
from $-7$ to $-3\%$ over 1 mm, measured perpendicular to the (0001) cleavage (Santosh et al. 2003). Once graphite acquires its carbon isotope composition, this composition may persist for over 10$^9$ years. Crustiform graphite from Borrowdale differs by almost 2\% in $\delta^{13}C$, layer-by-layer, over submillimeter distances (Barrenechea et al. 2009), providing a permanent record of changing conditions of graphite precipitation.

**WHAT’S NEXT?**

Accurate understanding of the dynamics of hydrothermal graphite deposition is currently curtailed by a conspicuous lack of information on the chronology of graphite deposits.

**REFERENCES**


in the examples cited above, information on the geologic age of host rocks is included but there is little data on the ages of mineralization. Detailed geochronologic data are needed to estimate rates of fluid flow and of temperature and pressure changes during graphite deposition.

Recent discoveries of graphite “nanostructures” (Jaszczak et al. 2003, 2007), carbon-coated diamonds in fluid inclusions (Frezzotti et al. 2011), and reaction skarns of graphite and wollastonite replacing quartz and calcite (Malvoisin et al. 2012; Galvez et al. 2013a) demonstrate that there are still surprises to be found in nature. Each of these discoveries fosters new directions in research. Painstaking work will be required to learn whether nanostructures are more prevalent than currently known. Fluid inclusions filled with an aqueous solution of SO$_2^2$, HCO$_3^-$, CO$_3^{2-}$, and Si(OH)$_4$ with little or no CO$_2$ and CH$_4$ raise questions about how adequately phase relations in the system C–O–H represent conditions of hydrothermal graphite precipitation. Future studies of graphite phase relations should consider aqueous solutions including not only molecular but also ionic species. These studies will be greatly aided by recent developments in electrochemistry that have extended the pressure–temperature range (Sverjensky et al. 2014) over which predictions of solvent–solute interactions in aqueous solutions can be made.

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Distribution of Y in a grain from granite of Cournols, France. Dated at 343±20 m.y by measuring Th, U, Pb and Y. Sample courtesy of Dr G. Wille, BRGM, France.
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