Graphite reaction weakening of fault rocks, and uplift of the Annapurna Himal, central Nepal

D. Craw¹ and P. Upton²
¹Geology Department, University of Otago, PO Box 56, Dunedin 9054, New Zealand
²GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand

ABSTRACT

Hydrothermal graphite has been added to a regional-scale postmetamorphic fault zone in the High Himalaya. Fault rocks contain graphite veins and cement that locally constitute >50% of the rock. Individual graphite veins are as much as 1 cm wide, and are locally almost pure graphite, with minor muscovite and anatase. Hydrothermal graphite grain size (10–500 µm) is substantially greater than background metamorphosed organic matter (~1 µm). The graphite is crystallographically disordered, and has maximum reflectance of ~3% with weak reflection pleochroism. This degree of crystallinity is consistent with formation under upper sub-greenschist facies conditions, similar to the metamorphic grade of the host rocks that are near the lower boundary of greenschist facies. The graphite formed during hydrothermal mixing of CO₂ and CH₄, both of which emanate from nearby active springs. The graphite deposition process in these low-grade rocks contrasts with graphite remobilization and structurally controlled redeposition, without enrichment, during greenschist facies metamorphism, and graphite oxidation and removal during amphibolite facies metamorphism elsewhere in the Himalayan orogen. The reverse fault zone that hosts the graphite formed during tight folding of interlayered carbonate and metapelitic (shale) rocks, and the inhomogeneous nature of these rocks has focused strain into weaker zones that anastomose around stronger rocks, at scales from millimeters to tens of meters. Graphite was emplaced during this fold and fault deformation into weaker zones, further weakening and lubricating the fault zone in a hydrothermally driven feedback system. Differential uplift across the reaction-weakened graphite fault zone has led to relative uplift of the Annapurna Himal and formation of a large (>2 km) and steep topographic step on the northern side of the high mountains.

INTRODUCTION

Carbonaceous material is a common, although minor, component of many metasedimentary rocks in low-grade metamorphic terranes. Physical and chemical changes (coalification or graphitization) to this carbonaceous material during prograde metamorphism have been used to quantify metamorphic grade changes of the host rocks, and even to provide high-resolution geothermometry in appropriate rock sequences (Landis, 1971; Teichmuller et al., 1979; Beysac et al., 2004, 2007). The presence of carbonaceous material also has an effect on rock properties, and can facilitate deformation and foliation development (Bini-Lal et al., 2003; Upton and Craw, 2008; Ooohashi et al., 2011). Carbonaceous material is disordered to some extent.

In addition to the primary carbonaceous material in low-grade metamorphic terranes, there is increasing evidence for mobility, deposition, and enrichment of carbonaceous material in some metamorphic rocks as part of metamorphic and hydrothermal processes (Luque et al., 1998, 2009; Evans et al., 2002; Bini-Lal et al., 2003; Pitcairn et al., 2005; Huizenga, 2011; Galvez et al., 2013; Marshall et al., 2014). The chemical processes that drive this carbon mobility are generally considered to involve volatile carbon compounds in metamorphic fluids (Holloway, 1984; Luque et al., 1998, 2009, 2014; Evans et al., 2002; Huizenga, 2011). Localized combination of these volatile components commonly requires structural control of differing, and ultimately intersecting, fluid pathways within the metamorphic rock pile. The nature of such fluid mixing processes is poorly understood in ancient metamorphic belts because the evidence for such processes becomes obscured by subsequent deformation and fluid flow during uplift and erosion.

Both the organic maturation processes and the inorganic hydrothermal processes can lead ultimately to formation of a crystalline mineral, graphite, provided temperatures are sufficiently high, typically in upper greenschist facies or amphibolite facies conditions (Landis, 1971; Teichmuller et al., 1979; Holloway, 1984; Pitcairn et al., 2005; Galvez et al., 2013; Luque et al., 2014). However, carbonaceous material that is crystallized or recrystallized at lower temperatures does not form fully crystalline graphite, but a crystalline form commonly called disordered graphite, as displayed by broadened and diffuse X-ray diffraction peaks located in similar positions to sharp peaks of fully crystalline graphite (e.g., Landis, 1971). This disordered graphite forms under low-temperature hydrothermal conditions as well as from maturation of organic matter (Henne and Craw, 2012). In this paper we refer to all the carbonaceous material we examine as “graphite,” even though all of it is disordered to some extent.

To further understand the processes and consequences of addition of this graphite to low-grade metamorphic rocks, this study focused on a young and active orogenic belt, the Himalaya, in which the underlying structural and metamorphic processes are relatively well constrained by current observations of the tectonic setting and associated deformation. Metamorphic rocks and related fluid systems are well exposed and relatively well understood because of abundant fresh rock exposure and lack of overprinting events. This study was conducted in response to predictions from previous studies in older metamorphic belts that mixing of CO₂ and CH₄ should yield graphite enrichment (Holloway, 1984; Luque et al., 1998; Craw, 2002; Evans et al., 2002; Huizenga, 2011; Henne and Craw, 2012). The Himalayan mountains have surface...
Graphite reaction weakening, Annapurna Himal, Nepal

discharges of both CO₂ and CH₄ (described in the following), so zones in which these fluids could mix were targeted in a search for evidence of graphite addition. We report here the results of this search, first by describing background graphitic rocks in which graphite enrichment has not occurred, and then describing some highly graphitic fault rocks. We then outline some structural, geochemical, and topographic implications for this late metamorphic graphite addition process in the active Himalayan orogen.

GENERAL SETTING

The Himalayan orogen has been forming because of collision between India and Tibet (Fig. 1) since the early Cenozoic, and shortening in the orogen continues at ~2 cm/yr (Yin and Harrison, 2000; Betinelli et al., 2006). The present surface deformation is focused in the low-relief southern margin of the orogen, but uplift and exhumation continue in the mountains as well, with current erosion rates of ~0.5–2 mm/yr (Yin and Harrison, 2000; Gabet et al., 2008). Continued uplift and exhumation have exposed high-grade metamorphic rocks on the southern side of the highest mountains, with transitions to lower grade rocks to the north and south (Vannay and Hodges, 1996; Yin and Harrison, 2000; Searle et al., 2008). Our study was conducted across the metamorphic gradients exposed on the vicinity of the Kali Gandaki valley of central Nepal, where access is relatively simple and there have been many studies of the basement rocks (Fig. 1; Colchen et al., 1980; Hodges et al., 1996; Vannay and Hodges, 1996, 2003; Searle et al., 2008; Larsen and Godin, 2009; Kellett and Godin, 2009; Searle, 2010).

The high-grade rocks in the Kali Gandaki area are amphibolite facies metasedimentary gneisses that include metapelites and calc-silicates interlayered with granitoid orthogneisses that were intruded into those metasediments (Hodges et al., 1996; Vannay and Hodges, 1996; Godin, 2003). These rocks make up most of the Greater Himalayan Series that is traceable across the entire Himalayan orogen (Vannay and Hodges, 1996, 2003; Searle et al., 2008). These Precambrian–Cambrian rocks were metamorphosed in the Eocene in the early stages of Himalayan collisional orogenesis, and exhumed rapidly starting in the Miocene (Vannay and Hodges, 1996). The high-grade rocks have been thrust over lower grade (greenschist facies) Precambrian metasediments (metapsammites, metapelites, quartzites, and carbonates) that were also metamorphosed during Cenozoic Himalayan collision (Vannay and Hodges, 1996; Godin, 2003; Larsen and Godin, 2009). The boundary between amphibolite facies and greenschist facies rocks is a prominent regional thrust that has been mapped as the Main Central thrust (MCT, in Fig. 1; Colchen et al., 1980; Vannay and Hodges, 1996). The underlying greenschist facies schists have been thrust on to subgreenschist facies metasediments by structures mapped by Larsen and Godin (2009) as a Main Central thrust strand (MCT₂ in Fig. 1). These greenschist facies rocks have been included in the Greater Himalayan Series, and the underlying subgreenschist facies rocks in the Lesser Himalayan Series as an orogen-wide feature (Searle et al., 2008; Larsen and Godin, 2009).

The amphibolite facies rocks of the Greater Himalayan Sequence are structurally overlain
by greenschist facies marine metasediments of the Paleozoic Tethyan Sequence (Fig. 1; Vannay and Hodges, 1996; Godin, 2003; Kellett and Godin, 2009). The boundary between these sequences is a ductile shear zone with normal sense of motion, the South Tibetan detachment system (Fig. 1; Vannay and Hodges, 1996; Godin, 2003; Larsen and Godin, 2009; Searle, 2010). The Tethyan metasediments, which are dominated by carbonate beds with subordinate metapsammitic and metapelitic beds, have been variably folded and faulted, and metamorphic grade decreases upsection to subgreenschist facies rocks in the upper Kali Gandaki valley (Fig. 1; Vannay and Hodges, 1996; Godin, 2003; Kellett and Godin, 2009). North-striking normal faults adjacent to the upper Kali Gandaki valley have formed a large sedimentary basin, the Thakkholra graben, with thick Pliocene–Pleistocene nonmarine fill (Fig. 1; Colchen, 1999; Godin, 2003).

CARBON IN HIMALAYAN OROGENIC FLUIDS

Numerous ambient and warm springs emanate from the basement rocks and thin gravel veneer in the High Himalaya (Craw, 1990; Becker et al., 2008; Evans et al., 2008; Perrier et al., 2009). The water in these springs has meteoric origin, and the springs also contain abundant CO₂ that is of metamorphic origin (Becker et al., 2008; Evans et al., 2008; Perrier et al., 2009). The CO₂ is presumed to have been derived from decarbonation metamorphic reactions and oxidation of organic material in the ductile region below the mountains, and mixes with shallower meteoric water along fracture networks leading to the surface (Craw, 1990; Kerrick and Caldeira, 1993; Becker et al., 2008; Evans et al., 2008; Perrier et al., 2009). Fluid inclusions in quartz veins in Greater Himalayan amphibolite facies gneisses contain as much as 70 mol% CO₂, attesting to the abundance of CO₂ migrating at depth beneath the Himalayan mountains (Craw, 1990). Methane is a minor or negligible component of fluids in these inclusions (Craw, 1990). Carbon dioxide is less abundant (typically 20–30 mol%) in fluid inclusions in veins in greenschist facies rocks of the Tethyan Sequence, and is mixed with basal brines derived from these lower grade marine metasediments (Craw, 1990).

Subgreenschist facies organic metasediments of both the Lesser Himalayan Sequence and the Tethyan Sequence are considered to be prospective for hydrocarbon generation because of their degree of maturation (Thakur et al., 2008; Mishra and Mukhopadhyay, 2012). Methane is reaching the surface in subgreenschist facies Tethyan Sequence rocks, attesting to ongoing maturation of organic matter in these rocks. A methane seep at Muktinath (Fig. 1) occurs in association with meteoric springs, and has reputedly been burning since first human occupation of the area. This site is managed as an important component of a combined Hindu and Buddhist temple complex. The occurrence of separate structurally controlled surface emanations of CH₄ and CO₂ in the Himalaya was the basis for our predictions of localized mixing and graphite precipitation that led to this study.

METHODS

Field work for this study involved examination of accessible outcrops and stream boulders along parts of the Kali Gandaki, and in valleys and passes adjacent to Dhaulagiri and to the north of Annapurna (Fig. 1). Graphitic rocks are highly friable and break up during erosion, so exposures of suitable material are rare and discovery relies on serendipity. Further, while graphite-bearing rocks are common in the area, textural evidence for graphite enrichment is generally equivocal. Therefore, this study focuses principally on a series of outcrops in which graphite enrichment has undoubtedly occurred.

Graphite was identified in the field in hand specimens, on the basis of color, hardness, and streak. Selected material was examined in polished thin sections, where graphite was confirmed from its optical properties. The abundant graphite at the Thini (Nepal) localities was characterized by X-ray diffraction (XRD), using a PANalytical X’Pert PRO X-ray diffractometer at University of Otago, New Zealand, with Cu Kα radiation. Sample preparation for XRD was via fine grinding with a mortar and pestle of ~1 g of material extracted from hand specimens, followed by mounting and drying of a slurry as a smear on a glass slide.

Graphite was characterized optically using quantitative reflectance with a Zeiss reflected light microscope fitted with a microphotometer. A 25x oil immersion objective and a microphotometer measurement spot size of 5 μm were used to avoid polishing scratches on graphite surfaces. Microphotometric measurements were made with polished monochromatic green light (λ = 546 nm) in oil with refractive index of 1.518, at 18 °C. Maximum and minimum microphotometric responses were measured for each grain after rotation in polarized light, and reflectance results were calibrated with a polished glass standard (Zeiss catalogue LaSF6–961–349) with reflectance of 1.672%. Polished surfaces of graphite can be distorted at the nanometer scale by the preparation procedures, but this can be overcome if light penetrates into the specimen below the surface (Pasteris, 1989). The relatively low reflectance of the disordered graphite examined in this study and associated low refractive index allowed substantial penetration of incident light. The preparation procedures in this study were identical to those used for hydrothermal disordered graphite described by Henne and Craw (2012), to which we compare the graphite in this study. The degree of disorder of hydrothermal graphite in these studies, as indicated by XRD, is consistent with the differences in reflectance for the same materials determined by standard methods for maturation of organic matter (Teichmüller et al., 1979), and this consistency gives confidence that the polishing procedure has not unduly affected the results.

Numerical models of interrelated graphite deposition and deformation were developed using FLAC® (Fast Lagrangian Analysis of Continua in Three Dimensions), with model geometry and input parameters that were described in detail in Upton and Craw (2008). Our models assume: (1) an initially inhomogeneous rock mass; (2) that deformation occurred by noncoaxial flow, with water-saturated rocks under near-lithostatic fluid pressure; (3) that deformation caused dynamically enhanced permeability; (4) that permeability increased with increasing strain rate; (5) that graphite precipitation from fluid occurred instantaneously compared to the rates of deformation in zones of deformation-induced dilatation; and (6) that graphite deposition lowered the strength of the rock during deformation. Models described in Upton and Craw (2008) were developed for a low-angle reverse fault, and these have been adapted for a steep reverse fault in this study.

METAMORPHIC CARBON

Greenschist facies clastic metasediments, both above and below the amphibolite facies zone, have remnants of bedding preserved, but this is mostly overprinted by foliation, which is commonly polyphase. The rocks are largely recrystallized with greenschist facies mineralogy, i.e., quartz, albite, and muscovite with subordinate chlorite and/or biotite. Many of these rocks are calcareous, especially those of the Tethyan Sequence in the High Himalaya, and most of the clastic metasediments have at least some metamorphic calcite. Graphite is an accessory mineral in most of these rocks, especially in metapelites where it locally defines foliations (Fig. 2A). Graphite grain size is typically micron scale or finer, but some carbonaceous metapelites have graphite grains as large as 10 μm, elongated parallel to foliations (Fig. 2A). Some of these graphitic host rocks have
focused deformation into narrow (meter scale) ductile shear zones with thrust senses of motion. The shear zones have recrystallized under greenschist facies conditions, although associated rocks, structurally immediately above and below the shear zones, are merely folded with pre-shear foliation progressively deformed into parallelism with the recrystallized shears.

Despite the intense deformation and recrystallization of graphitic rocks in the shear zones, there is no evidence for graphite enrichment in these rocks. Syn-shear metamorphic segregation and quartz vein formation locally dilutes some graphitic rock (Fig. 2A). Likewise, calcareous metapelites deformed under greenschist facies conditions have extensive remobilization of calcite, but no obvious graphite enrichment. Micron-scale graphite-rich seams occur along some new foliation surfaces where carbonate has been locally depleted, but similar or larger volumes of these rocks have had graphite diluted by foliation-parallel metamorphic calcite and calcite veins.

Amphibolite facies pelitic metasediments, including those that may be higher grade equivalents of the Lesser Himalayan Series, are distinctly lacking in graphite. Submicron dusty inclusions in some garnets and feldspars may be graphite, but no confirmation of this was possible in this study. Instead, most of these rocks contain no carbon minerals, apart from minor accessory calcite that occurs mostly as veinlets. Associated calc-silicate gneisses also contain metamorphic calcite and calcite veinlets.

**POSTMETAMORPHIC CARBON**

Postmetamorphic crenulations of foliation are widespread in greenschist facies rocks structurally above and below the amphibolite facies belt. These crenulations are typically centimeter-scale perturbations of the micaceous foliation, and can locally dominate the rock fabric. Crenulations are minor structures associated with larger scale postmetamorphic folds and/or faults that deform the foliation macroscopically, and kilometer-scale folds and associated fault zones are particularly prominent in the Tethyan Sequence ($D_2$ of Godin, 2003; Kellett and Godin, 2009). Crenulation fold axial surface cleavage pervades some metapelitic rocks (Fig. 2B). Crenulations and the associated fold axial surface cleavage in graphitic rocks have distinct darker seams along the new cleavage (Fig. 2B), but there is no evidence in polished thin section for enrichment of graphite along those seams, merely a decrease in graphite grain size. The dark cleavage seams in Figure 2B are dominated by fine-grained (1–10 µm) calcite and muscovite, with only scattered dusty graphite.

Tight postmetamorphic folds commonly have thrust or reverse faults developed in or near their hinge zones, at all scales (meters to kilometers).
These faults disrupt bedding and foliation, and these surfaces are commonly sheared with slickensided surfaces. Shears in graphitic rocks are commonly polished with slickensided graphite that has been smeared across fracture surfaces. Similar graphitic polishing occurs on the surfaces of broken clasts in cataclastic material in the fault zones. Graphitic smears are commonly accompanied by calcite veins, especially in carbonate-rich rock units. These rocks are too inhomogeneous to obtain meaningful carbon analyses to investigate potential graphite enrichment, but at least localized graphite mobility appears to have occurred throughout these fault zones. However, the fault zone near Thini village (Fig. 1), described in the following, provides unequivocal evidence for structurally controlled graphite enrichment.

GRAPHITE IN THE FAULT ZONE AT THINI

Fault Structure

The fault near Thini village is associated with a zone of tight postmetamorphic folding of interlayered (1–10 m scale) carbonate horizons and variably graphitic metapelites of the Tethyan Sequence (Fig. 1). These rocks have a weak lower greenschist to subgreenschist facies foliation that is subparallel to bedding, and this foliation is defined by fine-grained muscovite. The fault and fold zone is traceable for at least 30 km (Fig. 1), although individual strands and associated folds are discontinuous along the zone. The fault and fold zone approximately coincides with a major topographic change from the highest mountains (e.g., Nilgiri, Annapurna) to relatively low relief landscape that includes Lake Tilicho and the upper Marsyandi Khola catchment (Fig. 1).

The structure of the fault zone is strongly controlled by lithology; the most complex structure results from differential strain in interlayered carbonate and metapelite (Figs. 3A–3D). Some internal shearing of carbonate beds has occurred, especially in thick carbonate units, but most strain has been focused into interlayered metapelites (Figs. 3A–3D). The most highly strained metapelites are intensely cataclastic, and cataclastic zones as wide as 100 m occur locally along the fault zone. Thin (meter scale) carbonate beds have been variably folded and dismembered by deformation of enclosing metapelite to form irregularly shaped blocks surrounded by sheared and cataclastic metapelite (Figs. 3A–3C). Individual strands of the fault zone dip steeply to the north and south. The dip of the fault zone as a whole is not clear, but has been inferred to be steeply southward based on its general topographic interactions. Abundant folding within the fault zone attests to dominant reverse sense of motion, and stratigraphic offset, south side up (Vannay and Hodges, 1996; Godin, 2003), is also consistent with reverse motion. Slickenlines on sheared surfaces indicate dip-slip sense of motion.

Structurally Controlled Graphite

Most of the metapelitic rocks contain fine-grained (1–10 µm) dusty graphite dispersed along bedding or foliation with metamorphic phyllosilicates, as described in earlier sections. Slickensided graphite shear surfaces are also abundant throughout the fault and fold zone, and many of these appear to have had minor graphite enrichment. However, there has clearly been substantial addition of graphite veins to the fault rocks near Thini, along sheared surfaces and throughout cataclasites and associated fractured rocks. Vein graphite is most abundant along distinct fault surfaces that cut through sheared metapelite at the outcrop scale (Figs. 3B–3D). The maximum thickness of individual graphite vein zones along these faults is not discernable in outcrop because of the friable nature of the sheared zones, but highly graphitic material occurs in zones as much as 5 cm wide. Some of these graphitic fault surfaces also cut through carbonate blocks, and graphite veins persist into these blocks (Figs. 3B, 3C). The abundance of graphite is lower in sheared metapelite adjacent

Figure 3. Field sketches (based on photographs) of the graphitic fault zone in folded interlayered carbonate and metapelite (shale) near Thini (Nepal; Fig. 1). (A) Composite sketch across the best-exposed portions of the outcrop, showing disruption of folded carbonate beds in highly deformed metapelite. (B) Detailed section of the northern margin of the fault strand. (C) Oblique view (looking east, along strike) of a low-relief portion of the outcrop. (D) Detailed section of the hinge zone of a fold in carbonate rock, with folded and faulted metapelite.
Graphite reaction weakening, Annapurna Himal, Nepal

to the fault surfaces, although graphite cement and associated veinlets are still widespread and graphite can make up more than 50% of some cataclastic material.

Individual graphite veins are at least 1 cm thick in places, and are locally almost pure graphite, with minor dispersed muscovite, quartz, calcite, Ti-minerals, and angular rock fragments. Graphite pervades adjacent sheared metapelitic rocks in patches and shear-parallel seams and masses, locally forming a cement in cataclasites (Figs. 4A, 4B). The shear-parallel graphite seams and masses anastomose around quartz-rich cataclastic fragments at the thin-section scale (Fig. 4B), and at larger scales to at least 10 m. Early-formed graphite vein material in fault rocks has been subsequently refractured and dismembered, then recemented with later graphite generations (Figs. 5A, 5B).

Graphite Crystallinity

Unlike the dusty amorphous metamorphic graphite in the metapelites, the structurally controlled graphite vein material is sufficiently coarse grained that individual crystals can be discerned in polished thin sections. Grains and clusters of grains in graphite veins are sufficiently crystalline to show distinct anisotropy when rotated under near-crossed polars (Figs. 6A, 6B). Shear-parallel graphite seams contain graphite flakes and elongate graphite grains as much as 0.5 mm long (Figs. 4A, 4B), and some of these are single graphite crystals. However, most of the graphite vein material is finer grained, with a typical grain size of 10–50 µm (Figs. 6A, 6B). These grains are irregular, equant, and anhedral in shape, and form interlocking masses, with only localized shear-parallel crystallographic orientation (Figs. 6A, 6B).

Despite the strong anisotropy of the graphite, there is only weak reflection pleochroism in most grains. Maximum reflectance in green light is 1.9%–3.2%, and minimum reflectance is typically 1.2%–2.5% (Fig. 7A). These measured reflectances and associated pleochroism are low compared to fully crystalline graphite, which has maximum reflectance near 10% and minimum near 1% (Fig. 7A). The low Thini graphite reflectances imply only moderately crystalline material that has formed under subgreenschist facies conditions that are equivalent to the upper limits of coalification of vitrinite (Fig. 7A; Teichmüller et al., 1979). The observed reflectances are at the lower end of graphite reflectances from shear zones at the upper end of subgreenschist (pumpellyite-actinolite) facies rocks (Fig. 7A; Henne and Craw, 2012).

The relatively poorly crystalline nature of the vein graphite is also shown with XRD analysis (Fig. 7B). Graphite vein material was scraped from shear surfaces for this analysis, and all samples of this material were found to contain muscovite and anatase, as well as minor quartz. The graphite produces a very broad low peak between 22° and 28° 2θ with maximum near 26° (Fig. 7B). The broad graphite peak is asymmetrical, with gentle gradient on the low 2θ side and steeper gradient on the high 2θ side near the main crystalline graphite peak position (masked by muscovite in this material; Fig. 7B). This broad asymmetrical XRD pattern centered on ~26° 2θ is typical of disordered graphite formed under subgreenschist facies conditions (Landis, 1971). The Thini graphite is similar to, but more disordered than, hydrothermal graphite.
described in Henne and Craw (2012) (see Fig. 7B). The more disordered nature of Thini graphite is consistent with the observed differences in reflectance for these hydrothermal graphite localities (Fig. 7A).

DISCUSSION

Hydrothermal Graphite Formation

The graphite textures described here for the Thini fault zone provide strong evidence that there has been substantial addition of graphitic carbon to the rock during deformation, with graphite locally forming >50% of the rock as matrix, cement, and veins. These textures and the high proportions of graphite preclude passive graphite enrichment by dissolution of host rock, which would imply >50-fold removal of silicates. The strong tectonic fabric and evidence for repeated graphite addition, cementation, and brecciation preclude passive introduction of liquid hydrocarbons, such as pyrobitumen (Scott et al., 2009), as the predominant source of the carbon in the rock.

The structurally controlled and locally pervasive nature of the vein graphite hosted in what were permeable zones in the rock suggests that the graphite was derived from syndeformational passage of fluid through the fault zone. There are observed regional occurrences of separate CO₂ and CH₄ emanations at the surface, and widespread evidence for generation of these carbon compounds at depth in different parts of the orogen, as outlined here. The Thini area coincides with the general boundary between deep-sourced CO₂ beneath the high Himalaya, and methane emanations from maturation of organic-rich sediments. We therefore suggest that the Thini graphite deposition was a result of mixing of CO₂ and CH₄ within the fault zone, as depicted in Figure 8.

The CO₂ and CH₄ surface emanations are associated with meteoric springs, and it is highly likely that these gases were carried as dissolved components in hotter waters at depth. Becker et al. (2008) suggested that only 3% of metamorphic CO₂ dissolved in deeper waters remains in solution in surface springs, and the other 97% is degassed at shallow levels. The moderate crystallinity of Thini graphite implies that graphite deposition occurred at the higher temperature end of subgreenschist facies, near greenschist facies conditions (Figs. 7A, 7B; Landis, 1971; Teichmueller et al., 1979; Henne and Craw, 2012) and probably at ~150–200 °C. Under these conditions, CO₂ and CH₄ can coexist in solution at only very low levels, and graphite deposition is inevitable (Fig. 8; Holloway, 1984; Huizenga, 2011). These observations imply that the graphite addition was a hydrothermal process within the fault zone, precipitated by fluid mixing (Holloway, 1984; Craw, 2002; Evans et al., 2002; Pitcairn et al., 2005).

The moderate crystallinity of the graphite reflects formation conditions similar to the metamorphic grade of the host rocks, implying that graphite emplacement occurred during middle...
Cenozoic late metamorphic deformation (possibly D₄ of Godin, 2003), rather than during near-surface modern fault reactivation and warm spring activity. The low metamorphic grade, implied moderate temperature, and brecciated, cataclastic nature of the host rocks for the graphite all imply that graphite deposition occurred under brittle conditions in the fault zone, rather than under ductile conditions at greater depth. The fault zone was clearly highly permeable to fluid flow, the permeability consisting of open fractures and high-porosity breccias, some of which ultimately became cemented with graphite. This highly permeable environment has apparently permitted incursion and mixing of at least two fluids of differing compositions, so that CO₂ and CH₄ could combine to make graphite. We suggest that the ambient fluid was CO₂-bearing water, similar to that which occurs in most of the surface springs, and that either water with dissolved CH₄, or a CH₄ gas phase that had immiscibly separated from such a water (as at nearby Muktinath), was able to percolate into the fault zone from the margins. However, we cannot discount the possibility that the ambient water was CH₄ bearing, and that CO₂ gas or CO₂-bearing water percolated into the fault zone from the margins.

The proposed graphite deposition reaction in the Thini fault zone is the opposite of that inferred to have occurred in the amphibolite facies rocks during metamorphism, where primary graphite has apparently been removed from the rocks to contribute to the CO₂ component of the fluid (Fig. 8; Becker et al., 2008; Evans et al., 2008). Under amphibolite facies conditions, significant quantities of CO₂ and CH₄ can coexist in solution (Fig. 8; Holloway, 1984; Evans et al., 2002; Huizenga, 2011). In contrast, in the green-schist facies rocks to the north and south of the amphibolite facies belt, primary graphitic material appears to have been locally remobilized and recrystallized, but neither removed nor enriched (Figs. 2A, 2B). This implies localized graphite recrystallization that presumably involved dissolution and minor transport, followed by essentially immediate redeposition (Fig. 8).

### Structural and Geochemical Model of Graphite Deposition

Hydrothermal addition of soft weak graphite to parts of the Thini fault zone will have had profound effects on the rock strength during subsequent deformation (Binu-Lal et al., 2003; Upton and Craw, 2008; Oohashi et al., 2011). The common occurrence of slickensided graphitic shear surfaces along the fault zone attests to at least some localization of strain into graphitic zones. Graphitic shear zones anastomose around more competent, graphite poor, rock types at a range of scales (Figs. 3–5). Early-formed graphite became a locus of subsequent deformation and was recemented by more graphite as deformation continued (Figs. 5A, 5B). Ongoing deformation in the fault zone facilitated mixing of separate fluids, leading to hydrothermal graphite addition, which then facilitated further deformation and graphite addition in graphite-weakened fault rocks.

This process of graphite-induced reaction weakening and strain localization was modeled in Upton and Craw (2008) for a ductile shear zone, and similar processes probably operated in the Thini fault zone, albeit with different rock
parameters. The model involves a feedback system, whereby strain localization in inhomogeneous rocks increases shear strain rate and enhances permeability in the weakest rocks, allowing fluid penetration, mixing, and graphite deposition, which further weakens these rocks, further enhances permeability, and leads to further graphite deposition (Upton and Craw, 2008).

A set of results for this model has been superimposed on to a schematic Himalayan structure representative of the observed Thini fault zone (Fig. 9). These model results reflect the earliest stages of the development of the Thini fault zone, where the metapelites were relatively strong yet distinctly weaker than the carbonates, rock permeability was low, and graphite proportions were low but increasing (to 3%; Fig. 9). The feedback processes apparently continued until graphite made up more than 50% of some parts of the deformed rock mass on the centimeter scale.

Figure 7. Quantification of the crystallinity of graphite from the fault zone at Thini (Nepal). (A) Maximum and minimum reflectance of graphite grains (as displayed in Fig. 6) under plane-polarized green light. Three different symbols (triangles, squares, circles) are for three different specimens. Data are compared to coalification fields defined by Teichmuller et al. (1979), and hydrothermal graphite from low-grade rocks in New Zealand (light gray field). (B) Portion of an X-ray diffraction spectrum, showing the broad disordered graphite peak (cf. Landis, 1971) compared to fully crystalline graphite peak position.

Figure 8. Sketch cross section (after Colchen et al., 1980; Vannay and Hodges, 1996; Godin, 2003) through the Annapurna massif to Nilgiri and the fault zone near Thini (Nepal; Fig. 1; this study), showing the variations in relief, lithologies, and metamorphic grade across the High Himalaya. Orange zone between the STDS (South Tibetan detachment system) and MCT1 (Main Central thrust) is amphibolite facies. Dominant transformations involving carbonaceous material, including graphite, at the different metamorphic grades are indicated. Phase diagrams (truncated triangles) for the C-O-H system (after Holloway, 1984; Huizenga, 2011) show that amphibolite facies fluid can contain coexisting CH4 and CO2, whereas under greenschist facies conditions either CO2 or CH4 occur in the fluid, in equilibrium with graphite.
The graphitic Thini fault zone coincides with a prominent topographic step between the high mountains of the Annapurna Himal (7000–8000 m) and the lower and more subdued topography (4000–6000 m) to the north (Figs. 8 and 10). The high mountains are made up of carbonate rocks that are lithologically more competent than the shale-bearing rock sequence to the north (Fig. 8; Colchen et al., 1980; Godin, 2003). Therefore, the topographic step (Figs. 8 and 10) is partly a result of differential erosion of rocks of varying competence. However, the rocks of the high mountains (early Paleozoic) are older than those to the north (late Paleozoic–Mesozoic; Fig. 8), implying that there has been substantial differential uplift across the Thini fault zone. Similar stratigraphic and topographic steps occur along strike in central Nepal, such as north of Dhaulagiri (Fig. 1; Kellett and Godin, 2009), but the Annapurna Himal (Fig. 10) has the steepest step with the steepest topographic gradient.

The abundant graphite in the Thini fault zone has weakened the fault rocks and focused strain into these weaker rocks, as modeled in Figure 9. We suggest that this feedback between reaction weakening and strain localization is partially responsible for uplift of the Annapurna Himal relative to the mountains to the north, yielding the steep topographic step (Figs. 9 and 10).

**Carbon Repository in a Fault Zone?**

Maturation and/or oxidation of organic material and metamorphic devolatilization of carbonate-bearing rocks in the Himalaya are responsible for substantial flux of volatile carbon, especially CO₂, into the atmosphere (Kerrick and Caldeira, 1993; Becker et al., 2008; Evans et al., 2008). The CO₂ discharged from only one set of springs is equivalent to that from an active volcano, and an extrapolation across the entire Himalaya suggests that these springs are responsible for ~13% of all solid Earth CO₂ discharges (Becker et al., 2008; Perrier et al., 2009). These high levels of CO₂ discharge are reputed to be significant for ancient and modern climate change issues (Kerrick and Caldeira, 1993; Becker et al., 2008; Perrier et al., 2009).

The rate of carbon sequestration in graphite in the Thini fault zone is not known, but a general estimate of the total amount of carbon present in the fault zone can be made. A conservative assumption of graphite (density ~2 t/m³) with 5% cementation in a fault zone 10 m wide and 10 km long, and extending 2 km deep, yields a mass of $2 \times 10^7$ t of carbon, or $\sim 10^{12}$ moles. This is $\sim 100$ times the annual carbon discharge from springs in a Himalayan catchment (Evans et al., 2008). While these estimates are highly speculative, the fact that the processes have occurred, and may still be occurring, is entirely predictable from observations of the surface emanations of CO₂ and CH₄. These processes are most likely to occur in the part of the Himalaya where the separate CH₄ and CO₂ can mix, as is seen in the Thini fault zone. This is the general zone between the subgreenschist facies rocks in which organic maturation is sufficiently advanced to produce CH₄, and the higher grade part of the Himalaya where CO₂ is produced by metamorphic devolatilization (Fig. 8). More work is needed to quantify the amount of sequestration of carbon that has occurred, and presumably is occurring, in this zone. Without this process, the amount of CO₂ discharged to the atmosphere from the Himalaya may have been, and would still be, substantially greater than the current measurements suggest. Further, once the graphite has been deposited, it remains essentially inert during erosion, and can be permanently sequestered within the sedimentary system (Dickens et al., 2004).

**CONCLUSIONS**

Greenschist facies metasediments of the Greater Himalayan Sequence on the southern side of the High Himalayan mountains have variable amounts of graphite derived from organic material in their Precambrian protoliths. This graphite is fine grained (micron scale) and dispersed irregularly through the rock mass, controlled by metamorphic foliation. Graphitic metapelites have focused strain for Cenozoic shears into narrow zones, with development of new graphitic greenschist facies.
fabric locally, but there has been no discernable graphite enrichment during this process. Likewise, greenschist facies metapelites (shales) in the Paleozoic–Mesozoic Tethyan Sequence in, and to the north of, the highest mountains have fine-grained graphite derived from their protoliths, and this graphite has been remobilized, but has not been concentrated, by synmetamorphic to postmetamorphic deformation. In contrast, Greater Himalayan Sequence amphibolite facies metapelites, which have been thrust over greenschist facies rocks on the southern side of the mountains, have little or no graphite preserved, and any primary graphite has apparently been removed, possibly by oxidation reactions accompanying decarbonation of calcareous rocks.

A regional-scale fold and fault zone cuts Tethyan Sequence rocks near the poorly defined boundary between greenschist facies and sub-greenschist facies. The fault zone developed in a zone of tight folding of interlayered carbonate and metapelite (shale) layers. Strain was focused into strongly deformed zones of metapelite that now contains dismembered blocks of variably folded and faulted carbonate rock. The fault zone has been extensively impregnated by hydrothermal graphite, along shear zones, throughout cataclasite matrix, and in veins cutting both sheared rocks and cataclasites. Almost pure graphite veins as much as 1 cm thick occur locally, and some patches of cataclasites have >50% graphite. Graphite has been structurally controlled during deposition, with seams oriented parallel to shears and fractures. Early-formed graphite veins and impregnations have been subsequently redeformed, fragmented, and recemented by more graphite.

The hydrothermal graphite is moderately crystalline, with disordered structure, and has much coarser grain size (10–500 µm) than the original carbonaceous material in the metamorphic host. Reflectance values (to 3% in green light) are consistent with formation under upper subgreenschist facies conditions. The graphite was probably emplaced in the middle Cenozoic, rather than as part of modern near-surface hydrothermal systems. However, meteoric water springs in the High Himalaya are discharging abundant CO₂ and CH₄ from maturation and decarbonation reactions at depth, and mixing of these carbon species in the fault zone was probably responsible for graphite deposition. Therefore, the fault zone provides a repository for volatile carbon species that would otherwise have been released into the atmosphere.

Impregnation of the fault zone with graphite was initiated when fault movement and associated shear development and cataclasis enhanced the rock permeability, allowing ingress and mixing of hydrothermal fluids. Graphite deposition lowered rock strength and enhanced lubrication of fault movement, thereby creating more permeability, allowing more fluid ingress, and more graphite deposition. This feedback process has caused emplacement of the abundant hydrothermal graphite and substantially weakened the fault zone. This process has localized fault motion on the northern side of the Annapurna Himal, facilitating substantial differential uplift and formation of a large (>2 km) and steep topographic step.

Figure 10. Images of the prominent topographic step at the graphitic fault zone and associated folded zone on north side of Annapurna Himal. (A) Oblique view from north of Annapurna Himal from International Space Station (part of National Aeronautics and Space Administration image ISS 025-E-011510), showing the graphitic fault zone (red dashed line) and topographic step. (B) View southeastward (yellow arrow in A) across the fault zone to the Annapurna Himal. The direction of the view in A is indicated in Fig. 1, and direction of the view in B is indicated in A.
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