Textural changes of graphite by tectonic and hydrothermal processes in an active plate boundary fault zone, Alpine Fault, New Zealand

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Abstract

Graphitisation in fault zones is associated both with fault weakening and orogenic gold mineralisation. We examine processes of graphite emplacement and deformation in the Alpine
Fault Zone, New Zealand’s active continental tectonic plate boundary. Optical and scanning electron microscopic observations reveal a microstructural record of mobilisation of graphite as a function of temperature and ductile then brittle shear strain. Raman spectrometry allowed interpretation of the degree of maturity of carbonaceous material (CM), which reflects thermal and mechanical processes. In the amphibolite-facies Alpine Schist highly crystalline graphite, indicating peak metamorphic temperatures up to 640°C, occurs mainly on grain boundaries within quartzo-felspathic domains. The subsequent mylonitization process resulted in reworking of CM under lower temperature conditions (500°C – 600°C) in a structurally controlled environment, resulting in clustered (in protomylonites) and foliation aligned CM (in true mylonites). In the brittlely-deformed rocks (cataclasites derived from the mylonitised schists) graphite is most abundant (<50%) and has two different habits: inherited mylonitic graphite and less mature patches of potentially hydrothermal graphite. Tectonic-hydrothermal fluid flow was probably important in deposition of graphite throughout the examined rock sequences. The increasing abundance of graphite may be a significant source of fault weakening, allowing strain localisation, as the fault rocks are progressively exhumed.

Keywords

Graphite is a common component of orogenic and Carlin style gold deposits around the world, where it is intimately associated with hydrothermal deposits (Bierlein et al. 2001; Kribeck et al. 2008; Large et al. 2007, 2011). Graphite may be inherited from the host rocks, in which case it acts as a chemical reductant that facilitates precipitation of gold and associated sulphide minerals from younger hydrothermal fluids (Cox et al. 1995; Bierlein et al. 2001; Large et al. 2007, 2011).
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Graphite may also be added to the mineralising systems as a result of chemical interactions between hydrothermal fluids and the host rocks (Pitcairn et al. 2005; Kribeck et al. 2008; Huizenga 2011; Luque et al. 1998, 2009, 2014). Hydrothermal gold deposits are commonly intimately associated with zones of focussed deformation (i.e. the deposits are “structurally controlled”) and graphite derived from both these origins commonly becomes involved in later deformation including fault zone inception and evolution. Graphite is frictionally weak, thus, its presence affects fault mechanics because it can preferrentially accommodate localized shear and result in further structurally-controlled mineralization (Binu et al. 2003; Upton & Craw 2008; Oohashi et al. 2011; Kuo et al. 2014; Craw & Upton 2014). For this reason, processes of deformation of graphite in fault zones are of interest in understanding both gold deposits and rheology. Furthermore, flaky crystalline graphite is increasingly recognised as an important mineral resource in its own right (Beyssac & Rumble, 2014). However, the graphite we have studied is not sufficiently concentrated to present an economically viable resource – a function of the structural setting that we carefully describe here to facilitate future development of realistic models of graphite distribution around various typical geological structures.

On a larger scale, the close spatial relationship between graphite and hydrothermal gold deposits can be of relevance for developing exploration strategies in prospective regions. This is because graphite is a highly electrically conductive mineral, and if it forms linked networks it may contribute to a low-resistivity geophysical signal in graphite bearing rocks (Haak & Hutton, 1986; Jiracek et al., 2007). Consequently, graphitic rocks and associated graphitic structures can be detected using regional scale geophysical methods such as airborne electromagnetic or magnetotelluric surveys (Won 1983; Gautneb & Tvetin, 2000; Dentith & Barrett, 2003; Heinson et al. 2006; Dentith et al. 2013). The relative roles of conductive fluids versus minerals such as graphite in forming electrically conductive fault zones at depth has been debated by
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geophysicists interpreting magnetotelluric profiles through major ore-hosting terranes (Wang & Chamalaun, 1996; Heinson et al., 2006; Dentith et al., 2013).

Finally, the crystallinity of carbonaceous material (CM) has been calibrated as a geothermometer (Beyssac et al., 2002a), that is increasingly employed to understand both P-T evolution of metamorphic zones (Beyssac et al., 2016), and to determine fault strength based on estimates of frictional heating that accompanied shear (Kaneki et al., 2016). However, mechanical processes might also modify graphite structure, significantly reducing the accuracy of thermometric estimates.

In this study, we document the behaviour of graphite during progressive ductile-to-brittle deformational processes in an active, self-exhuming fault zone in South Island, New Zealand. The most important processes we identify involve both mechanical reworking of inherited graphite in deformed host rocks, and addition of new graphite to fault rocks by syndeformational hydrothermal activity. The fault zone is not known to contain significant gold deposits, although orogenic gold deposits have formed, and are still forming, elsewhere in the hangingwall of the Alpine Fault (Johnstone et al. 1990; Craw et al. 2009; Upton & Craw 2014). Our observations here instead focus on the various ways in which graphite interacts with an evolving structure, as they were extracted from the active fault zone during recent scientific drilling. We link these observations to inferred processes of formation of orogenic gold deposits in the nearby hangingwall, and in older deposits in the same host rocks including the world-class Macraes orogenic gold mine (Craw 2002; Craw et al. 2009).

Geological Setting

Alpine Fault zone
The oblique-slip Alpine Fault (Fig. 1a) accommodates up to 75% of the 37 mm/yr relative motion at the Australian – Pacific plate boundary, manifest as uplift of the fault hangingwall at ~8 mm yr\(^{-1}\) and dextral strike slip at 27 ± 5 mm yr\(^{-1}\) (Norris & Cooper, 2001; Herman, et al., 2009). At least 20 km of vertical uplift and exhumation has occurred along the fault, with total strike-separation of ~480 km (Norris et al., 1990; Norris & Cooper, 1995). The transform plate boundary fault strikes NE-SW and dips at 30 –50\(^{\circ}\) to the SE. At 35 km depth, it soles out into a major crustal decollement (Norris et al., 1990; Norris & Cooper, 1995; Kleffman et al., 1998; Little et al., 2007).

Uplift and erosion of the fault zone has exhumed ductile mylonitic rocks from the middle crust, while on-going near-surface deformation continues to form, and rework, cataclasites and gouges which only partially overprint the older, deeper-formed mylonites (Fig. 1b). Thus, rocks formed at the full range of depths over which shearing occurs in the fault zone outcrop at the surface (Fig. 1b; Table 1). The active slip zone is marked by a thin (<5 cm) clay gouge layer, forming the base of a 10 to 50 m-thick cataclasite unit composed of crushed angular mylonitic clasts in a fine-grained matrix (Fig. 1b). These brittle rocks are now structurally overlain by a ~1 km thick mylonite zone (Fig. 1b; Table 1). Based on degree of grain size reduction and transposition of the original protolith fabric, these mylonitic rocks can be subdivided into ultramylonites, mylonites and protomylonites (Toy et al., 2011). This mylonite zone subdivision reflects the relative magnitude of finite ductile shear strain accommodated by those variably foliated and lineated rocks, with increasingly higher strains accommodated nearer to the fault. Most samples were collected on either sub-horizontal or vertical outcrop surfaces or borehole samples. The Alpine Fault and its mylonitic foliation have an average attitude of 055/45 SE (Norris & Cooper, 2007). The mylonitic foliation is a spaced foliation largely inherited from the protolith amphibolite facies quartzo-feldspathic Alpine Schist, and later (in the Neogene) was cross-cut by extensional (C’) shear bands (e.g., Little et al., 2002). The fabric
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gradually changes from spaced to continuous with increasing proximity to the fault and ductile
finite strain magnitude. The protolith is well exposed in the non-mylonitic part of the Southern
Alps to the east of the fault zone (Fig. 1b). Farther east the Alpine Schist decreases in
metamorphic grade across the Southern Alps mountains, from oligoclase-zone amphibolite
facies through garnet, biotite and chlorite zones to pumpellyte-actinolite and prehnite-
pumpellyte facies (Little et al., 2005; Cox et al., 2012).

Thermal profile and hydrothermal system

Thermobarometric data from the central Alpine Fault zone, based on garnet-biotite
thermometers and garnet-plagioclase barometers in the mylonitic rocks, indicate they
equilibrated to P-T conditions of 600 –700 °C at 9.2 –10 kbar (Table 1; Cooper, 1980; Grapes
& Watanabe, 1992; Grapes, 1995). A few kilometres to the south-east of the fault the P-T
estimates decrease to 400 – 540°C at 4–7 kbar (Cooper, 1980; Grapes, 1995). Recently, Beyssac
et al. (2016) determined temperatures in excess of 640°C close to the Alpine Fault by Raman
thermometry. The mineral assemblages in the cataclasites indicate equilibrium at greenshist
facies conditions (< 530 °C; Warr & Cox, 2001), however, a pervasive chloritisation occurred
under sub-greenschist facies conditions (< 320 °C) and most clay minerals grew at much lower
temperatures (<120 °C) (Warr & Cox, 2001).

Rapid uplift of hot, tectonically advected rocks along the Alpine Fault has resulted in
giothermal gradients of >60°C km⁻¹ in the upper 3–4 km of the crust, and the brittle-ductile
transition (BDT) is inferred to be only be 8–10 km below the surface (Sutherland et al., 2012).
Furthermore, a pervasive tectonically-induced fracture network in the fault rocks, together with
topographically driven fluid pressure gradients, has allowed meteoric water to penetrate down
to at least 6 km depth through this hot rock and to rise again beneath the valleys (Koons, 1987;
Koons et al., 1998; Menzies et al., 2014), producing hot springs with temperatures greater than
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50°C (Barnes et al. 1978; Koons, 1987). Isotopic data also suggest metamorphic fluids mingle with meteoric water within this system (Jenkin, 1994; Upton et al., 1995, 2003; Cox et al., 1997; Koons, 1998).

Sample Description and Analytical Methods

Samples

We have examined samples recovered from boreholes that were drilled during the two phases of the Alpine Fault – Deep Fault Drilling Project (DFDP-1A and 1B, and DFDP-2B) (Fig. 1). During DFDP-1, undertaken at Gaunt Creek in early 2011, the Alpine Fault was cored in two shallow-depth boreholes, namely DFDP-1A (100.6 m) and DFDP-1B (151.4 m) (Sutherland et al., 2012). Thin sections were prepared from blocks cut perpendicular to the foliation within these cores. In 2014, the DFDP-2B cuttings (chips) were obtained during rotary drilling operations at up to 800 m actual (vertical) depth at Whataroa Valley. These include the non-mylonitic quartz-feldspathic Alpine Schist wall rock, and the Alpine mylonite zone (protomylonites and mylonites). These cuttings thin-sections were prepared from randomly orientated rock chips mounted in resin.

For the aims of the current study we used a sample set of 22 thin sections from DFDP-2B, equally distributed with depth, and five DFDP-1 thin sections, representing the principal slip zone of the Alpine Fault, New Zealand. In the current manuscript we present data from samples DFDP-2B 266 (schist), DFDP-2B 518 (protomylonite), DFDP-2B 890 (mylonite), DFDP-1A 69.1 (cataclasite) and DFDP-1A 69-2.61 (cataclasite). Sample nomenclature includes the name of the corresponding drilling phase together with the drill depth in meters.

Petrographic methods
Petrographic and microstructural characteristics of the samples were investigated using transmitted and reflected light optical microscopy. Based on these microstructural observations samples with representative graphite were selected for further, more detailed analysis. The structure and composition of the rocks were analysed on TESCAN MIRA3 field emission scanning electron microscope (FESEM) at John de Laeter Centre, Curtin University, Perth, Australia. The instrument was operated at 20 kV using a working distance (WD) of 15 mm. Energy-dispersive X-ray spectroscopy (EDS) maps were collected using an Oxford Instruments X-MaxN 150 mm² silicon drift detector (SDD). The EDS spectra were acquired and processed using Oxford Instruments Aztec software.

**Raman Spectrometry of Carbonaceous Material (RSCM)**

Raman spectroscopy was performed using a Reinshaw® inVia Raman Microscope with a 514 gr/mm Spectra Physics argon laser in circular polarization and a Peltier cooled RENCAM CCD detector, located at IMPMC, Paris, France. The laser was focused on the samples by a DMLM Leica microscope with a 100X objective, NA of 0.90 and ND filter of 10 %, producing final laser power of 1 – 2 mW.

Raman spectra were collected in the 800 – 1800 cm⁻¹ range in order to capture the first-order region. In order to avoid potential orientation and polishing effects, recognized as the main constraints of RSCM (Beyssac et al., 2003b; Beyssac & Lazzeri, 2012), we performed only in-depth measurements of carbonaceous material (CM) (Pasteris, 1989) in 30 µm – thick thin sections, orientated as close to perpendicular to the foliation as possible. Because of the nature of the cuttings samples, additional precautions were taken i.e. a quarter waveplate was used to remove potential polarization effects (Beyssac & Lazzeri, 2012).

Spectra decomposition and analysis were implemented by fitting procedures with the computer program PeakFit. Initially, the baseline was manually corrected by creating splines and
removing the background. Afterwards, curves representing Raman bands were fitted with a combination of Lorentzian and Gaussian functions (Voigt profiles), known to yield the best results (Beyssac & Lazzeri, 2012). As an outcome the parameters of the identified peaks were calculated, as well as R1 and R2 ratios (defined below), and the peak metamorphic temperatures.

Applications of Raman Spectrometry of Carbonatious Material

Raman spectroscopy has been established as a reliable quantitative method for characterizing the degree of organization of CM. The transformation of organic matter into crystalline graphite is induced by compositional and structural changes during diagenesis and metamorphism, known as graphitization, which is considered to be irreversible. Consequently, characteristics of Raman spectra are used as an indicator of peak metamorphic temperature (Wopenka & Pasteris, 1993; Beyssac et al. 2002a, 2002b, 2004).

Fully crystalline graphite consists of hexagonal planes of carbon atoms (space group D$_{6h}^4$ = P6$_3$/mmc) that result in vibration of E$_{2g}$ in-plane mode, observed as a high frequency Raman peak at ~1580 cm$^{-1}$ (G band) (Wopenka & Pasteris, 1993). Any disorders or defects in the graphite structure give rise to numerous additional bands, resulting in Raman spectra with first and second-order regions. In the first-order region (1100–1800 cm$^{-1}$), except for the G band, out of plane defects result in the appearance of peaks at ~1350 cm$^{-1}$ (D1 band) and ~1620 cm$^{-1}$ (D2 band). The D2 band forms a shoulder on the G band (Wopenka & Pasteris, 1993; Beyssac et al. 2002a, 2002b, 2003a, 2003b; Sforna et al., 2014). Very poorly organized CM characteristically has additional bands at ~1500 cm$^{-1}$ (D3) and ~1150 cm$^{-1}$, and a shoulder on D1. The second-order region (2200–3400 cm$^{-1}$) is represented by several bands at ~2400,
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~2700 (S1), ~2900 and ~3300 cm$^{-1}$, associated with overtone and combination scattering (Wopenka & Pasteris, 1993; Beyssac et al. 2002a, 2002b, 2003a, 2003b).

Quantification of CM is achieved by decomposition and analysis of the first-order region, more precisely – position, intensity, area (integrated area) and width (full width and half maximum) of the G and D bands (Wopenka and Pasteris, 1993; Beyssac et al. 2002a, 2002b, 2003a, 2003b).

Various correlations of these parameters are used to identify the structural order of CM. The most reliable are the intensity ratio between D1 and G bands ($R_1 = I_{D1}/I_G$) [where $I_i$ = intensity of the $i$th peak] and the area ratio ($R_2 = A_{D1}/(A_G + A_{D1} + A_{D2})$) [where $A_i$ = area of the $i$th peak], introduced by Beyssac et al. in 2002a. Peak temperature in the range 330–650˚C can be estimated to ±50˚C by the linear correlation $T = -445R_2 + 641$ (Beyssac et al., 2002b).

Petrographic Characteristics of the Alpine Fault Rocks

Alpine Schist

In the amphibolite-facies Alpine Schist there is a grain shape fabric in both quartz and/or feldspar domains and micaceous lamellae parallel to the planar spaced foliation. Large biotite porphyroblasts and garnets are scattered throughout (Fig. 2, Table 1). Quartz grains with mostly irregular, lobate boundaries, show pronounced sweeping undulose extinction, general absence of colour changes on rotation of the stage with the sensitive tint plate inserted (indicating a crystallographic preferred orientation is not present) and average geometric-mean grain size of 0.18 mm (based on a linear intercept method as described by Berger et al. (2011). Accessory opaque minerals with tabular habit are ilmenite and pyrrhotite. Graphite occurs as opaque particles at micrometer scale, and it is most commonly distributed on grain boundaries and as inclusions in biotite porphyroblasts (Fig. 3a).

Mylonites
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The mylonites and schists have nearly identical modal mineralogies. However, mylonitic rocks have a more uniform quartzo-feldspathic lithology in comparison to the Alpine Schist i.e. the main mineral phases appear as more evenly distributed with less variable grain sizes and shapes in the mylonitic rocks than in the schists. However, the schists’ planar foliation is gradually transformed to a wavy and anastomosing foliation then with increasing proximity to the fault a typical macroscopically continuous mylonitic fabric is developed. Throughout the protomylonite sequence shear bands subtend a low angle to the foliation (45° to 15°), and they become increasingly abundant and more closely spaced (spacing ranges from 500 to 145 micrometers) in the true mylonite zone (Gillam et al., 2013) (Table 1).

In the lowest strain protomylonites (Toy et al., 2012), sampled in the shallower DFDP-2 borehole samples, quartz grains show two predominant colours on rotation of the stage with the sensitive tint plate inserted (indicating bimodal distribution) and a geometric-mean ranging from 0.06 to 0.23 mm. Elongated quartz grains (a few hundred micrometers long) with irregular grain shapes, lobate boundaries and undulose extinction form an oblique shape fabric. They are mantled by aggregates of more equant smaller grains with mostly straight grain boundaries and uniform extinction, indicating strain free areas (Norris & Cooper, 2003). In the higher strain mylonites, sampled at greater depths in the DFDP-2 borehole, most quartz grains are smaller (geometric grain size ranging from 0.06 to 0.12 micrometers), more equigranular, and have well-defined grain boundaries. Quartz grains show more uniform colours on rotation of the stage with the sensitive tint plate inserted with increasing sample depth, indicating transformation of a weak CPO to a very strong and definite CPO.

Fine micaceous material coexists with biotite porphyroblasts, platy muscovite flakes, and mica fish. The biotite porphyroblasts are smaller than the ones observed in the shist rocks, their margins are reworked by the foliation, and there are occasional domino structures. At the protomylonite-mylonite transition, biotite is locally chloritised due to retrogressive
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Graphite appears as an accessory mineral throughout the Alpine Schist and mylonite succession. In the amphibolite facies schists, fine-grained single crystals (typically at one

267  metamorphism with this chloritic alteration becoming even more prevalent in the true mylonite section. Also in the transition from protomylonite to mylonite, garnet porphyroblasts become
268  more fractured, with chlorite filling the cracks. These garnet porphyroblasts contain spiralled
269  inclusion trails of the precursor non-mylonitic fabric, and typically have asymmetric strain
270  shadows, but in the true mylonites only fragments of these garnets are found, some of which
271  contain remnants of the inclusion trails. Opaque accessory minerals remain with the same
272  chemical composition and in relatively the same amount as in the schist rocks.
273
274  *Cataclasites*
275
276  The cataclasites consist chiefly of intensely crushed mylonites, the fragments of which float in
277  very fine to dusty-grained dark matrix. Asymmetric angular clasts up to 100 µm in size are
278  bounded by a cataclastic foliation, and there is an anastomosing network of dark hairline layers
279  (Table 1). Porphyroclastic quartzo-feldspathic mylonitic fragments, ranging up to a few
280  hundred micrometers in size, are internally fracured with sub-rounded, irregular shapes. These
281  fragments are cemented by a mixture of calcite and clay minerals with significant titanite and
282  graphite, causing dark appearance. These clay minerals are very fine-grained, and some have
283  been identified as illite, kaolinite and chlorite by using XRD in previous studies; kaolinite
284  locally dominates (Warr & Cox, 2001; Boulton et al., 2012; Schleicher et al., 2015). Smectite
285  has been identified in the thin, latest stage fault gouges (Boulton et al., 2012; Schleicher et al.,
286   2015).
287
288  **Graphite Textures**
289
290  Graphite appears as an accessory mineral throughout the Alpine Schist and mylonite
291  succession. In the amphibolite facies schists, fine-grained single crystals (typically at one
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Micrometer scale or finer) are dispersed mainly along grain boundaries in quartz-feldspathic
domains (Fig. 3a, b). Some randomly oriented graphite inclusions occur within large brown
biotite porphyroblasts or in quartz or feldspar domains. Aggregates of graphite grains constitute
larger flakes (Fig. 3a, b), which can reach a length up to ~30 µm long. Occasionally,
concentrations of graphite appear as elongated seams along grain boundaries (Fig. 3b).

In the mylonitic rocks, graphite persists with similar grain size to that in the metamorphic
protoliths. In the protomylonite section, clusters of graphite grains commonly occur within
silicate minerals, especially quartz and feldspar. These appear to have formed by aggregation
of the once more dispersed graphite grains that typify the protolith schists (Fig. 3c, d). In the
mylonites, graphite grains are also clustered into aggregates that are broadly aligned with the
foliation (Fig. 3e, f). In contrast to the non-mylonitic rocks, in the mylonites graphite is most
abundant at grain and sub-grain boundaries of recrystallised quartz-feldspathic domains (Fig.
3c, f), but we also observed dusty graphitic concentrations that are spatially associated with
iron oxides (Fig. 3c, d), especially in the protomylonites. Graphite inclusions are rare in remnant
biotite porphyroblasts. Phyllosilicate minerals are commonly aligned with fine-grained
graphite, and recrystallized matrix material (Fig. 3e, f). In Fig. 3e, an ilmenite porphyroclast
has inclusions of graphite grains parallel to the old metamorphic foliation, and other graphite
grains are aligned along the overprinting mylonitic foliation.

In the cataclastic rocks, mylonitic clasts enveloped by the cataclastic matrix preserve some of
the pre-existing mylonitic fabric, and have graphite textures identical to those described above.
In addition, the cataclastic matrix is locally filled and cemented by fine grained graphite
(approximately one micrometer across). This graphite generally aggregated to form larger
graphitic patches (a few hundred micrometers across) in the cataclasites, which locally
constitute ~50% of the rock volume (Fig. 4a-e). On a thin section scale, some of these
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aggregates are aligned as part of an anastomosing network of dark-coloured shear surfaces
decorated by slickensides (Fig. 4f).

Graphite Crystallinity and Raman Thermometry

Raman spectra

Raman spectra acquired from graphitic grains in the Alpine Fault rocks show typical G and D1
bands, respectively at ~1580 cm\(^{-1}\) and ~1350 cm\(^{-1}\), which allowed us to analyse the degree of
crystallinity in the CM (Fig. 5). In schist (Fig. 5a) and mylonite samples (Fig. 5b, c) D1 bands
show low intensity in comparison with the G bands (Fig. 5), and correspondingly low and
relatively consistent R1 values (between 0.02 and 0.26), suggesting well-organized graphite
with slight structural variations throughout the successions. The overall spectra analysis shows
that the schist CM material has achieved slightly higher maturity in comparison with the
mylonite zone (Fig. 5 a, b, c).

In contrast, R1 in the examined cataclasites (Fig. 5d, e, f) ranges between 0.13 and 0.8,
indicating significant variations in the graphite structures. Highly mature graphite, showing
identical spectra with the mylonite samples (Fig. 5d), was identified in preserved mylonitic
porphyroclasts. Simultaneously, the dusty graphite aggregates and veins appear to be composed
of less organized CM (in comparison with CM in schist and mylonite rocks) with variable
degree of maturity (Fig. 5e, f). In graphitic patches spectra comparable with the mylonitic CM
(Fig. 5e) coexist with spectra showing extremely high D1 peaks (Fig. 5f), indicating very poorly
organized CM is present.

RSCM thermometry
Textural changes of graphite

From the Raman spectra we are able to estimate the temperature conditions in the Alpine Fault rocks, based on the R2 ratio values. We estimate peak metamorphic temperatures up to 640°C with maximum error of ± 50°C in the non-mylonitic amphibolite facies schist (Fig. 5a). Estimated temperatures in the mylonites are slightly lower (between 500°C and 600°C). However, the Raman-based geothermometry method relies on progressive maturation of originally organic CM (Beyssac et al. 2002a, b; 2003). Hence, application of this geothermometry method in the deformed Alpine Fault rocks may not be valid because of possible recrystallisation of the CM (see discussion below). Similarly, temperature estimates in the cataclasites could indicate a range of 400 - 500°C (Fig. 5d), but these temperature estimates have no real meaning if the CM has been recrystallised.

Discussion

Deformation of metamorphic graphite

Graphite associated with the Alpine Fault zone manifests itself as very fine (1 to 5 microns) to dusty grains, arranged in a variety of textures and crystallinity, as a result of ongoing metamorphic and deformation-related processes. Initially, metamorphic graphite has grown predominantly on grain boundaries in the Alpine Schist, where RSCM thermometry indicates temperatures typical for amphibolite facies metamorphism – up to 640 ± 50°C (Cooper, 1980; Grapes & Watanabe, 1992; Grapes, 1995, Toy et al., 2010, Beyssac et al., 2016). The subsequent mylonitization of the schist rock resulted in partial recrystallisation of the rock volume under slightly lower temperatures (500 – 600°C from RSCM thermometry), which coincide with previous temperature estimates in the Alpine Fault mylonites (Toy, et al., 2010). Under these conditions, remobilisation of CM apparently took place, and graphite with lower maturity (in comparison with the schist protolith) was redeposited in quartzo-feldspathic
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domains in structurally controlled settings. Previous observations on graphite textures in
greenschist facies and at lower metamorphic grade schists, in equivalent non-mylonitic schists
further to the east of the Southern Alps, have identified graphite in close association with
metamorphic micaceous minerals (Craw 2002; Henne & Craw, 2012; Hu et al. 2015). However,
our study demonstrates that graphite mainly occurs within, or along grain boundaries of
quartzofeldspathic domains, both in the protolith schists and in the mylonitic rocks (Fig. 3).
The principal exceptions are the graphitic inclusions in relict biotite porphyroblasts, which are
progressively reworked and recrystallised with increasing strain (Toy et al. 2010).

In the cataclasites, our Raman data and textural observations (Fig. 4, 5) show that two highly
crystalline graphite types with non-identical crystallinity and distribution coexist, indicating
two structurally different generations of graphite. The first generation of graphite, preserved in
remnants of mylonitic clasts, carries the textural and crystallographic arrangement of graphite
in the mylonitic rocks (Fig. 4b, c). In contrast, the second generation of graphite has been
accumulated in the cataclastic matrix and in slickenside-rich shear surfaces, forming localised
graphite enrichment (Fig. 4). The first generation of graphite is clearly inherited from mylonitic
rocks, and the graphite textures or Raman signals of this generation have not been significantly
affected by cataclasis.

The abundance and textures of the second generation of graphite that occurs in the cataclasite
matrix supports observations on the silicate matrix that there has been extensive fluid-driven
modification in these rocks (Boulton et al., 2012). Locally abundant CM in these rocks (Fig. 4)
may result from either residual concentration during extensive dissolution of the silicate matrix,
or hydrothermal addition of graphite by the alteration fluids (Beyssac & Rumble, 2014; Galvez
et al., 2013a, b). Without detailed microchemical analyses of these CM-bearing rocks,
distinguishing these possibilities is difficult. However, petrographic observations of the
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cataclasites show that while the metamorphic silicates have been variably transformed to aluminous clay minerals, there has not been an associated residual increase in relatively insoluble minerals such as zircons in the vicinity of the matrix CM. Further, the matrix CM has a distinctly different Raman signal from that of the parent amphibolite facies schists and mylonites (Fig. 5). On the basis of these observations, we tentatively conclude that the matrix CM was added to the rocks hydrothermally. Similar interpretations have also been made in other fault zones, such as Annapurna Himal, Central Nepal (Craw & Upton, 2014) and Hidaka metamorphic belt, Hokkaido, Japan (Nakamura et al., 2015). More conclusive demonstration of the formation of hydrothermal graphite in these rocks remains a goal for future research.

The variations in the crystallographic order of the second generation of graphite can also signify hydrothermal graphite formation by consecutive pulses of fluids with variable temperatures. However, we also acknowledge the possibility of amorphization of CM as a result of intense shear deformation (Nakamura et al., 2015). There is evidence in our samples for deformation of the graphite pools into elongate shears within the cataclasite (Fig. 4), but we have no local, high resolution RSCM data to provide evidence for amorphization in these shears. Nevertheless, the sheared graphite may weaken these parts of the cataclasites, and causes further strain accommodation along localised slip surfaces, as modelled by Upton and Craw (2008).

Hydrothermal alteration of cataclasite

The alteration of sub-amphibolite facies protoliths (Fig. 1b) to the lower metamorphic grade mineral assemblages commonly documented in the cataclasite sequence is due to fluid-rock interaction across a range of temperatures as the fault rocks have been exhumed up the Alpine Fault. Deformation-driven, episodic enhancement of permeability facilitated hydrothermal fluids flowing in the hangingwall to penetrate the lower permeability fault zone and infill
fractures and pore spaces with secondary minerals. This resulted in multiple generations of
alteration and precipitation of secondary minerals in the fault zone over a range of temperatures
(Table 1). Chloritic alteration can occur at temperatures up to 320–360 °C (Warr & Cox, 2001).
Fluid inclusion microthermometry yields estimates of precipitation temperatures of deformed
quartz veins containing chlorite of 325 ± 15 °C (Toy et al. 2010; Menzies et al., 2014). The
temperatures at which the documented secondary minerals may precipitate from fluids with the
chemical composition of local spring waters from the hangingwall hydrothermal system (Reyes
et al., 2010) can be estimated by calculating the saturation indices of the secondary minerals in
the fluid using PHREEQC and the Ilul database (Parkhurst & Appelo, 1999). These calculations
(Parkhurst & Appelo, 1999) indicate that the mineral assemblage may be near equilibrium with
hot spring waters at ~90–100 °C (Fig. 6), which represents the latest stage mineralisation of
the fault zone. The hydrothermally altered cataclasite matrix is dominated by the latter minerals,
which co-exist with the CM in the matrix. We infer that hydrothermal precipitation of graphite,
if such did occur, was an accompaniement of this lower temperature alteration process (Fig. 6,
7).

Significance of hydrothermal graphite addition

Our preliminary conclusion in the previous section that there has been hydrothermal graphite
addition to the cataclasites raises some important structural and geochemical issues. Open
fractures in brittlely deformed cataclasites induce high permeability potentially allowing high
temperature fluids to be transported from middle to lower crust during earthquake events
(Oohashi et al., 2011). If graphite precipitates from these fluids, further fault rock weakening
and lubrication of fault movements may occur, creating more permeability, and additional
deposition of graphite (Upton & Craw, 2008). Carbon-bearing fluids with both meteoric and
metamorphic origins propagate through the Alpine Fault rocks (Jenkin, 1994; Upton et al.,
1995; Upton & Craw, 2003; Cox et al., 1997; Menzies et al., 2014). Meteoric waters dominate
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in the Southern Alps hydrothermal system right down to the brittle-ductile transition (Menzies et al. 2014) and therefore dominates in the cataclastic zone. These fluids contain both carbon dioxide and methane (Barnes et al. 1978), although CH₄ is subordinate to CO₂ (Jenkin et al. 1994).

Previous studies from greenschist-facies schist to the east of the Southern Alps (with similar composition to Alpine Schist) suggest that hydrothermal precipitation of graphite resulted from mixing of CO₂ and CH₄ fluids during Mesozoic metamorphism (Craw, 2002; Henne & Craw, 2012). Graphite deposition from a C – O – H bearing fluid is inevitable below 400 °C, because CO₂ and CH₄ at these temperatures can coexist in very small amounts only (Holloway 1984; Craw 2002; Huizenga 2011). Hydrothermal graphite can be deposited under these conditions via the reaction:

$$\text{CO}_2 + \text{CH}_4 = 2\text{C}_{\text{graphite}} + 2\text{H}_2\text{O} \quad (1)$$

This process may also be occurring in the modern Alpine Fault zone. However, the relative scarcity of CH₄ in the Alpine Schist fluids suggests that some additional reactions may be occurring, involving reduction of the abundant CO₂. A small but significant amount of pyrrhotite in the Alpine Schists is being transformed to pyrite during uplift, and this pyrite is widespread in the cataclasites (Fig. 2; Johnstone et al. 1990). This sulphide mineral transformation involves oxidation of sulphur, and coeval reduction of CO₂ to graphite may occur as part of this process, perhaps according to the following reactions (Fig. 7):

$$4\text{FeS} + 4\text{H}_2\text{S} + \text{CO}_2 = 4\text{FeS}_2 + 2\text{H}_2\text{O} + \text{H}_2 + \text{C}_{\text{graphite}} \quad (2)$$

$$4\text{FeS} + \text{CO}_2 = 2\text{FeS}_2 + 2\text{FeO}_{\text{silicates}} + \text{C}_{\text{graphite}} \quad (3)$$

Retrogressive or hydrothermal chlorite in the cataclasites (Fig. 2) is the most likely recipient of the FeO component in Equation 3. Irrespective of the actual reaction(s) involved, our
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Observations provide firm evidence that hydrothermal graphite is being deposited under near-greenschist facies conditions in the Alpine Fault zone cataclasites.

We also have evidence for transformation of fine-grained metamorphic graphite under ductile conditions at depth within the mylonitic zone of the Alpine Fault (Fig. 3). Dusty graphite along grain boundaries in amphibolite facies Alpine Schist coincides with the principal fluid flow permeability along grain boundaries in these rocks (Craw & Norris 1993). Hence, it is likely that at least some recrystallisation of metamorphic graphite has occurred, to emplace that graphite along grain boundaries. Furthermore, this dusty graphite becomes concentrated into clusters within the silicate minerals as they recrystallise in the mylonitic rocks nearer to the Alpine Fault (Fig. 3), which implies further remobilisation and recrystallisation of graphite. The scale of these remobilisation and recrystallisation processes may be small (micrometers to millimetres), but they are sufficient to completely transform the metamorphic graphite textures (Fig. 3). Since these amphibolite facies rocks were pervaded by CO$_2$-bearing fluid, with minor CH$_4$ (Craw & Norris 1993; Jenkin et al., 1994), the graphite formation probably occurred via Equation 1 (Fig. 7). However, CO$_2$ and CH$_4$ can coexist in higher concentrations under amphibolite facies conditions than in greenschist facies fluids (Holloway, 1984; Huizenga, 2011). Hence, the graphite formation process probably involved Equation 1 operating in both directions, resulting in localised remobilisation with no net increase in graphite contents of these rocks.

Significance for conductive geophysical signals

Magnetotelluric surveys in the central section of the Southern Alps demonstrate the existence of a high-conductivity zone in the mid-crust (at ~8 km depth), coinciding with the down-dip projection of the Alpine Fault (Wannamaker et al., 2002; Caldwell et al., 2012, 2013). This zone has been interpreted as a ductile shear zone, perhaps resulting from the presence of fluid
or interconnected graphite. The topic is of particular interest because the conductive zone in the ductile lower crust underlays the seismogenic zone of the Alpine Fault. Thus, a relationship between the two has been inferred and it was assumed that seismic events in the brittle zone might be triggered by stress response or fluid escape from the underlying ductile zone (Wannamaker et al., 2002; Caldwell et al., 2012, 2013).

The electrically conductive zone is relevant to the current study because of the potential role of graphite. Wannamaker et al. (2002) argued it is unlikely that interconnected graphite remains structurally coherent at greater depth and suggested that a combination of fluid and graphite is more likely to be the reason for the presence of highly conductive zone. But convincing evidence has not yet been documented for either of these cases. We observed locally connected dusty graphite at slickensided surfaces in the Alpine Fault cataclasites (Fig. 5f), but we do not have evidence that this graphite occurs on a larger scale, or could be preserved under ductile conditions.

Significance for gold mineralisation processes

Orogenic gold deposits in ancient metamorphic belts have formed from some combination of metamorphic, magmatic and meteoric fluids, and are typically hosted in greenschist facies rocks (Cox et al. 1995; Groves et al. 2003; Goldfarb et al. 2005; Large et al. 2011). The active hydrothermal system in the Southern Alps of New Zealand provides a modern analogue for many components of orogenic gold emplacement systems (Johnstone et al. 1990; Craw et al. 2009; Upton & Craw 2014; Pitcairn et al. 2014). Beneath the Southern Alps, metamorphic transformation from greenschist to amphibolite facies is releasing water, Au, As, and related metals from the rocks into the orogen-scale hydrothermal system, to be emplaced as small gold deposits at shallower levels (Craw et al. 2009; Upton & Craw 2014; Pitcairn et al. 2014). There
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is no associated modern-day magmatism, and the mineralising hydrothermal fluid is a mixture of metamorphic and meteoric water (Craw et al. 2009; Pitcairn et al. 2014; Menzies et al. 2014).

Some of the gold deposits in the hangingwall of the Alpine Fault are localised in graphitic greenschist facies schists, and the metamorphic graphite has apparently been responsible for facilitating reductive deposition of sulphide minerals and gold (Craw et al. 2009). However, no previous evidence has been found in any of the hydrothermal deposits for hydrothermal graphite deposition, with or without gold. The present study provides the first tentative evidence for hydrothermal graphite deposition in near-greenschist facies conditions from mixed metamorphic and meteoric fluids of the Alpine Schist active hydrothermal system. As yet, we have no evidence for coeval gold deposition associated with this hydrothermal graphite. However, our inference of the emplacement of hydrothermal graphite in the Alpine Fault cataclasites provides yet another component to the Southern Alps hydrothermal system as an analogue for ancient orogenic gold deposit formation processes.

The world-class Macraes orogenic gold mine (Craw 2002) is located east of the Southern Alps and is hosted in lower greenschist facies rocks, equivalent to, but of lower metamorphic grade than, the Alpine Schist described above. This deposit formed in a shear zone during uplift from ductile to brittle conditions in the latter stages of Mesozoic deformation and metamorphism. A distinctive feature of this deposit is the abundant hydrothermal graphite that was added to the shear zone during gold mineralisation (Craw 2002; Pitcairn et al. 2005; Hu et al. 2015). Deformation, fluid flow, and mineralisation were all facilitated by this hydrothermal graphite addition, and the graphite therefore contributed to the large scale of the mineralisation in the hosting structure (Craw 2002; Upton & Craw 2008). Our Alpine Fault observations show that similar metamorphic-hydrothermal graphite recrystallisation, emplacement, and subsequent deformation is occurring under near-greenschist facies conditions as these rocks are uplifted from ductile to brittle conditions.
Conclusions

We have documented the crystallinity and microstructural occurrence of graphite in the active Alpine Fault zone as a function of varying temperature and shear strain magnitude. Our study demonstrates that ongoing deformation processes and hydrothermal fluid flow resulted in deposition of graphite with different textural and structural characteristics throughout the examined rock sequences. Highly crystalline graphite, carried by the non-mylonitic amphibolite-facies Alpine Schist rocks, has apparently recrystallized during mylonitization of the metamorphic protolith. Brittle cataclasis associated with tectonic movements along the fault zone allowed penetration of C-bearing hydrothermal fluids. These fluids have extensively altered the silicates in the cataclasites and may have deposited hydrothermal graphite. We identified two coexisting generations of graphite in the Alpine Fault cataclasites on the basis of petrographic textures and Raman signals: (i) inherited graphite, in remnants of mylonitic clasts that carry the textural arrangement of mylonitic graphite; and (ii) less crystalline graphite which has accumulated in large dusty aggregates in the hydrothermally altered matrix of the cataclasites. RSCM thermometry of CM indicates peak metamorphic temperatures in the parent amphibolite facies schists consistent with previous studies in samples, representing the Alpine Schist and mylonite rocks. However, CM in the Alpine Fault cataclasites has a distinctly different Raman signal from that of the parent rocks, and we infer a hydrothermal origin for that material. Hydrothermal deposition of graphite in the fault zone may cause structural weakening if connected on a significant scale. Connected graphite could also result in higher electrical conductivity in a fault zone, enhancing a magnetotelluric signal.

Acknowledgement
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Table captions

Table 1 – Summary of petrographic and microstructural observations, and Raman data interpretations in the Alpine Fault rocks.

Figure captions

Figure 1 - (a) Tectonic setting of New Zealand, with the plate boundary, which is the Alpine Fault trace through the South Island, delineated by bold black line. Bathymetric map compiled by the National Institute of Water and Atmospheric Research of New Zealand. Red square indicates the study area. (b) Schematic cross section of typical Alpine Fault rock sequence, modified after Norris and Cooper (2007).

Figure 2 - Paragenetic diagram showing the distribution of mineral phases in the different Alpine Fault rock types. The diagram was created for the purpose of the current study.

Figure 3 - Backscattered SEM images of polished thin sections showing typical graphite textures in the Alpine Fault rocks. (a), (b) schist; (c), (d) protomylonite; and (e), (f) mylonite.
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Dark material labeled ‘Gr’ is graphite. White materials are labelled with Ox for oxide and Ilm for ilmenite.

*Figure 4* - Backscatter SEM images of polished thin sections of cataclasites from the Alpine Fault zone. Dark material labeled ‘Gr’ is graphite. It occurs either as pools (c), veins (a), or cements (b, d, e); or (f) seams we infer are equivalent to slickensided shear surfaces observed on rock chips.

*Figure 5* - Representative Raman spectra of graphite from the different types of Alpine Fault rocks.

*Figure 6* – Schematic diagram illustrating the temperatures of the the secondary minerals estimated by calculating the saturation indices of these minerals in the fluid using PHREEQC and the IIlnl database (Parkhurst & Appelo, 1999).

*Figure 7* – Schematic diagram illustrating the conditions under which we infer graphite is precipitated in the Alpine Fault zone. The diagram was created for the purpose of the current study.

References


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