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-feldspathic 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, hydrothermal, tectonic, fault, cataclasite, Raman, Alpine Fault – Deep Fault Drilling Project (DFDP).

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). 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 distibution 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 elecrically 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

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 focuss 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

99 The oblique-slip Alpine Fault (Fig. 1a) accommodates up to 75% of the 37 mm/yr relative
100 motion at the Australian – Pacific plate boundary, manifest as uplift of the fault hangingwall at
101 ~8 mm yr^{-1} and dextral strike slip at 27 ± 5 mm yr^{-1} (Norris & Cooper, 2001; Herman, et al.,
102 2009). At least 20 km of vertical uplift and exhumation has occurred along the fault, with total
103 strike-separation of ~480 km (Norris et al., 1990; Norris & Cooper, 1995). The transform plate
104 boundary fault strikes NE-SW and dips at 30 –50° to the SE. At 35 km depth, it soles out into a
105 major crustal decollement (Norris et al., 1990; Norris & Cooper, 1995; Kleffman et al., 1998;
106 Little et al., 2007).

107 Uplift and erosion of the fault zone has exhumed ductile mylonitic rocks from the middle crust,
108 while on-going near-surface deformation continues to form, and rework, cataclasites and
109 gouges which only partially overprint the older, deeper-formed mylonites (Fig. 1b). Thus, rocks
110 formed at the full range of depths over which shearing occurs in the fault zone outcrop at the
111 surface (Fig. 1b; Table 1). The active slip zone is marked by a thin (<5 cm) clay gouge layer,
112 forming the base of a 10 to 50 m-thick cataclasite unit composed of crushed angular mylonitic
113 clasts in a fine-grained matrix (Fig. 1b). These brittle rocks are now structurally overlain by a
114 ~1 km thick mylonite zone (Fig. 1b; Table 1). Based on degree of grain size reduction and
115 transposition of the original protolith fabric, these mylonitic rocks can be subdivided into
116 ultramylonites, mylonites and protomylonites (Toy et al., 2011). This mylonite zone
117 subdivision reflects the relative magnitude of finite ductile shear strain accommodated by those
118 variably foliated and lineated rocks, with increasingly higher strains accommodated nearer to
119 the fault. Most samples were collected on either sub-horizontal or vertical outcrop surfaces or
120 borehole samples. The Alpine Fault and its mylonitic foliation have an average attitude of
121 055/45 SE (Norris & Cooper, 2007). The mylonitic foliation is a spaced foliation largely
122 inherited from the protolith amphibolite facies quartzo-feldspathic Alpine Schist, and later (in
123 the Neogene) was cross-cut by extensional (C') shear bands (e.g., Little et al., 2002). The fabric

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-mylonitc 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 geothermal 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

148 50° C (Barnes et al 1978; Koons, 1987). Isotopic data also suggest metamorphic fluids mingle
149 with meteoric water within this system (Jenkin, 1994; Upton et al., 1995, 2003; Cox et al.,1997;
150 Koons, 1998).
151

152 Sample Description and Analytical Methods

153 *Samples*

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

164 For the aims of the current study we used a sample set of 22 thin sections from DFDP-2B,
165 equally distributed with depth, and five DFDP-1 thin sections, representing the principal slip
166 zone of the Alpine Fault, New Zealand. In the current manuscript we present data from samples
167 DFDP-2B 266 (schist), DFDP-2B 518 (protomylonite), DFDP-2B 890 (mylonite), DFDP-1A
168 69.1 (cataclasite) and DFDP-1A 69-2.61 (cataclasite). Sample nomenclature includes the name
169 of the corresponding drilling phase together with the drill depth in meters.

170 *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 collectedusing an Oxford Instruments X-Max^N 150 mm^2 silicon drift detetctor (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^4_{6h} = $P6_3/mmc$) 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,

~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 ($R1=I_{D1}/I_G$) [where I_i = intensity of the *i*th peak] and the area ratio ($R2=A_{D1}/(A_G+A_{D1}+A_{D2})$) [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= - 445R2 + 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

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

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

263 Fine micaceous material coexists with biotite porphyroblasts, platy muscovite flakes, and mica
264 fish. The biotite porphyroblasts are smaller than the ones observed in the shist rocks, their
265 margins are reworked by the foliation, and there are occasional domino structures. At the
266 protomylonite-mylonite transition, biotite is locally chloritised due to retrogressive

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 more fractured, with chlorite filling the cracks. These garnet porphyroblasts contain spiralled inclusion trails of the precursor non-mylonitic fabric, and typically have asymmetric strain shadows, but in the true mylonites only fragments of these garnets are found, some of which contain remnants of the inclusion trails. Opaque accessory minerals remain with the same chemical composition and in relatively the same amount as in the schist rocks.

Cataclasites

The cataclasites consist chiefly of intensely crushed mylonites, the fragments of which float in very fine to dusty-grained dark matrix. Asymmetric angular clasts up to 100 μm in size are bounded by a cataclastic foliation, and there is an anastomosing network of dark hairline layers (Table 1). Porphyroclastic quartzo-feldspathic mylonitic fragments, ranging up to a few hundred micrometers in size, are internally fracured with sub-rounded, irregular shapes. These fragments are cemented by a mixture of calcite and clay minerals with significant titanite and graphite, causing dark appearance. These clay minerals are very fine-grained, and some have been identified as illite, kaolinite and chlorite by using XRD in previous studies; kaolinite locally dominates (Warr & Cox, 2001; Boulton et al., 2012; Schleicher et al., 2015). Smectite has been identified in the thin, latest stage fault gouges (Boulton et al., 2012; Schleicher et al., 2015).

Graphite Textures

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

micrometer scale or finer) are dispersed mainly along grain boundaries in quartzo-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 quartzo-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

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. Simultaniously, 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

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 geothermomentry method relies on progressive maturation of originallly 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

360 domains in structurally controlled settings. Previous observations on graphite textures in
361 greenschist facies and at lower metamorphic grade schists, in equivalent non-mylonitic schists
362 further to the east of the Southern Alps, have identified graphite in close association with
363 metamorphic micaceous minerals (Craw 2002; Henne & Craw, 2012; Hu et al. 2015). However,
364 our study demonstrates that graphite mainly occurs within, or along grain boundaries of
365 quartzo-feldspathic domains, both in the protolith schists and in the mylonitic rocks (Fig. 3).
366 The principal exceptions are the graphitic inclusions in relict biotite porphyroblasts, which are
367 progressively reworked and recrystallised with increasing strain (Toy et al. 2010).

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

377 The abundance and textures of the second generation of graphite that occurs in the cataclasite
378 matrix supports observations on the silicate matrix that there has been extensive fluid-driven
379 modification in these rocks (Boulton et al., 2012). Locally abundant CM in these rocks (Fig. 4)
380 may result from either residual concentration during extensive dissolution of the silicate matrix,
381 or hydrothermal addition of graphite by the alteration fluids (Beyssac & Rumble, 2014; Galvez
382 et al., 2013a, b). Without detailed microchemical analyses of these CM-bearing rocks,
383 distinguishing these possibilities is difficult. However, petrographic observations of the

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 acknolwedge 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 permeabilty 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 percipitation 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 llnl 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 respresents 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 brittely 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 percipitates 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

433 in the Southern Alps hydrothermal system right down to the brittle-ductile transition (Menzies
434 et al. 2014) and therefore dominates in the cataclastic zone. These fluids contain both carbon
435 dioxide and methane (Barnes et al. 1978), although CH_4 is subordinate to CO_2 (Jenkin et al.
436 1994).

437 Previous studies from greenschist-facies schist to the east of the Southern Alps (with similar
438 composition to Alpine Schist) suggest that hydrothermal precipitation of graphite resulted from
439 mixing of CO_2 and CH_4 fluids during Mesozoic metamorphism (Craw, 2002; Henne & Craw,
440 2012). Graphite deposition from a C – O – H bearing fluid is inevitable below 400 ˚C, because
441 CO_2 and CH_4 at these temperatures can coexist in very small amounts only (Holloway 1984;
442 Craw 2002; Huizenga 2011). Hydrothermal graphite can be deposited under these conditions
443 via the reaction:

444 $$CO_2 + CH_4 = 2C_{graphite} + 2H_2O \quad (1)$$

445 This process may also be occurring in the modern Alpine Fault zone. However, the relative
446 scarcity of CH_4 in the Alpine Schist fluids suggests that some additional reactions may be
447 occurring, involving reduction of the abundant CO_2. A small but significant amount of
448 pyrrhotite in the Alpine Schists is being transformed to pyrite during uplift, and this pyrite is
449 widespread in the cataclasites (Fig. 2; Johnstone et al. 1990). This sulphide mineral
450 transformation involves oxidation of sulphur, and coeval reduction of CO_2 to graphite may
451 occur as part of this process, perhaps according to the following reactions (Fig. 7):

452 $$4FeS + 4H_2S + CO_2 = 4FeS_2 + 2H_2O + H_2 + C_{graphite} \quad (2)$$

453 $$4FeS + CO_2 = 2FeS_2 + 2FeO_{silicates} + C_{graphite} \quad (3)$$

454 Retrogressive or hydrothermal chlorite in the cataclasites (Fig. 2) is the most likely recipient of
455 the FeO component in Equation 3. Irrespective of the actual reaction(s) involved, our

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

480 or interconnected graphite. The topic is of particular interest because the conductive zone in the
481 ductile lower crust underlays the seismogenic zone of the Alpine Fault. Thus, a relationship
482 between the two has been inferred and it was assumed that seismic events in the brittle zone
483 might be triggered by stress response or fluid escape from the underlying ductile zone
484 (Wannamaker et al., 2002; Caldwell et al., 2012, 2013).

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

493 *Significance for gold mineralisation processes*

494 Orogenic gold deposits in ancient metamorphic belts have formed from some combination of
495 metamorphic, magmatic and meteoric fluids, and are typically hosted in greenschist facies rocks
496 (Cox et al. 1995; Groves et al. 2003; Goldfarb et al. 2005; Large et al. 2011). The active
497 hydrothermal system in the Southern Alps of New Zealand provides a modern analogue for
498 many components of orogenic gold emplacement systems (Johnstone et al. 1990; Craw et al.
499 2009; Upton & Craw 2014; Pitcairn et al. 2014). Beneath the Southern Alps, metamorphic
500 transformation from greenschist to amphibolite facies is releasing water, Au, As, and related
501 metals from the rocks into the orogen-scale hydrothermal system, to be emplaced as small gold
502 deposits at shallower levels (Craw et al. 2009; Upton & Craw 2014; Pitcairn et al. 2014). There

503 is no associated modern-day magmatism, and the mineralising hydrothermal fluid is a mixture
504 of metamorphic and meteoric water (Craw et al. 2009; Pitcairn et al. 2014; Menzies et al. 2014).

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

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

Conclusions

We have documented the crystallinity and microstructural occurance of graphite in the active Alpine Fault zone as a function of varying temperature and shear stain 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 hydrothermall 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.

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559 Raman data.

560

561 Table captions

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

564

565 Figure captions

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

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

573 *Figure 3* - Backscattered SEM images of polished thin sections showing typical graphite
574 textures in the Alpine Fault rocks. (a), (b) schist; (c), (d) protomylonite; and (e), (f) mylonite.

575 Dark material labeled ‘Gr’ is graphite. White materials are labelled with Ox for oxide and Ilm
576 for ilmenite

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

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

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

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

589

590 ## References

591 Barnes, I., Downes, C.J. & Hulston, J.R. 1978. Warm springs, South Island, New Zealand, and
592 their potential to yield laumontite. *American Journal of Science* 278, 1412–1427.

593 Berger, A., Herwegh, M., Schwarz, J. O. & Pultiz, B. 2011. Quantitative analysis of
594 crystal/grain sizes and their distributions in 2D and 3D. *Journal of Structural Geology* vol. 33
595 (12) pp. 1751-1763

596 Beyssac, O., Goffe´, B., Chopin, C. & Rouzaud, J. N. 2002a. Raman spectra of carbonaceous
597 material in metasediments: a new geothermometer. *Journal of Metamorphic Geology*, 20, 859–
598 871.

599 Beyssac, O., Rouzaud, J.-N., Goffe´, B., Brunet, F. & Chopin, C. 2002b. Graphitization in a
600 high-pressure, low-temperature metamorphic gradient: a Raman microspectroscopy and
601 HRTEM study. *Contributions to Mineralogy and Petrology*, 143, 19–31.

602 Beyssac, O., Goffe´, B., Petitet, J.-P., Froigneux, E., Moreau, M. & Rouzaud, J.-N. 2003a. On
603 the characterization of disordered and heterogeneous carbonaceous materials by Raman
604 spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 59,
605 2267–2276.

606 Beyssac, O., Brunet, F., Petitet, J.P., Goffe´, B. & Rouzaud, J.N. 2003b. Experimental study of
607 the microtextural and structural transformations of carbonaceous materials under pressure and
608 temperature. *European Journal of Mineralogy*, 15, 937–951.

609 Beyssac, O., Bollinger, L., Avouac, J.-P. & Goffe´, B. 2004. Thermal metamorphism in the
610 lesser Himalaya of Nepal determined from Raman spectroscopy of carbonaceous material.
611 *Earth and Planetary Science Letters*, 225, 233–241.

612 Beyssac, O & Lazzeri, M. 2012. Application of Raman spectroscopy to the study of graphitic
613 carbons in the Earth Sciences. *EMU Notes in Mineralogy*, Vol. 12, Chapter 12, 415–454

614 Beyssac, O & Rumble, D. 2014 Graphitic Carbon: A Ubiquitous, Diverse, and Useful
615 Geomaterial. *Element. An International Magazine of Mineralogy, Geochemistry and Petrology.*
616 Vol. 10, p. 415-420, doi:10.2113/gselements.10.6.415

617 Beyssac, O., Cox, S., Vry, J., Herman, F. 2016. Peak metamorphic temperatures and thermal
618 history of the Southern Alps (New Zealand). *Tectonophysics*, doi:10.1016/j.tecto.2015.12.024

619 Bierlein F.P., Cartwright I. & McKnight S. 2001. The role of carbonaceous “indicator” slates
620 in the genesis of lode gold mineralization in the western Lachlan Orogen, Victoria, southestern
621 Australia. *Econ Geol* 96: 431-451

622 Binu, L.S.S., Kehelpannala, K.V.W., Satish, K.M. &Wada, H. 2003. Multistage graphite
623 precipitation through protracted fluid flow in sheared metagranitoid, Digana, Sri Lanka:
624 evidence from stable isotopes. *Chemical Geology*, v. 197, p. 253-270.

625 Boulton, C., Carpenter, B.M., Toy, V. & Marone, C. 2012. Physical properties of surface
626 outcrop cataclastic fault rocks. *Geochem. Geophys. Geosyst.*, 13, Q01018,
627 doi:10.1029/2011GC003872

628 Caldwell, T.G., Bannister, S., Bourguignon, S., Hill, G.J., Bertrand, E.A., Bennie, S., L.,
629 Heise1, W., Ogawa, Y. & Bibby, H.M. 2012. EQC project ‘Electrical conductivity structure of
630 the Alpine Fault and its relationship to seismicity and seismogenesis’.

631 Caldwell, T.G., Heise, W., Ogawa, Y., Hill, G.J., Bertrand, E., A., Bennie, S.L., Bibby, H.M.
632 & Jiracek, G.R 2013. Electrical conductivity structure of the Alpine Fault, New Zealand – a 3D
633 anisotropic problem. *5th International Symposium on Three-Dimensional Electromagnetics,*
634 *Sapporo, Japan*, May 7-9, 2013.

635 Cooper, A.F. 1980. Retrograde alteration of chromian kyanite in metachert and amphibolite
636 whiteschist from the Southern Alps, New Zealand, with implications for uplift on the Alpine
637 Fault: *Contributions to Mineralogy and Petrology*, v. 75, p. 153–164,
638 doi:10.1007/BF00389775.

639 Cox, S.F., Sun, S-S., Etheridge, M.A., Wall, V.J., & Potter, T.F. 1995. Structural and
640 geochemical controls on the development of turbidite-hosted gold quartz vein deposits, Wattle
641 Gully mine, central Victoria, Australia. *Economic Geology*, v. 90, p. 1722-1746.

642 Cox, S. C., Craw, D. & Chamberlain, C. P. 1997. Structure and fluid migration in a late
643 Cenozoic duplex system forming the Main Divide in the central Southern Alps, New Zealand.
644 *New Zealand Journal of Geology and Geophysics*, 40, 359–373.

645 Cox, S.C., Stirling, M.W., Herman, F., Gerstenberger, M. & Ristau, J. 2012. Potentially active
646 faults in the rapidly eroding landscape adjacent to the Alpine Fault, central Southern Alps, New
647 Zealand. *Tectonics*, 31, TC2011.

648 Craw, D. & Norris, R.J. 1993. Grain boundary migration of water and carbon dioxide during
649 uplift of garnet-zone Alpine Schist, New Zealand. *Journal of Metamorphic Geology* 11: 371-
650 378.

651 Craw, D. 2002. Geochemistry of late metamorphic hydrothermal alteration and graphitisation
652 of host rock, Macraes gold mine, Otago Schist, New Zealand. *Chem Geol* 191: 257-275.

653 Craw, D., Upton, P. & MacKenzie, D.J. (2009) Hydrothermal alteration styles in ancient and
654 modern orogenic gold deposits, New Zealand. *New Zealand Journal of Geology and*
655 *Geophysics* 52: 11-26.

656 Craw, D. & Upton P. 2014. Graphite reaction weakening of fault rocks, and uplift of the
657 Annapurna Himal, central Nepal. *Geosphere* 10: 720-731.

658 Dentith, M. & Barrett, D. 2003. Geophysical exploration for graphite at Uley, South Australia.
659 *ASEG Special Publications* (3) 47 - 57

660 Dentith, M., Evans, S., Thiel, S., Gallardo, L., Joly, A. & Romano, S. (2013) A magnetotelluric
661 traverse across the southern Yilgarn Craton. *Geological Survey of Western Australia* Report
662 121, 43 pp.

663 Galvez, M., Beyssac, O., Martinez, I., Benzerara, K., Chaduteau, C., Malvoisin, B. &
664 Malavieille, J. 2013a. Graphite formation by carbonate reduction during subduction. *Nature*
665 *geoscience*, doi:10. 1038/NGEO1827

666 Galvez, M., Martinez, I., Beyssac, O., Benzerara, K., Agrinier, P. & Assayag, N. 2013b.
667 *Contrib Mineral Petrol* 166:1687–1708, doi:10.1007/s00410-013-0949-3

668 Gautneb H. & Tveten E. 2000. The geology, exploration and characterisation of graphite
669 deposits in the Jennestad area, Vesterålen, northern Norway. *NGU Bulletin* 436: 67-74.

670 Gillam, B. G., Little, T., A., Smith, E. & Toy, V., G. 2013. Reprint of Extensional shear band
671 development on the outer margin of the Alpine mylonite zone, Tatare Stream, Southern Alps,
672 New Zealand. *Journal of Structural Geology*, Volume 64, July 2014, Pages 115-134

673 Goldfarb, R.J., Baker, T., Dube, B., Groves, D.I., Hart, C.J. & Gosselin, P. 2005.Distribution,
674 character and genesis of gold deposits in metamorphic terranes. In: Hedenquist, J.W.,
675 Thompson, J.F.H., Goldfarb, R.J., Richards, J.P., (Eds.), *Economic Geology* 100th Anniversary
676 Volume, 407-450.

677 Grapes, R.H. & Watanabe, T. 1992. Metamorphism and uplift of Alpine Schist in the Franz
678 Josef– Fox area of the Southern Alps, New Zealand: *Journal of Metamorphic Geology*, v. 10,
679 p. 171–180, doi:10.1111/j.1525-1314.1992.tb00077.x.

680 Grapes, R. H. 1995. Uplift and exhumation of Alpine Schist, Southern Alps, New Zealand:
681 thermobarometric constraints. *New Zealand Journal of Geology & Geophysics*, 38, 525–533.

682 Groves, D.I., Goldfarb, R.J., Robert, F. & Hart, C.J. 2003. Gold deposits in metamorphic belts:
683 overview of current understanding, outstanding problems, future research, and exploration
684 significance. *Economic Geology* 98, 1-29.

685 Haak, V. & Hutton, R. 1986. Electrical resistivity in continental lower crust, in Nature of Lower
686 Continental Crust *Geological Society Special Publications*, 24, 35– 49

687 Heinson, G. S., Direen, N. G. & Gill, R. M. 2006. Magnetotelluric evidence for a deep-crustal
688 mineralizing system beneath the Olympic Dam iron oxide copper-gold deposit, southern
689 Australia. *Geology* 34: 573-576.

690 Henne, A. & Craw, D. 2012. Synmetamorphic carbon mobility and graphite enrichment in
691 metaturbidites as a precursor to orogenic gold mineralization, Otago Schist, New Zealand.
692 *Mineralium Deposita*, v. 47, p. 781-797.

693 Herman, F., Cox, S. C. & Kamp, P. J. J. 2009. Low-temperature thermochronology and
694 thermokinematic modeling of deformation, exhumation and development of 1061 topography
695 in the central Southern Alps, New Zealand. *Tectonics*, 28, TC5011, 1062
696 doi:10.1029/2008TC002367.

697 Holloway, J. R. 1984. Graphite-CH4-H2O-CO2 equilibria at low-grade metamorphic
698 conditions. *Geology*, v. 12, p. 455-458.

699 Hu, S., Evans, K., Craw, D., Rempel, K., Bourdet, J., Dick, J. & Grice, K. 2015. Raman
700 characterization of carbonaceous material in the Macraes orogenic gold deposit and
701 metasedimentary host rocks, New Zealand. *Ore Geology Reviews* 70: 80-95.

702 Huizenga, J-M. 2011. Thermodynamic modelling of a cooling C–O–H fluid–graphite system:
703 implications for hydrothermal graphite precipitation. *Mineralium Deposita*, v. 46, p. 23-33.

704 Jenkin, G. R. T., Craw, D. & Fallick, A. E. 1994. Stable isotopic and fluid inclusion evidence
705 for meteoric fluid penetration into an active mountain belt; Alpine Schist, New Zealand.
706 *Journal of Metamorphic Geology* 12, 429–444.

707 Jiracek, G. R., Gonzalez, V. M., Caldwell, T. G., Wannamaker, P. E. & Kilb, D. 2007.
708 Seismogenic, electrically conductive, and fluid zones at continental plate boundaries in New
709 Zealand, Himalaya, and California. A Continental Plate Boundary: Tectonics at South Island,
710 New Zealand. *AGU Geophysical Monograph* 175, 347-369.

711 Johnstone, R. D., Craw, D. & Rattenbury, M. S. 1990. Southern Alps Cu-Au hydrothermal
712 system, Westland, New Zealand. *Mineralium Deposita* 25 : 118-125.

713 Kaneki, S., Hirono, T., Mukoyoshi, H., Sampei, Y., Ikehara, M. 2016. Organochemical
714 characteristics of carbonaceous materials as indicators of heat recorded on an ancient plate-
715 subduction fault. *Geochemistry, Geophysics, Geosystems*, doi: 10.1002/2016GC006368.

716 Kleffmann, S., Davey, F. & Melhuish, A. 1998. Crustal structure in the central South Island,
717 New Zealand, from the Lake Pukaki Seismic Experiment. *New Zealand Journal of Geology*
718 *and Geophysics* 41 (1), 39–49.

719 Koons, P. O. 1987. Some thermal and mechanical consequences of rapid uplift: an example
720 from the Southern Alps, New Zealand. *Earth and Planetary Science Letters* 86, 307–319.

721 Koons, P. O., Craw, D., Cox, S. C., Upton, P., Templeton, A. S. & Chamberlain, C. P. 1998.
722 Fluid flow during active oblique convergence: a Southern Alps model from mechanical and
723 geochemical observations. *Geology*, 26, 159–162.

724 Kribeck, B., Sykorova, I., Machovic, V. & Laufek, F. 2008. Graphitization of organic matter
725 and fluid-deposited graphite in Paleoproterozoic (Birimian) black shales of the Kaya-Goren
726 greenstone belt (Burkina Faso, West Africa). *J Metam Geol* 26: 937-958

727 Kuo, L-W., Li, H., Smith, S. A. F. , Di Toro, G., Suppe, J., Song, S-R., Nielsen, S., Sheu, H-
728 S. & Si, J. 2014. Gouge graphitization and dynamic fault weakening during the 2008 Mw 7.9
729 Wenchuan earthquake. *Geology* 42: 47-50.

730 Large, R. R., Maslennikov, V. V., Robert, F., Danyushevshy, L. V. & Chang, Z. 2007.
731 Multistage sedimentary and metamorphic origin of pyrite and gold in the giant Sukhoi Log
732 deposit, Lena Gold Province, Russia. *Econ Geol* 105: 1233-1267

733 Large, R. R., Bull, S. W. & Maslennikov, V. V. 2011. A carbonaceous sedimentary source-rock
734 model for Carlin-type and orogenic gold deposits. *Econ Geol* 106: 331-358

735 Little, T. A., Holcombe, R. J. & Ilg, B. R. 2002. Kinematics of oblique collision and ramping
736 inferred from microstructures and strain in middle crustal rocks, central Southern Alps, New
737 Zealand. *Journal of Structural Geology*, v. 24, p. 219–239, doi:10.1016/S0191-8141(01)00060-
738 8.

739 Little, T. A., Cox, S. C. , Vry, J. K. & Batt, G. 2005. Variations in exhumation level and uplift-
740 rate along the oblique-slip Alpine Fault, central Southern Alps, New Zealand. *Geological*
741 *Society of America Bulletin*, 117(5), 707−723.

742 Little, T. A., Wightman, R., Holcombe, R. J. & Hill, M. 2007. Transpression models and ductile
743 deformation of the lower crust of the Pacific Plate in the central Southern Alps, a perspective
744 from structural geology, in A Continental Plate Boundary: Tectonics at South Island, New
745 Zealand edited by D. Okaya, T. Stern, F. Davey. *AGU Geophysical Monograph Series*, 175,
746 271-288.

747 Luque, F. J., Pasteris, J. D., Wopenka, B., Rodas, M., & Barrenechea, J. F. 1998. Natural fluid-
748 deposited graphite: mineralogical characteristics and mechanisms of formation. *American*
749 *Journal of Science*, v. 298, p. 471-498.

750 Luque, F. J., Ortega, L., Barrenechea, J. F., Millward, D., Beyssac, O. & Huizenga, J-M., (2009)
751 Deposition of highly crystalline graphite from moderate-temperature fluids. *Geology*, v. 37, p.
752 275-278.

753 Luque, F. J., Huizenga, J-M., Crespo-Feo, E., Wada, H., Ortega, L. & Barrenechea, J. F. 2014.
754 Vein graphite deposits: geological settings, origins, and economic significance. *Mineralium*
755 *Deposita*, v. 49, p. 261-277.

756 Menzies, C. D., Teagle, D. A. H., Craw, D., Cox, S. C., Boyce, A. J., Barrie, C. D. & Roberts,
757 S. 2014. Incursion of meteoric waters into the ductile regime in an active orogen. *Earth and*
758 *Planetary Letters* 399: 1-14

759 Nakamura, Y., Oohashi, K., Toyoshima, T., Satish-Kumar, M. & Akai, J. 2015. Strain-induced
760 amorphization of graphite in fault zones of the Hidaka metamorphic belt, Hokkaido, Japan.
761 *Journal of Structural Geology* 72: 142 – 161.

762 Norris, R. J., Koons, P. O. & Cooper A. F. (1990) The obliquely convergent plate boundary in
763 the South Island of New Zealand: implications for ancient collision zones, New Zealand.
764 *Journal of Structural Geology*, 12, 715-725.

765 Norris, R. J. & Cooper, A. F. 1995. Origin of small scale segmentation and transpressional
766 thrusting along the Alpine fault, New Zealand. *Geological Society of America Bulletin*, v. 107,
767 p. 231–240, doi:10.1130/0016-7606(1995)107 <0231:OOSSSA>2.3.CO;2.

768 Norris, R. J. & Cooper, A. F. 2001. Late Quaternary slip rates and slip-partitioning on the
769 Alpine Fault, New Zealand. *Journal of Structural Geology* 23, 507–520.

770 Norris, R. J. & Cooper, A. F. 2003. Very high strains recorded in mylonites along the Alpine
771 Fault, New Zealand: implications for the deep structure of plate boundary faults. *Journal of*
772 *Structural Geology* Vol.25(12), pp.2141-2157

773 Norris, R. J., &Cooper, A. F. 2007. The Alpine fault, New Zealand: Surface geology and field
774 relationships. *American Geophysical Union Geophysical Monograph* 175, p. 157–175.

775 Oohashi, K., Hirose, T., & Shimamoto, T. 2011. Shear-induced graphitization of carbonaceous
776 materials during seismic fault motion: Experiments and possible implications for fault
777 mechanics. *Journaal of Structural Geology*, v. 33, p. 1122-1134.

778 Parkhurst, D. L. & Appelo, C. A. J. 1999. User's guide to PHREEQC (Version 2) : a computer
779 program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical
780 calculations. *U.S. Geological Survey : Earth Science Information Center, Open-File Reports*
781 *Section [distributor], Water-Resources Investigations Report* 99-4259, xiv, 312 p. :ill. ;28 cm.

782 Pasteris, J. D. 1989. In situ analysis in geological thin-sections by laser Raman microprobe
783 spectroscopy: a cautionary note. *Applied Spectroscopy*, 43, 567–570.

784 Pitcairn, I. K., Roberts, S., Teagle, D. A. H. & Craw, D. 2005. Detecting hydrothermal graphite
785 deposition during metamorphism and gold mineralisation. *J Geol Soc London* 162: 429-432

786 Pitcairn, I. K., Craw, D. & Teagle, D. A. H. 2014. The gold conveyor belt: Large-scale gold
787 mobility in an active orogen. *Ore Geology Reviews* 62, 129-142.

788 Reyes, A. G., Christenson, B. W. & Faure, K. 2010. Sources of solutes and heat in low-enthalpy
789 mineral waters and their relation to tectonic setting, New Zealand. *Journal of Volcanology and*
790 *Geothermal Research* 192, 117-141.

791 Schleicher, A. M., Sutherland, R., Townend, J., Toy, V. G. & Pluijm, B. A. 2015. Clay mineral
792 formation and fabric development in the DFDP-1B borehole, central Alpine Fault, New
793 Zealand. *Journal of Geology and Geophysics*, DOI: 10.1080/00288306.2014.979841

794 Sforna, M., van Zuilen, M. & Philippot, P. 2014. Structural characterization by Raman
795 hyperspectral mapping of organic carbon in the 3.46 billion-year-old Apex chert, Western
796 Australia. *Geochimica et Cosmochimica Acta* 124: 18-33, doi:10.1016/j.gca.2013.09.031

797 Sutherland, R., Toy, V. G., Townend, J., Cox, S. C., Eccles, J. D., Faulkner, D. R., Prior, D. J.,
798 Norris, R. J., Mariani, E., Boulton, C., Carpenter, B. M., Menzies, C. D., Little, T. A., Hastings,
799 M., De Pascale, G. P., Langridge, R. M., Scott, H. R., Lindroos, Z. R., Fleming, B. & Kopf, A.
800 J. 2012. Drilling reveals fluid control on architecture and rupture of the Alpine fault, New
801 Zealand. *Geology, 40(12):* 1143-1146; doi: 10.1130/G33614.1

802 Toy, V. G., Craw, D., Cooper, A. F., Norris, R. J. 2010. Thermal regime in the central Alpine
803 Fault zone, New Zealand : constraints from microstructures, biotite chemistry and fluid
804 inclusion data. *Tectonophysics*, 485(1-4): 178-192;doi:10.1016/j.tecto.2009.12.013

805 Toy, V. G., Ritchie, S. & Sibson, R. 2011. Diverse habitats of pseudotachylytes in the Alpine
806 Fault Zone and relationships to current seismicity. *Geological Society London, Special*
807 *Publications*, v. 359, p. 115-133, doi: 10.1144/SP359.7

808 Toy, V. G., Prior D. J., Norris, R. J., Cooper, A. F. & Walrond, M. 2012. Relationships between
809 kinematic indicators and strain during syn-deformational exhumation of an oblique slip,
810 transpressive, plate boundary shear zone: The Alpine Fault, New Zealand. *Earth and Planetary*
811 *Science Letters*. Volumes 333–334, p. 282 – 292, doi:10.1016/j.epsl.2012.04.037Upton, P.,
812 Koons, P. O. & Chamberlain, C. P. 1995. Penetration of deformation-driven meteoric water

into ductile rocks: isotopic and model observations from the Southern Alps, New Zealand. *New Zealand Journal of Geology and Geophysics* 38, 535–543.

Upton, P. & Craw, D. 2003. Upper crustal fluid flow in the outboard region of the Southern Alps, New Zealand. *Geofluids*, 3, 1–12.

Upton P. & Craw D. 2008. Modelling the role of graphite in development of a mineralised mid-crustal shear zone, Macraes mine, New Zealand. *Earth Planet Sci Letters* 266: 245-255

Upton P. & Craw D. 2014. Modelling of structural and lithological controls on mobility of fluids and gold in orogenic belts, New Zealand. In: Garofalo PS, Ridley JR (eds) Gold-Transporting Hydrothermal Fluids in the Earth's Crust. *Geological Society of London Special Publication* 402: 231-253.

Wang L. J. and Chamalaun F. H. 1996. A magnetotelluric traverse across the Adelaide Geosyncline. *Exploration Geophysics* 26: 539 – 546.

Wannamaker, P. E., Jiracek, G. R., Stodt, J. A., Caldwell, T. G., Gonzalez, V. M., McKnight, D. & Porter, A. D. 2002. Fluid generation and pathways beneath an active compressional orogen, the New Zealand Southern Alps, inferred from magnetotelluric data. *Gournal of geophysical research*, vol. 107, No. B6, 10.1029/2001JB000186, 2002

Warr, L. N. & Cox, S. C. 2001. Clay mineral transformations and weakening mechanisms along the Alpine Fault, New Zealand. p. 85-101 IN: Holdsworth, R.E.; Strachan, R.A.; Magloughlin, J.F.; Knipe, R.J. The nature and tectonic significance of fault zone weakening. London. *Geological Society of London special publication* 186.

Won I. J. 1983. A sweep-frequency electromagnetic exploration method. Chapter 2. *Developments in Geophysical Exploration Methods-4* (AA Fitch, Ed).

835 Wopenka, B. & Pasteris, J. D. 1993. Structural characterization of kerogens to granulite-facies
836 graphite: applicability of Raman microprobe spectroscopy. *American Mineralogist* 78, 533–
837 557.