



Raman characterization of carbonaceous material in the Macraes orogenic gold deposit and metasedimentary host rocks, New Zealand



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ABSTRACT

Raman spectroscopic and petrographic analyses were performed on samples collected from zones distal and proximal to the Macraes gold deposit in the Otago Schist of New Zealand to characterize the features and possible origins of Carbonaceous Material (CM) and to assess the potential role of CM in the formation of gold deposits. CM is a common component in meta-sedimentary orogenic gold deposits, and it has been proposed that CM contributes to gold mineralization processes, but the details of the mechanisms responsible are not fully understood. Documentation of the origins of the Otago schist CM will improve our understanding of the role of CM in gold deposits.

This work has identified four types of CM of varying thermal maturity and origins from prehnite–pumpellyite grade to lower greenschist grade samples. In prehnite–pumpellyite and pumpellyite–actinolite grade rocks, low-maturity CM 1 coexists with framboidal pyrite, indicating an in-situ, sedimentary origin, with a potential association with the source of gold. Low crystallinity CM 2 is also found in low grade samples and is likely to have been deposited from fluids unrelated to gold mobilization. CM 3 is the highest maturity CM recognized. CM 3 is found in samples from the highest metamorphic grades studied (lower greenschist facies), where bands of CM 3 cross cut the foliation, CM 3 is therefore thought to have been transported by fluids, though possibly only at short length scales. CM 4 is less mature than CM 3 and is found in mineralized rocks in association with sulfide minerals and gold. CM 4 is likely to have a depositional origin but its precise role with respect to gold mineralization has not been identified.

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1. Introduction

Carbonaceous material (CM) is commonly associated with gold in metasediment-hosted orogenic and Carlin-type gold deposits (Bierlein et al., 2001; Cox et al., 1995; Large et al., 2011; Thomas et al., 2011). Detrital CM, especially in organic-matter (OM)-rich shales, can contribute to the sequestration of metals during sediment deposition, and these OM-rich sediments can then act as sources for metals during subsequent metamorphic processes (Large et al., 2011, 2012; Peters et al., 2007; Zhang et al., 1997). During ore deposition, the presence of CM in metasedimentary host rocks may facilitate precipitation of gold from hydrothermal fluids by chemical reduction (Bierlein et al., 2001; Cox et al., 1995; Craw et al., 2010; Goldfarb et al., 2007; Zoheir et al., 2008). Alternatively, CM may be deposited from hydrothermal fluids containing volatile organic compounds during gold deposit formation

(Craw, 2002; Gu et al., 2012; Huizenga, 2011; Luque et al., 1998; Luque et al., 2009; Vallance et al., 2003).

Because of the close associations between CM and gold in metasedimentary terranes, it is important to understand the nature of changes in CM during the transitions that occur with increasing metamorphism and associated fluid migration, and between primary source rocks and gold depositional systems. Metamorphism of detrital CM has been well studied in several metasedimentary belts (Beysac et al., 2002, 2003a; Landis, 1971; Pasteris and Wopenka, 1991; Rahl et al., 2005). However, links between organic maturation, CM mobility, and regional gold mineralization processes have received less attention.

The texture and structure of CM can be used to assess whether it has been remobilized, and to infer the role of CM in metal mobilization and deposition (Luque et al., 1998). The usual analytical methods employed to provide structural characterization of CM are quantitative reflectance, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and Raman microspectroscopy (Beysac et al., 2002, 2003a; Henne and Craw, 2012; Wopenka and Pasteris, 1993). With the advantages of in-situ analysis and high resolution data acquisition, Raman microspectroscopy has become increasingly popular (e.g.,

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Beyssac et al., 2002, 2003a; Jehlička et al., 2003; Pasteris and Wopenka, 2003; Quirico et al., 2005, 2009; Rahl et al., 2005). It has long been observed that Raman spectra are sensitive to changes in crystallinity and structure of CM, which largely depend on temperature during metamorphism. The graphitization is presumed to be an irreversible process (Beyssac et al., 2002; Wopenka and Pasteris, 1993). Beyssac et al. (2002), Lahfid et al. (2010) and Rahl et al. (2005) found a linear relationship between quantifiable features in the Raman spectra of CM and peak metamorphic temperature, and used this relationship to develop a geothermometer for metamorphic samples, which was calibrated for temperature ranges of 330–650 °C, 200–320 °C and 100–700 °C by the respective authors. However, few studies have combined the characteristics of Raman spectra with the petrographic features of CM in metamorphic rocks as a means to trace the origins of CM. It is the aim of this paper to use a combination of Raman and petrographic analysis to document the CM transformations that occurred during prograde metamorphism in a metamorphic belt in which Au is thought to have been mobilized by the same regional metamorphic processes (Large et al., 2012). The results are used to quantify the changes that have occurred to the CM within the linked metamorphic and hydrothermal systems.

Gold-bearing rocks used for this study are taken from the vicinity of the world-class Macraes orogenic gold deposit, which is hosted by the Otago Schist in southern New Zealand (Craw, 2002). The gold in this deposit was emplaced by metamorphic–hydrothermal fluids in the latter stages of metamorphism (Craw, 2002), and is thought to have been generated by metamorphism of host metasediments that contained gold accumulated during diagenesis (Large et al., 2012; Pitcairn et al., 2006). There is abundant CM throughout the host rock sequence, from low grade metamorphic schists to the gold deposit itself where hydrothermal enrichment of up to 3 wt.% carbon has occurred (Craw, 2002; Henne and Craw, 2012).

2. Geological setting and regional gold mobility

The Otago Schist is a Mesozoic metasedimentary belt with a core zone of upper greenschist facies rocks flanked on either side by zones

of progressively lower grade rocks (Fig. 1; Mortimer, 1993, 2000). The protoliths for the schist belt are Paleozoic turbidites which were metamorphosed to prehnite–pumpellyite facies in the Jurassic (Mackinnon, 1983; Mortimer, 1993). There is a generally symmetrical regional increase in metamorphic grade of these protolith metaturbidites through pumpellyite–actinolite facies and lower greenschist facies towards the core zone of the schist belt (Fig. 1; Mortimer, 1993). The rocks become progressively more recrystallized and foliated through this increase in metamorphic grade, and the schists in the core of the belt have been pervasively recrystallized with several generations of folding and foliation development (Mortimer, 1993). Amphibolite facies rocks underlie the core upper greenschist facies rocks, and these have been tectonically exposed farther to the northwest of the main belt (Mortimer, 2000; Pitcairn et al., 2006). In detail, the boundaries between metamorphic zones are commonly post-metamorphic structures, especially extensional faults that were initiated in the middle Cretaceous (Fig. 1; Deckert et al., 2002; Henne and Craw, 2012).

The consistent protolith composition that persists across the whole schist belt has enabled geochemical comparison of metal and metalloid contents at different metamorphic grades, in order to quantify metamorphogenic mobilization of these elements (Pitcairn et al., 2006, 2010, 2014). Gold and arsenic, in particular, have been demonstrably mobilized on a regional scale during metamorphism, with prominent decreases in contents of these elements in the transition from the lower greenschist facies to amphibolite facies (Pitcairn et al., 2006, 2014). These elements were initially weakly enriched compared to the average crustal concentrations, on a regional scale, in diagenetic pyrite in the prehnite–pumpellyite facies protoliths, and prograde metamorphic recrystallization of that pyrite facilitated mobilization of Au and As (Large et al., 2012; Pitcairn et al., 2006, 2010, 2014). Minor intercalated metabasic layers in the metamorphic pile did not contribute significantly to the amount of mobilized Au, and were local sinks for mobilized As (Pitcairn et al., 2014). The regional scale metamorphogenic mobilization of Au and As, along with other elements commonly associated with orogenic hydrothermal deposits, such as Sb, W, and Hg, has been responsible for widespread formation of orogenic

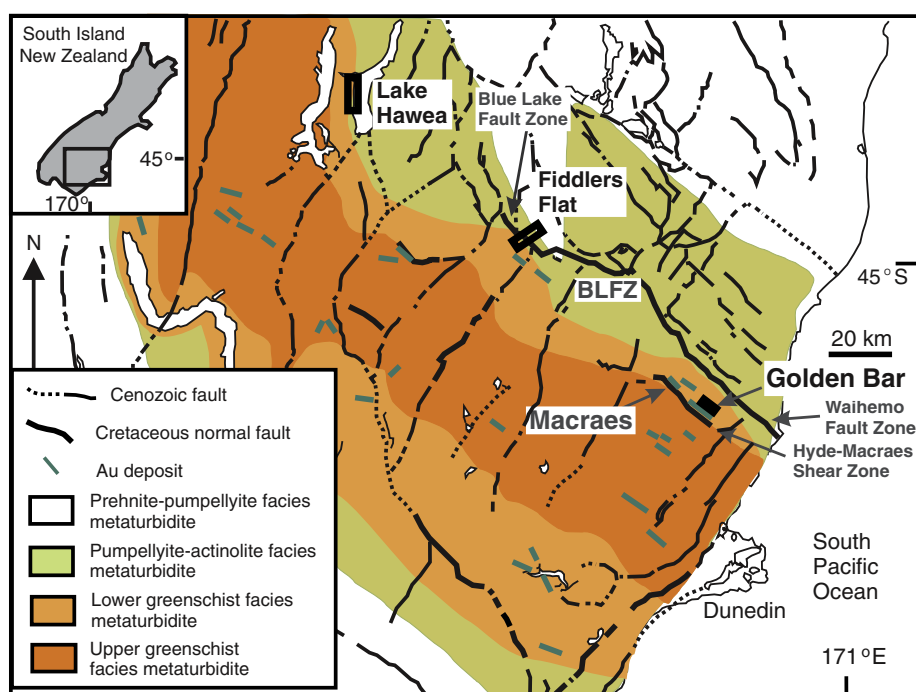


Fig. 1. Geological map of the Otago Schist in New Zealand (modified from Henne and Craw, 2012 and Pitcairn et al., 2005); the highlighted areas with black boxes are sampling locations, i.e., Lake Hawea, Fiddlers Flat and Golden Bar.

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