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Carbon dioxide generation and drawdown during active orogenesis of siliciclastic rocks in the Southern Alps, New Zealand

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A B S T R A C T

Collisonal mountain building influences the global carbon cycle through release of CO2 liberated by metamorphic reactions and promoting mechanical erosion that in turn increases chemical weathering and drawdown of atmospheric CO2. The Southern Alps is a carbonate-poor, siliciclastic mountain belt associated with the active Australian Pacific plate boundary. On-going, rapid tectonic uplift, metamorphism and hydrothermal activity are mobilising carbon. Here we use carbon isotope measurements of hot spring fluids and gases, metamorphic host rocks, and carbonate veins to establish a metamorphic carbon budget. We identify three major sources for CO2 within the Southern Alps: (1) the oxidation of graphite; (2) consumption of calcite by metamorphic reactions at the greenschist–amphibolite facies boundary, and (3) the dissolution of groundmass and vein-hosted calcite. There is only a minor component of mantle CO2 arising on the Alpine Fault. Hot springs have molar HCO3 /Ca2+ ∼ 9, which is substantially higher than produced by the dissolution of calcite indicating that deeper metamorphic processes must dominate. The total CO2 flux to the near surface environment in the high uplift region of the Southern Alps is estimated to be 6.4 × 109 mol/yr. Approximately 87% of this CO2 is sourced from coupled graphite oxidation (25%) and disseminated calcite decarbonation (62%) reactions during prograde metamorphism. Dissolution of calcite and mantle-derived CO2 contribute ∼ 10% and ∼ 3% respectively. In carbonate-rich orogens CO2 production is dominated by metamorphic decarbonation of limestones. The CO2 flux to the atmosphere from degassing of hot springs in the Southern Alps is 1.9 × 108 mol/yr, which is 30–50% of the flux to the near surface environment. By contrast, the drawdown of CO2 through surficial chemical weathering ranges between 2.7 and 20 × 108 mol/yr, at least an order of magnitude greater than the CO2 flux to the atmosphere from this orogenic belt. Thus, siliciclastic mountain belts like the Southern Alps are net sinks for atmospheric CO2, in contrast to orogens involving abundant carbonate rocks, such as the Himalaya, that are net CO2 sources.

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1. Introduction

Collisonal mountain belts may have been significant sources and/or sinks of atmospheric CO2 over geological time through the generation of CO2 in metamorphic reactions and drawdown of CO2 during enhanced chemical weathering of silicates. Uplift of the Himalaya and Tibetan plateau and resulting enhanced weathering over the past 40 Myr has been attributed as a driving force for global late Cenozoic cooling (Raymo and Ruddiman, 1992), and orogenic cycles have undoubtedly influenced the global carbon cycle (Bickle, 1996), but the balance between CO2 drawdown and release is poorly constrained and the overall effect results from variations in local climate, tectonic setting, rock type, and duration of the mountain building.

Active orogenic belts are estimated to currently be adding equivalent amounts of CO2 to that from volcanoes (Kerrick et al., 1995; 0.7 to 3.5 × 1012 mol/yr of CO2 from mid ocean ridges, and 1.5–3.6 × 1012 mol/yr from volcanic arcs, Kelemen and Manning, 2015). The presence of metamorphic calc-silicate minerals in high grade rocks and abundant limestones in many orogenic belts, such as the North American Cordillera, the Himalaya, the
European Alps, and numerous portions of the SW Pacific Rim in Indonesia and New Guinea, is evidence that organic CO₂ is mainly generated by metamorphic decarbonation as described by the simplified Ca-endmember reaction: limestone + quartz = wollastonite + CO₂. In the Himalaya high grade decarbonation reactions produce abundant CO₂, most (~70%) of which migrates to the surface via thermal springs (0.9 × 10⁻¹² mol CO₂/yr for the Himalayan orogen; Becker et al., 2008; Evans et al., 2008).

Active tectonics, steep slopes, and orographic effects mean that mountain belts are sites of rapid physical erosion. The resulting comminution and generation of fresh mineral surfaces can lead to elevated rates of chemical weathering. Weathering of calcium silicates generates a sink for CO₂ through reactions of the form: 2CaO + H₂O + CaAl₂Si₂O₈ (anorthite) → Ca²⁺ + Al₂Si₂O₅(OH)₄ (kaolinite) + 2HCO₃⁻ where two moles of CO₂ are drawn down during weathering reactions although one mole is subsequently released if the precipitation of marine carbonates occurs (Brady, 1991). The effectiveness of such silicate weathering reactions and net drawdown of CO₂ remain debated, but the best estimate of CO₂ removal rate for the present day is ~11.7 × 10⁻¹² mol CO₂/yr by silicate weathering and ~24 × 10⁻¹² mol CO₂/yr total including carbonate weathering (Gaillarret et al., 1999). Approximately 0.27 × 10⁻¹² mol CO₂/yr is drawn down through weathering reactions in the Himalayan Ganges–Brahmaputra basin (Galy and France-Lanord, 1999), a factor of three to four lower than the estimated release from metamorphic reactions in this region (Becker et al., 2008; Evans et al., 2008).

In contrast, some active mountain belts, such as in Taiwan and the Southern Alps, New Zealand, contain relatively few carbonate rocks and comprise siliciclastic metasediments with low carbon contents (~<2 wt.% C, Pitcairn et al., 2006). These rocks contain carbon as variably matured organic debris, and metamorphic interstitial carbonate and veins. However, CO₂-effusing warm springs are also common in these mountain belts (Barnes et al., 1978; Upton et al., 2011). The contribution of these low-carbon rocks to the global CO₂ budget is poorly constrained and likely to be small. Nevertheless, the crustal processes that generate this CO₂ in low-carbon orogenic belts are of interest, as they may also be operating in the major carbonate-bearing mountain chains but are obscured by the overwhelming supply of limestone-derived CO₂. The proportion of the total metamorphic CO₂ flux these processes constitute will depend on the mineralogy and organic carbon content of the metamorphic pile. In this paper, we evaluate the potential deep sources for CO₂ in the active low carbon orogen of the Southern Alps, New Zealand. We define the relative contributions of different key metamorphic reactions, and provide estimates of the likely fluxes of CO₂ to the surface environment from the various deep sources within the active mountain belt. This flux is then compared with estimates of CO₂ drawdown through weathering for this area to estimate the net CO₂ balance for a siliciclastic orogenic belt.

1.1. Geological and tectonic setting

The South Island of New Zealand lies astride the Pacific-Australian plate boundary, and is being deformed by oblique dextral collision of these plates (Cox and Sutherland, 2007). The basement rocks are Palaeozoic–Mesozoic siliciclastic metasedimentary rocks that were variably metamorphosed in the Mesozoic during terrane accretion on the margin of Gondwana (Mortimer, 2004). Since the onset of convergence along this plate boundary in the Miocene (Sutherland et al., 2000), these basement rocks are being reformed and metamorphosed to amphibolite facies as they pass through the modern orogen in a 5 km thick zone beneath the Southern Alps (Pitcairn et al., 2014).

The metasedimentary rocks are being uplifted to form the >3000 m Southern Alps orogenic belt on the hangingwall of the Alpine Fault, the main plate boundary structure (Cox and Sutherland, 2007). Long-term, multiple-earthquake, uplift rates vary from >8 mm/yr adjacent to the Alpine Fault, to <1 mm/year in the high mountains (Main Divide region) and their eastern slopes (Outboard Zone, Fig. 1) (Norris and Cooper, 2007; Teagle et al., 1998). Erosion rates in the Inboard Zone near the Alpine fault are similar to uplift rates, so that the western slopes of the mountains retain a near steady state topographic profile, and upper greenschist to amphibolite facies metasediments are being rapidly exhumed from the middle crust (Koons, 1989). This rapid exhumation results in a high geothermal gradient, with temperatures of 350 °C as shallow as 6–8 km (Koons, 1987). Consequently the brittle-ductile transition has been raised from a regional normal of 10–12 km to form a shallow base to the seismogenic zone at ~8–10 km depth (Boese et al., 2012).

The high mountains and their eastern slopes consist of low grade (greenschist facies and lower) Mesozoic metasediments that are dominated by metagreywackes (lithic sandstones) with interlayered meta-argillites and minor metabasites (Cox and Barrell, 2007; Grapes and Watanabe, 1992) that are lithologically and geochemically similar to the high grade rocks that are being exhumed along the Alpine Fault (Fig. 1).

The principal slip zone of the Alpine Fault acts as a barrier to cross fault fluid flow throughout the crust (Menzies et al., 2016; Sutherland et al., 2012) and combined with the steep topography and the high geothermal gradient results in geothermal circulation in the Alpine Fault hangingwall (Menzies et al., 2016). Hot springs occur in deeply-incised valleys up to 17 km east of the Alpine Fault and deeper fluid flow causes deposition of hydrothermal veins from the near-surface to the middle crust (Fig. 1) (Menzies et al., 2014). The hot spring fluids commonly effervesce CO₂, and trapped metamorphic fluids studied in fluid inclusions in quartz veins contain abundant CO₂ (up to 5 mol% end member fluid, Craw and Norris, 1993).

2. Methods

To investigate the behaviour of carbon in the Southern Alps orogenic belt, we have analyzed basement rock samples spanning an exhumed crustal cross section from prehnite–pumpellylite facies to garnet–oligoclase amphibolite facies for total carbon content, total organic carbon and carbonate content, δ¹³C values of organic carbon/graphite and δ¹³C values of active geothermal fluids and calcite veins throughout the crust. This study has made use of a well characterised collection of rock samples taken from the full suite of metamorphic grades through the Mesozoic and Cenozoic orogens (Pitcairn et al., 2006). Samples were obtained from fresh outcrops in road cuts and river gorges. Samples of Cenozoic calcite-bearing veins were collected from amphibolite facies rocks in river gorges and glaciated exposures near the Alpine Fault (Menzies et al., 2014).

Spring waters were collected following Menzies et al. (2016) and river waters were sampled following the same protocols, although alkalinity titrations were carried out using 0.01 N HNO₃. Major cations in river water samples were analyzed by a Perkin Elmer Optima 4300 DV ICP-OES at the National Oceanography Centre Southampton following Menzies et al. (2016). Precision and accuracy were assessed using internal reference solution SLR54 and in-house reference solution Sco2/15 resulting in precision better than 7% and accuracy better than 6%.

Total carbon contents and total organic carbon contents were analyzed on bulk rock powders on an elemental analyzer (EA). Traces of carbonate C were removed by reaction with dilute (3N) HCl, followed by washing in distilled H₂O (Könitzer et al., 2012).
Fig. 1. a) Geological map of South Island, New Zealand coloured by metamorphic grade of the Haast Schist. Sample locations and numbers are marked. Dashed line indicates location of resistivity cross section in part b and shaded dashed box outlines the area of modern day rapid uplift. b) Cross section of central South Island along dashed line A to B from Menzies et al. (2016). Zone of active metamorphism is shown as a “crustal root” beneath the orogen and down dip of the resistivity anomaly.
The $\delta^{13}$C of TOC and TC were determined at the University of Michigan with a Costech EA coupled to a Thermo Scientific Delta V plus isotope ratio MS (IRMS), using IAEA 600 Caffeine ($\delta^{13}$C = −27.77‰ VPDB) and IAEA-CH-6 Sucrose (−10.45‰) as calibration standards. Rock powders were degassed at 100 °C and stored under vacuum to minimize adsorption of atmospheric CO$_2$. Duplicate analyses of low-C content samples (<500 ppm) were within ±70 ppm and ±0.5‰ $\delta^{13}$C. Carbon blanks are less than 6% of reported C contents.

3. Results

3.1. Carbon in river and spring waters

River waters and shallow recharge groundwaters typically contain 123 to 899 μmol/L dissolved HCO$_3^−$ (Table S1) and show a 2:1 relationship between dissolved HCO$_3^−$ and Ca$^{2+}$ that reflects calcite dissolution that involves atmospheric CO$_2$ as carbonic acid (Fig. 2). This trend is distinctly different from one which involves calcite dissolution via acid reactions that is typical of deeper groundwaters and has a 1:1 molar relationship (Fig. 2). In contrast, spring waters show a strong trend towards high dissolved HCO$_3^−$, ranging up to 19,000 μmol/L at relatively low Ca$^{2+}$ concentrations (Fig. 2A, Menzies et al., 2018). The dissolved carbon concentrations of these springs are minima because many effervescence of CO$_2$ and precipitate calcite as they upwell. The abundant rain on the west side of the mountains contains low concentrations of dissolved carbon (<20 μmol/L HCO$_3^−$, Fig. 2; Cox et al., 2015; Jacobson et al., 2003).

When carbon is released during metamorphic decarbonation reactions the molar HCO$_3^−$/Ca$^{2+}$ ratio of the resulting metamorphic fluids would be significantly greater than 2 as CO$_2$ is released from carbonates and Ca sequestered in calcium silicates (Fig. 2). The high HCO$_3^−$/Ca$^{2+}$ ratios of warm springs in the Southern Alps (7–19) may indicate that decarbonation reactions are occurring even though carbonate is a minor component of the rock mass.

3.2. Rock organic carbon contents and isotope compositions

The total organic carbon (TOC) contents of the rocks are typically <0.3 wt% at all metamorphic grades, although our data suggest that the upper greenschist and amphibolite facies rocks have slightly lower TOC contents than lower grade rocks (Fig. 3a), but the difference is insignificant above 72% confidence levels. Organically derived graphic carbon occurs in a wide range of textures across the spectrum of metamorphic grades formed during the Mesozoic (Beyssac et al., 2016). In the lowest grade rocks, the carbonaceous material is typically irregularly shaped 1–10 μm particles distributed through the relict sedimentary rock textures (Hu et al., 2015). FT-IR spectra identify significant less-well-ordered kerogen in carbonaceous material from unmetamorphosed greywacke to Greenschist Facies schist (Pitcairn et al., 2005). Carbonaceous material also occurs in rocks of higher metamorphic grade and in general most of this material is more mature with fewer short chain hydrocarbons, although carbonaceous material from some Amphibolite Facies Alpine Schist retain immature kerogen as shown by FT-IR spectra (Pitcairn et al., 2005). The presence of immature hydrocarbons in carbonaceous material at greenschist and amphibolite facies may facilitate oxidation of rock mass carbon. Several studies have shown carbonaceous material from such metamorphic facies display evidence of graphite remobilisation in ductile and brittle shear structures (Henne and Craw, 2012; Hu et al., 2015; Kirilova et al., in press; Pitcairn et al., 2005).

The $\delta^{13}$C values of the graphitic material range between −29.5 and −17.2‰ (Table 1; Fig. 4). As inferred Mesozoic metamorphic temperatures of the rocks increase, the $\delta^{13}$C values of the graphitic material in the rocks also increase, from −26.1‰ (average, n = 6) in low grade to prehnite–pumpellyite facies rocks to −20.4‰ (average, n = 8) in upper greenschist and amphibolite facies rocks. Rayleigh distillation calculations suggest that the carbonaceous material matured during the Mesozoic metamorphism by CH$_4$ production as opposed to CO$_2$ loss (Fig. 4). Upper greenschist facies graphic material entering the Cenozoic Southern Alps orogen has $\delta^{13}$C = −22.5 to −20.3‰ and the resulting amphibolite facies schists exhumed adjacent to the Alpine Fault have...
graphitic material with $\delta^{13}$C values ranging between $-22.0$ and $-18.5\%$ ($n = 4$) (Fig. 4).

3.3. Calcite contents and carbon isotope composition

Calcite is a minor constituent of the rock mass in the Southern Alps and commonly occurs in veins (Jenkin et al., 1994; Menzies et al., 2014). The carbonate concentration of the rocks does not vary significantly across metamorphic grades (Fig. 3b), the difference is insignificant above 50% confidence levels. In the modern orogen, this calcite was remobilised in the Alpine Fault hangingwall, and calcite is found as a vein mineral from the brittle to ductile transition zone to the near surface in the Alpine Fault Zone and extends further east into the Main Divide (Menzies et al., 2014). This calcite precipitated at a wide range of temperatures and depths ($<1$ km to $>6$ km depth) (Jenkin et al., 1994; Menzies et al., 2014).

Mesozoic metamorphic calcite has $\delta^{13}$C values ranging between $-11 \text{ and } -6\%$ (Templeton et al., 1998), in equilibrium with CO$_2$ having $\delta^{13}$C values of $-9.7 \text{ to } -4.7\%$ at 250°C (using fractionation equation of Bottinga (1968)). In the Alpine Fault Zone the $\delta^{13}$C values of CO$_2$ in equilibrium with calcite range between $-10.1 \text{ and } -3.8\%$ (Fig. 5). Modern day hot springs in the Southern Alps have $\delta^{13}$C$_{CO2}$ values ranging between $-16.8 \text{ and } -5.7\%$ with an average of $-9.1 \pm 4\%$ (Fig. 5, Menzies et al., 2016), indicating CO$_2$ in the springs and Cenozoic veins may be in part derived from the remobilisation of Mesozoic calcite (Fig. 5). However, high HCO$_3$ to Ca$^{2+}$ ratios in the springs (Fig. 2) preclude calcite dissolution being the sole source for CO$_2$, unless significant calcium is removed by metamorphic reactions. An alternative would be the shallow precipitation beneath the springs of secondary non-carbonate calcium minerals, but this has not been observed.

4. Discussion

4.1. Metamorphic reactions producing CO$_2$ in Alpine Schist

The principal reactions involving Ca-bearing phases that occur in the Alpine orogenic metamorphism from greenschist to amphibolite facies schist are the formation of oligoclase and breakdown of epidote and replacement of titanite by ilmenite (eq. (2)) (Grapes and Watanabe, 1992). Either or both of the two carbon-bearing minerals, graphite and calcite, may be involved in reactions at this metamorphic transition, but modal changes must be small as their abundances are statistically similar in both greenschist facies rocks and amphibolite facies hangingwall schists next to the Alpine Fault (Table 1; Fig. 3). Hence, we restrict our calculations to $<10\%$ calcite and/or graphite loss (see mass balance below, Table 2).

Dissolved oxygen in metamorphic fluids near the greenschist-amphibolite facies transition, in the presence of graphite, is negligible, with log fo$_2 \sim -45$ (calculated using Geochemist’s Workbench). Consequently, oxidation of graphite requires redox reactions that do not involve free oxygen. The reduction of epidote ferric iron to ferrous iron-bearing ilmenite provides a potential redox partner for the oxidation of graphite. Greenschist facies quartzofeldspathic schist contains $\approx 4\%$ epideite and minor greenschist facies metabasic schist contains $\approx 10\%$ wt.% epidote (Grapes and Watanabe, 1992). This epidote is typically $P_s = 20$ at greenschist facies, so contains $\approx 6\%$ Fe$^{2+}$ (Grapes and Watanabe, 1992).

CO$_2$ generated during such reactions at the greenschist-amphibolite facies transition ($\sim 550^\circ C$) would have $\delta^{13}$C values of $-14.4 \text{ to } -7.8\%$ which is similar to the range of recorded $\delta^{13}$C$_{CO2}$ values in spring waters ($-16.8 \text{ to } -5.7\%$), and to $\delta^{13}$C values of CO$_2$ in equilibrium with calcite veins ($-11.7 \text{ to } -3.8\%$) (Fig. 5).

Metamorphic decarbonation of calcite is the other principal potential source of metamorphic CO$_2$ (Table 2). Quartzofeldspathic schist is calcium-poor, typically containing $\sim 2\%$ wt.% CaO (Pitcairn, 2004). In greenschist facies rocks, Ca is present as calcite ($\sim 1-5$ modal %), epidote ($\sim 4\%$) and titanite ($\sim 1-2\%$), with rare actinolite. Prograde metamorphism to amphibolite facies in the Alpine orogen generates $\sim 20\%$ oligoclase of An$_{20}$ from the breakdown of epidote and titanite and replacement of albite. This reaction may also involve the breakdown of calcite (Grapes and Otsuki, 1983) consuming Ca and releasing CO$_2$. Minor metasomatisch schists have $\sim 10\%$ wt.% CaO and undergo similar mineralogical changes at the greenschist to amphibolite facies transition, although they have a greater proportion of epidote (10%) which breaks down to form hornblende (20%) and oligoclase (20%) at amphibolite facies.

4.2. Mass balance at the greenschist to amphibolite facies transition

The greenschist to amphibolite facies metamorphic transformation may facilitate the release of CO$_2$, whilst consuming Ca, in order to satisfy the elevated HCO$_3$/Ca ratios measured in modern day spring waters. This can be summarised with the following
reaction that includes the major components in appropriate proportions (based on measured mineral modes) that consumes minor amounts of both calcite and graphite:

\[ 5.3\text{NaAlSi}_{3}O_{8}\text{(Albite)} + 0.3\text{CaTiSiO}_{5}\text{(Titanite)} + 0.7\text{CaAl}_{2.5}\text{Fe}_{0.5}\text{Si}_{3}\text{O}_{12}\text{(OH)}\text{( Epidote)} + 0.2\text{CaCO}_{3}\text{(Calcite)} + 0.08\text{C}\text{(Graphite)} = 5.83\text{Na}_{0.8}\text{Ca}_{0.2}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_{5}\text{(Oligoclase)} + 0.3\text{FeTiO}_{3}\text{(Ilmenite)} + 0.28\text{CO}_{2} + 1.87\text{SiO}_{2} + 0.33\text{H}_{2}\text{O} + 0.32\text{Na}_{2}\text{O}\text{(goes into paragonite in mica)} + 0.33\text{O}_{2} \]  

(2)

This reaction consumes no more than 10% of the calcite or graphite present and liberates 4.2 mmol (0.18 g) of CO₂ per 100 g of rock (Table 2).

**Table 2**

Summary of changes in mineralogy at the greenschist to amphibolite facies transition and associated reactions that generate CO₂ based on mineral proportions outlined in eq. (2) and consuming no more than 10% of the carbon-bearing minerals.

| Sample | Lith. | Met. | T (°C) | TOC (wt.%) | TC (wt.%) | CaCO₃ wt.% | δ¹³C_graphite (%) |
|--------|-------|------|--------|------------|-----------|------------|------------------|
| C46    | GR_E  | Porters Pass | GW | Low P–P | 100 | 0.07 | 0.09 | 0.03 | −26.2 |
| C47    | GR_E  | Porters Pass | GW | Low P–P | 100 | 0.02 | 0.06 | 0.05 | −26.1 |
| C29    | 2009000 | 5457500 | Taieri | Low P–P | 100 | 0.54 | 0.55 | 0.01 | −22.1 |
| A68    | 2120000 | 5626000 | Hawea | Pel | P–P | 200 | 0.37 | 1.01 | 0.64 | −25.0 |
| A3     | 2265000 | 5582000 | Oturehua | Pel | P–P | 200 | 0.24 | 0.33 | 0.09 | −27.4 |
| B84    | 2150000 | 5570500 | Glenorchy | Pel | P–P | 200 | 0.06 | 0.15 | 0.09 | −29.3 |
| B14    | 2070500 | 5632500 | Hawea | Pel | Chlor GS | 300 | 0.23 | 0.42 | 0.19 | −22.3 |
| B92    | 2155000 | 5563000 | Glenorchy | Pel | Chlor GS | 300 | 0.20 | 0.22 | 0.07 | −24.1 |
| B52    | 2180900 | 5567000 | Remarks | Psam | Chlor GS | 400 | 0.02 | 1.07 | 1.05 | −22.5 |
| C72    | 2219700 | 5613800 | Pleasant Flat | QFS | Chlor GS | 400 | 0.01 | 0.22 | 0.20 | −25.3 |
| C68    | 2222900 | 5668500 | Haast | QFS | Biot GS | 500 | 0.70 | 0.87 | 0.17 | −21.0 |
| C35    | 2382844 | 5829246 | Rocky Point | QFS | Biot GS | 500 | 0.22 | 0.37 | 0.15 | −21.7 |
| C64    | 2218700 | 5681100 | Haast | QFS | Garn GS | 550 | 0.15 | 0.28 | 0.14 | −17.2 |
| C50    | 2281200 | 5674989 | Haast | QFS | Garn GS | 550 | 0.17 | 0.18 | 0.01 | −21.0 |
| C59    | 2208700 | 5687900 | Haast | QFS | G–O Amph | 600 | 0.12 | 0.13 | 0.01 | −21.1 |
| C56    | 2090900 | 5668800 | Haast | QFS | G–O Amph | 600 | 0.08 | 0.15 | 0.07 | −19.6 |
| C75    | 2107200 | 5609050 | Haast – AF | QFS | G–O Amph | 600 | 0.04 | 0.14 | 0.09 | −18.5 |
| C36    | 2368700 | 5820000 | Northern – AF | PM | G–O Amph | 600 | 0.15 | 0.31 | 0.16 | −22.0 |
| C70+   | 2223100 | 5686300 | Haast | QFS | Gs – Chlor | 450 | 0.11 | nd | nd | −22.5 |
| C84    | 2219200 | 5687000 | Haast | QFS | Gs – Biot | 500 | 0.25 | nd | nd | −20.3 |
| C74    | 2216100 | 5688400 | Haast | MB | Gs – Biot | 500 | 0.01 | nd | nd | −26.2 |
| C66    | 2225500 | 5686700 | Haast | QFS | Gs – Biot | 500 | 0.29 | nd | nd | −22.5 |
| C76    | 2209000 | 5688800 | Haast | QFS | Gs – Garn | 550 | 0.11 | nd | nd | −23.9 |
| C77    | 2209000 | 5688800 | Haast | QFS | Gs – Garn | 550 | 0.11 | nd | nd | −21.6 |
| C50    | 2282100 | 5746989 | Franz Josef – AF | QFS | Gs – Garn | 550 | 0.22 | nd | nd | −21.2 |
| C61    | 2218000 | 5688100 | Haast | QFS | Gs – Garn | 550 | 0.18 | nd | nd | −21.8 |
| C75    | 2197200 | 5690500 | Haast – AF | QFS | Gs – Garn | 600 | 0.15 | nd | nd | −20.4 |
| C75    | 2197200 | 5690500 | Haast – AF | QFS | Gs – Garn | 600 | 0.08 | nd | nd | −19.3 |

Notes: GW = Greywacke, Pel = Pelite, Psam = Psammite, QFS = Quartzofeldspathic Schist, PM = Protomylonite, MB = metabasite, Low P–P = Low prehnite pumppelitie, P–P = Prehnite pumppelitie, Chlor GS = Chlorite Greenschist, Biot GS = Biotite Greenschist, Garn GS = Garnet Greenschist, G–O Amph = Garnet Oligoclase Amphibolite. nd = not determined, AF = Alpine Fault Lith. = Lithology of the sample, Met. Grade = Metamorphic grade of the sample, Met T. = Estimated maximum metamorphic temperature the sample experienced. Samples with an * are from Hilton et al. (2008).
decarbonation and the oxidation of graphite during greenschist to amphibolite facies metamorphism, which is equivalent to 2.5 $\times$ 10$^7$ kg/yr (5.7 $\times$ 10$^8$ mol/yr) CO$_2$ for the Southern Alps orogen.

Alternatively, infiltrating meteoric waters have been suggested as a source of dissolved oxygen to oxidise graphite at relatively low temperatures ($\sim$150°C, Jenkin et al., 1994). However, the calculated $\delta^{13}$C value of CO$_2$ generated would be greater than 0% which is substantially heavier than $\delta^{13}$C values measured in warm springs or hydrothermal mineral veins. The ambient redox below the water table is sufficiently low that pyrite is stable and widespread implying that the amount of dissolved oxygen is too low ($\sim$ log fO$_2$ of $\sim$45, calculated in Geochemist’s Workbench) to permit graphite oxidation. Therefore we discount oxidation of graphite at shallow levels by oxygen dissolved in meteoric waters as a source of CO$_2$ in the orogen. In addition, the oxidation of carbonaceous material in the surficial weathering environment is also discounted as a CO$_2$ source since there is limited weathering of eroded carbonaceous material with no oxidation rinds on clasts due to short residence times (Nibourel et al., 2015).

4.3. Composition of crustal fluids and total CO$_2$ flux to the near surface

The greenschist to amphibolite facies metamorphism results in a whole rock loss of total volatiles of $\sim$1 wt.% (Pitcairn et al., 2006) equating to 1.35 $\times$ 10$^8$ kg/yr of volatiles. When combined with our mass balance calculations (Section 4.2) this yields a fluid containing $\sim$75 mol.% CO$_2$, similar to fluid inclusions in metamorphic quartz veins ($\sim$5 mol.%, Craw and Norris, 1993). There is a minor mantle CO$_2$ flux from the hangingwall directly adjacent ($\sim$1 km) to the Alpine Fault of 2 $\times$ 10$^7$ mol/yr (Menzies et al., 2016) and including this gives a total deep flux of 5.9 $\times$ 10$^8$ mol/yr CO$_2$. However, because Southern Alps hot springs have HCO$_3^-$/Ca$^{2+}$ ratios of $\sim$9 this indicates that in addition to eq. (2) there must be a minor ($\sim$10%) component of calcite dissolution either at depth, or at shallow levels in the active geothermal system ($<$150°C). Hence the total CO$_2$ flux is 6.4 $\times$ 10$^8$ mol/yr, of which 87% is sourced from metamorphic graphite oxidation (25%) and decarbonation of calcite (62%) at the greenschist to amphibolite facies transition, with $\sim$10% from the shallow congruent dissolution of calcite, and 3% mantle-derived.

4.4. CO$_2$ flux to the atmosphere

The flux calculated in sections 4.2 and 4.3 quantifies the amount of carbon released into the near surface environment. To estimate the flux of CO$_2$ to the atmosphere from this reservoir, it is necessary to quantify the proportion of CO$_2$ degassed from geothermal waters (Becker et al., 2008; Evans et al., 2008). We use measured $\delta^{13}$C values of both DIC and CO$_2$ from two hot springs and combine these data with carbon isotopic fractionation factors from Mook et al. (1974) for HCO$_3^-$–CO$_2$(g) and Rayleigh fractionation modelling combined with a Monte Carlo approach to estimate the likely proportion of CO$_2$ gas that is lost to the atmosphere from upwelling and effusing hydrothermal waters. In the Monte Carlo simulation, the proportion of CO$_2$ degassed at each temperature step was randomly generated between 0 and 10% over 1000 iterations of the model. This approach enabled exploration of the range in possible degassing scenarios as the spring waters cool and upwell that result in the measured HCO$_3^-$ concentrations, and $\delta^{13}$C$_{DIC}$ and $\delta^{13}$C$_{CO_2}$ values (Fig. 6). From these simulations we are able to give realistic maximum and minimum proportions of dissolved CO$_2$ degassed at each spring. The calculations are constrained by $\delta^{13}$CO$_2$ values of $\sim$8.8% and $\delta^{13}$DIC values of $\sim$3.6% and $\sim$4.8% for Fox Spring; and $\delta^{13}$CO$_2$ values of $\sim$7.2% and $\delta^{13}$DIC values of $\sim$4.9% and $\sim$5.9% for Copland Spring (Menzies et al., 2016). The difference in DIC values between the springs, and differences
between CO₂ and DIC δ¹³C values is likely due to temperature differences between the spring waters; Fox is ∼30–40 °C and Copland ∼60 °C at the surface, and isotopic fractionation factors are higher at lower temperatures (Becker et al., 2008). Silica geothermometry suggests these spring waters equilibrated with rock at ∼120 °C (Menzies et al., 2016). The model predicts that for Fox Spring degassing while cooling from 120 to 40 °C results in a net difference between DIC and CO₂δ¹³C values of 5.2‰. This corresponds to degassing of 30 to 50% of the total CO₂ during upwelling, with the higher values representing greater degassing at depth owing to smaller fractionation factors at higher temperatures. For Copland Spring the net difference between DIC and CO₂δ¹³C values is smaller, 2.3‰, which may be obtained through 20–30% degassing. Our data indicate that there is greater fractionation at Fox Spring, and it is unlikely that the differences in δ¹³C values of DIC between the springs, and consequently their degassing history, is anything other than temperature-related. This indicates that greater degassing has occurred at Fox Spring, at lower temperatures, and that both fluids shared a similar deep fluid history with degassing between 20–30% followed by a further 10–20% degassing at lower temperatures at Fox Spring. Copland Spring has deposited a large travertine terrace during degassing of CO₂ at the surface indicating that further CO₂ loss occurs after it reaches the surface and it likely releases >20–30% of its initial total dissolved CO₂ to the atmosphere.

Using these estimates, between 30–50% of mantle and metamorphic CO₂ carried in hydrothermal fluids as dissolved CO₂ is liberated as CO₂ gas to the atmosphere, and the rest is added to the riverine HCO₃⁻ budget. It is likely that there is further, limited degassing of such fluids as they flow to join the rivers, but given our wide range in estimated proportion of degassing we assume it is accounted for within this range. This allows us to revise our mountain belt CO₂ flux to the atmosphere from metamorphic and mantle sources to 1.9 to 3.2 × 10⁶ mol/yr over a 10 × 10 km area (1.9 to 3.2 × 10⁵ mol/km²/yr). For comparison the flux of metamorphic CO₂ to the atmosphere from the Himalaya is estimated at 0.9 × 10¹² mol/yr over a 2500 × 300 km area (1.2 × 10¹⁰ mol/km²/yr) (Becker et al., 2008), an order of magnitude greater than the Southern Alps. The Southern Alps CO₂ flux calculated here is similar to the lower range of greenschist facies metamorphic CO₂ fluxes (0.5 to 7 × 10⁶ mol/km²/yr) modelled from carbonation reaction textures in the predominantly silicilastic Dalradian metasedimentary belt in the SW Scottish Highlands (Skelton, 2011).

4.5. CO₂ drawdown by weathering processes

To estimate the overall influence of Southern Alps orogenesis on the global atmospheric CO₂ budget we compare our estimated CO₂ flux to the atmosphere (Section 4.4) with the estimated short term rates of CO₂ drawdown during silicate and carbonate chemical weathering (Fig. 7, Table 3). Major ion concentrations of rivers draining to the west of the Main Divide have total, short term atmospheric CO₂ consumption rates of 7.5 to 39 × 10⁵ mol/km²/yr (Table 3, S1 following Jacobson and Blum (2003)). Relatively high Ca/Ca+Mg+Na indicates that carbonate dissolution is the dominant chemical weathering reaction (4.2 to 31 × 10⁵ mol/km²/yr). The carbonate that contributes to this weathering flux is likely sourced from disseminated carbonate veins that were deposited from hydrothermal fluids at depth, similar to what has been observed in the Himalaya (Blum et al., 1998). This is accompanied by silicate weathering (1.1 to 7.4 × 10⁵ mol/km²/yr) at rates similar to or up to an order of magnitude higher than the global mean silicate weathering rate (9 × 10⁴ mol/km²/yr, Table 3). In contrast, rivers draining to the east of the Main Divide have silicate chemical weathering rates of 0.5 to 1.3 × 10⁵ mol/km²/yr (Jacobson and Blum, 2003), similar to global mean weathering rates. An additional carbon sink is the burial of particulate organic carbon exported from the mountain belt by rivers to the ocean which is estimated at 32.5 mol/km²/yr and 10% of this is estimated to be stored in marine sediments on geological timescales (Hilton et al., 2008).

High rates of mechanical erosion in the Southern Alps due to rugged relief and orographic precipitation occur over a ∼200 km region parallel to the Alpine Fault that extends 25 km east to the Main Divide (Jacobson and Blum, 2003). This is larger than the ∼100 × 10 km region of modern convergence-related metamorphism in the most rapidly uplifting portion of the Alpine Fault hangingwall, that includes numerous warm springs that are effusing CO₂ to the atmosphere (Fig. 1). For this extended region west of the Main Divide the short term weathering drawdown is 0.3 to 2 × 10¹⁰ mol/yr of which 5.5 to 37 × 10⁸ mol/yr is due to silicate weathering. This is two to ten times higher than the orogenic flux of CO₂ from the mountain belt to the atmosphere (1.9 to 3.2 × 10⁸ mol/yr).

In the Himalaya CO₂ drawdown by chemical weathering is a factor of three lower than the estimated metamorphic output and therefore the Himalaya is a net source for atmospheric CO₂ (Becker et al., 2008). In contrast, in the Southern Alps CO₂ consumption by weathering is greater than CO₂ production, indicating that orogenic belts with low proportions of carbonate rocks may be CO₂ sinks. As a consequence, major continental collision events through geological time that involved dominantly silicilastic rocks deposited before the widespread occurrence of marine carbonate sediments (Early Proterozoic, Ronov, 1964) may have been net sinks for CO₂ and had the opposite influence to the modern Himalaya that dominates the modern carbon cycle (Bickle, 1996).

5. Conclusions

1. The Southern Alps is a low carbon silicilastic mountain belt developed along the transcurrent Australian Pacific plate boundary with modern uplift, metamorphism and hydrothermal activity that is mobilising carbon.

2. Hot spring HCO₃⁻/Ca²⁺ = 9 which is substantially higher than expected for the dissolution of calcite (1–2), indicating the op-
Fig. 7. Summary of the processes generating CO₂ in the Southern Alps orogen compared with rates of CO₂ drawdown through weathering reactions driven by elevated topography and associated enhanced erosion rates. Over short time scales the Southern Alps are a significant sink for CO₂ through weathering reactions, and even when considering long timescales where precipitation of marine carbonates may occur the mountain belt still acts as a net CO₂ sink.

1. The total CO₂ flux to the atmosphere from degassing of hot springs is 1.9 to 3.2 × 10⁸ mol/yr, which is 30–50% of the flux to the near surface environment. The balance (3.2–4.5 × 10⁸ mol/yr) is either precipitated in subsurface veins, travertine terraces or flows into the river system as a minor component (<1–10%) of the dissolved HCO₃⁻.

2. Rapid uplift and orographic precipitation in the Southern Alps enhances mechanical erosion, the comminution of rocks, and exposure of new reactive surface area leading to elevated rates of chemical weathering. The drawdown of CO₂ through this weathering ranges between 2.7 and 20 × 10⁹ mol/yr, which is at least an order of magnitude greater than the CO₂ flux to the atmosphere from the orogenic belt. In addition the rapid removal of particulate organic carbon from the mountain belt removes a further 16.3 × 10⁹ mol/yr of carbon (Hilton et al., 2008).

3. There are three active principal sources of CO₂: oxidation of graphite and decarbonation of calcite at the greenschist-amphibolite facies boundary (T and P), and dissolution of rock mass calcite at shallower levels. There is only a minor component of mantle CO₂ coming up the Alpine Fault.

4. The total CO₂ flux to the near surface environment is 6.4 × 10⁸ mol/yr, of which 87% is sourced from graphite (25%) and decarbonation of calcite (62%) at the greenschist to amphibolite facies transition, 10% is from congruent dissolution of calcite, and 3% is mantle-derived.

5. The CO₂ flux to the atmosphere from degassing of hot springs is 1.9 to 3.2 × 10⁸ mol/yr, which is 30–50% of the flux to the near surface environment. The balance (3.2–4.5 × 10⁸ mol/yr) is either precipitated in subsurface veins, travertine terraces or flows into the river system as a minor component (<1–10%) of the dissolved HCO₃⁻.

6. Rapid uplift and orographic precipitation in the Southern Alps enhances mechanical erosion, the comminution of rocks, and exposure of new reactive surface area leading to elevated rates of chemical weathering. The drawdown of CO₂ through this weathering ranges between 2.7 and 20 × 10⁹ mol/yr, which is at least an order of magnitude greater than the CO₂ flux to the atmosphere from the orogenic belt. In addition the rapid removal of particulate organic carbon from the mountain belt removes a further 16.3 × 10⁹ mol/yr of carbon (Hilton et al., 2008).

7. Although graphite oxidation and associated coupled decarbonation processes described above are also likely to occur in carbonate-rich orogens, decarbonation of limestone overwhelmingly dominates CO₂ production in these systems. Siliciclastic mountain belts such as the Southern Alps of New
Zealand, are net sinks for atmospheric CO₂, in contrast to orogens involving abundant carbonate rocks, such as the Himalaya, that are net CO₂ sources.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2017.10.010.

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Table 3

Summary of CO₂ drawdown through silicate and carbonate weathering, and export of particulate organic carbon (POC) from west of the Main Divide in the Southern Alps and total short term drawdown (silicate + carbonate + POC) and total long-term effective drawdown (half of silicate weathering + 10% of POC) compared with crustal CO₂ generation and of CO₂ which reaches the atmosphere.

| Material Type                                      | Area (km²) | CO₂ × 10⁹ (mol/(km²)yr) | CO₂ × 10⁹ (mol/yr) |
|---------------------------------------------------|------------|--------------------------|-------------------|
| Silicate Weathering, west of the Main Divide      | max        | 5000                     | 7.4               |
|                                                   | min        | 5000                     | 1.1               |
| Carbonate Weathering, west of the Main Divide     | max        | 5000                     | 1.1               |
|                                                   | min        | 5000                     | 0.55              |
| Biogenic POC, west of the Main Divide             | max        | 5000                     | 32.5              |
|                                                   | min        | 5000                     | 16.3              |
| Total Short-term drawdown                         | max        | 5000                     | 67.5              |
|                                                   | min        | 5000                     | 37.3              |
| Total Long-term drawdown                          | max        | 5000                     | 6.95              |
|                                                   | min        | 5000                     | 3.8               |
| Metamorphic CO₂ generation                        | max        | 1000                     | 6.4               |
|                                                   | min        | 1000                     | 1.9               |
| Metamorphic CO₂ reaching atmosphere               | max        | 1000                     | 3.2               |
|                                                   | min        | 1000                     | 0.19              |

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