Features of seafloor hydrothermal alteration in metabasalts of mid-

ocean ridge origin from the Chrystalls Beach Complex

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Abstract

 The Taieri Mouth locale of the Chrystalls Beach Complex (CBC) in the South Island of New Zealand includes well preserved to strongly deformed pillow lavas. Flattened veins of epidote, quartz and chlorite intercalated with basalt flows and volcanoclastic breccias. The tectonic affinity for the rare igneous portion of the predominantly sedimentary CBC has not been well established in the context of its regional metamorphic geology. New field, petrographic, geochemical and isotopic observations suggest a mid-ocean ridge origin for the Taieri metabasalts. Further, paleo-vertical networks of epidote-quartz-chlorite veins and cross- cutting faults suggest timing of seafloor fluid-flow. Altered pillows and epidote separates have δ^{18} O isotope values ranging from 9.3 to 13.1‰. This indicates slightly enriched δ^{18} O 42 fractionation resulting from seafloor weathering and low-temperature $(\langle 250^{\circ} \text{C} \rangle)$ exchange 43 between seawater and hydrothermal fluids in basaltic fractures. Age-corrected $87\text{Sr}/86\text{Sr}$ ratios between 0.704135 and 0.70624 show low temperature fluid-rock interactions where the altered pillows and veins did no succumb to major mineralogic changes or isotopic re-equilibration after formation. In contrast, compressed s-fold epidote and coarse quartz veins near metasediments are suggestive of the elevated temperatures and pressures during accretion. We differentiate between episodic seafloor venting and accretional wedge-related alteration recorded within these metabasalts.

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- 50 Keywords: Otago region, metabasalts; seafloor hydrothermal alteration; mid-
51 coean ridge processes; veins; epidote; petrology; geochemistry; trace element ocean ridge processes; veins; epidote; petrology; geochemistry; trace elements; isotopic analysis; ophiolite

Introduction

The Chrystalls Beach Complex (CBC) (Nelson 1982; Coombs et al. 2000; Fagereng and

55 Cooper 2010a,b) crops out a <1000 km² region on the coast in southeast Otago between

- Barrier Range and Dunedin. The complex comprises of deformed sub-greenschist facies
- greywacke, chert, and minor metabasalt in a pelitic matrix. Radiolarian fossils
- (Campbell and Campbell 1970) and detrital zircon ages (Adams et al. 2007) place the
- sedimentary protolith in the Early-Late Triassic with peak metamorphic ages in the
- Middle-Late Jurassic (Nishimura et al. 2000). With features such as soft sediment pull-
- aparts, weakly developed slaty cleavage, folds in dismembered bedding, and quartz-
- fibre lineated surfaces, the CBC has been interpreted to be an accretionary mélange
- within the Otago Schist (Fig. 1a; Nelson 1982).

 Due to variable metasediment geochemistry (Coombs et al. 2000), lithologies, and U/Pb zircon ages (Adams et al. 2007), the CBC's relationship to the terranes relevant to the origin of the Otago Schist has been a discussed area of problematic affinity. Straddling in between well-studied terranes of the Otago Schist, the CBC block 68 reported initial ${}^{87}Sr/{}^{86}Sr$ ratios intermediate to known values of the Caples and Torlesse terranes (Adams and Graham 1997). The emplacement of CBC has been referred to as an autochthonous subunit of the Caples terrane despite its silica-rich contents exhibiting greater similarity to the metasedimentary and felsic rocks of the Torlesse Terrane (Mortimer and Roser 1992). Amongst the minor igneous portions of three localities referred to as Taieri Mouth, Akatore Beach, and Watsons Beach within the CBC, normal- to enriched- mid-ocean ridge (N-MORB to E-MORB) and oceanic island (OIB) affinities have been proposed (Fig. 1b; Fagereng and Cooper 2010b, Pearce 1984).

 We focus on the igneous portion of the CBC and test whether the metabasalts and in-situ alteration veins from Taieri Mouth (Fig. 1a) originated as syn-accretionary volcanism (Mortensen et al. 2010), or at a seamount or mid-ocean ridge (Fagereng and Cooper 2010b). Recent field observations of the fault distribution, structures, and fracture morphotypes around brecciated pillow margins challenge prior interpretations of the tectonic-volcanic origin and settings of fluid-flow. Closer look at the structures of veins and faulting at Taieri Mouth suggest a history of episodic fluid-rock interactions from both low-temperature seafloor alteration as well as later metamorphism related to accretion. The main purpose of this paper is to differentiate: (1) the tectonic affinities of the metabasalts, and (2) low-temperature seafloor verses metamorphic/accretionary wedge-related alteration signals from the veins based on texture and compositional variations of hydrothermal minerals as well as geochemical data including major and trace element concentrations and stable isotope compositions.

Geological setting

The Otago Schist is composed of amalgamated terranes that merged on an orogenic belt

in the Mesozoic (Fig. 1a; Mortimer 2000). These terranes were exhumed from the

accretionary prism formed by subduction under the paleo-Pacific Gondwana margin

(Coombs et al. 1976; Mortimer 1993), and are predominantly metasedimentary, with

minor intercalations of mafic rocks (Mortimer 2000). However, we focus on the

metamorphosed volcanics within the CBC in this study. The metamorphic rocks grade

- into volcanogenic sediments of the Caples Terrane to the south and the
- quartzofeldspathic Torlesse Terranes to the northeast. Metamorphic grade varies from
- pumpellyite-actinolite to greenschist facies in the east and increases to amphibolite
- facies in the west (Mortimer 2000; Fig. 1a). Even though most of these rocks were
- subjected to similar penetrative deformation and metamorphic recrystallisation, Coombs
- et al. (2000) suggests that the igneous rocks within the CBC may be a separate,
- tectonically bounded fragment that has a different history from nearby terranes based on petrographic and geochemical data and radiolarian age determinations.
- The focused locality within the CBC in this study, Taieri Mouth beach (Fig. 1b), is bounded by the Rakaia Terrane schists to the north and Caples Terrane schists to the west (Nelson 1982). The metavolcanic band within Taieri Mouth consists majorly (>90%) of deformed altered mafic rocks metamorphosed up to the pumpellyite- actinolite facies (Nelson 1982) and volcanic breccia with fractures filled with secondary minerals such as quartz, albite, epidote and chlorite. A small portion (<10%) of outcrops, however, exhibit relict primary pillow lava textures indicating subaqueous eruption and crystallisation (Fagereng and Cooper 2010b). The active Akatore Fault, one of the Otago region's most active faults for the last 15,000 years with an average slip rate of 1.3 mm/year, runs just inland of the Taieri outcrops (Litchfield and Lian 2004). Faulting from surface-ruptures and displacements as well as other tectonic events may have since influenced structural features of the studied outcrops (Taylor-Silva et al. 2019).

Methods

 The studied outcrops of CBC at Taieri Mouth beach are located ~37 km south of Dunedin and were mapped and sampled in June 2018 (Fig. 2). Vein and major fault orientations were documented and tilt-corrected, which was determined for each outcrop by locating the downward-pointing "V" at the bottoms of preserved lava pillows.

 Transmitted and reflected light petrography was done with a Leica DM2500P microscope. The SEM imaging and qualitative chemical analyses were completed using a FEI Scanning Electron Microscope with a set of silicate and oxide standards to quantify EDS spectra. Mineral identifications were supplemented by (Table 1) X-ray diffraction using the PANalytical X'Pert PRO MPD system at the University of Otago.

 Total whole-rock major oxides and trace element concentrations were determined for 14 powdered samples by Bureau Veritas using ICP-AES and ICP-MS, respectively.

 Oxygen isotope ratios were measured on 7 epidote concentrates and whole rock powders at the University of Texas at Austin, USA. Individual epidote fragments were hand-picked from bulk rock samples and crushed. Approximately 2.0 mg of material was analysed using the laser fluorination method of Sharp (1990). Samples were heated 134 by a CO_2 laser in the presence of BrF 5 in order to produce O_2 gas, the analyte introduced into the ThermoElectron MAT 253. Garnet standard UWG-2 (δ 18 O value 136 = $+5.8\%$) (Valley et al. 1995) and an in-house quartz standard Lausanne-1 (δ 18 O 137 value $= +18.1\%$) were analysed along with samples to monitor the precision and accuracy of oxygen isotope analyses. δ 18 O values are reported relative to VSMOW, where the δ 18 O value of NBS-28 is +9.6‰. The precision on each oxygen isotope 140 analysis is $\pm 0.1\%$ (1 σ), based on the long-term analyses of standards. Sr isotopic compositions and Rb and Sr abundances were performed on the same 7 powdered epidote separates at the University of Southampton, UK. Concentrations were determined on a Thermo Fisher Scientific XSeries 2 ICP-MS using synthetic mixed element standards with Be, In and Re as internal standards, following standard clean dissolution methods. The powders were analysed with standard reference materials (SRM) and unknowns (PM-S and BCR-2). These standard reference materials have good agreement with GeoReM values. The mother solutions were subsampled to give approximately 1 μg Sr and the Sr isolated using ~50 μL Sr-Spec resin columns, the column blanks were <0.1 ng. The dried samples were loaded onto a single Ta filament 150 with a Ta activator solution. ${}^{87}Sr/{}^{86}Sr$ was analyzed using static routine with amplifier rotation on a Thermo Fisher Scientific Triton Plus Thermal Ionization Mass 152 Spectrometer with a beam size of ${}^{88}Sr = 2V$. ${}^{87}Sr/{}^{86}Sr$ measurements were normalized to $86Sr/88Sr = 0.1194$. The long-term average $87Sr/86Sr$ for NIST SRM987 on the 154 instrument is 0.710245 ± 0.000025 (2sd) on 161 analyses.

Field Observations

The Taieri Mouth locale of the CBC (Fig. 2) stretches about 350 m along the intertidal

- zone of the sandy beach, structurally above and below metasediments (Coombs et al.
- 2000; Nelson 1982). We divide the studied area of metabasalts and foliated schists into

 three zones (Fig. 2): headland (least deformed), pillow island, and deformed zone (most deformed).

161 The headland is a <100 m long metabasaltic outcrop that contains a major 162 normal fault that dips at 20°NE (Suppl. Fig. 1a) as well as non-foliated, fine-grained 163 ellipsoidal lava pillows dipping at 18°W with aspect ratio (V to H) ranging from \sim 2:1 to 3:2 (Fig. 2, 3a). A thrust fault with 5 m strike length dipping almost vertically within the pillow lavas is distinct towards the eastern side of the headland (Fig. 3a; Suppl. Fig. 1b). This lava flow structure hosts a meshed surface network of epidote veins flattened within the basalt with orientations dipping sub-vertical to vertical on the pillow bedding plane (Fig. 3b, c). Although the metabasalts here are chloritized and sheared, the main structural and alteration features of the lava flow are relatively well-preserved. Curved green epidote and chlorite-rich veins rim and cut across the pillows, and in the most concentrated zone, nearly filled up the entirety of a 2m x 2m reference square (Fig. 3a).

 The pillow island is another outcrop of relict lava flow with pillows dipping similarly at 18° W and separated from the headland by modern beach deposits. However, this 0.5-meter tall basaltic outcrop is placed in the intertidal with only the top cross- section of pillows exposed (Suppl. Fig. 1c, d), which makes structural observations of contacts almost impossible. Despite similarities to the headland in terms of lithology and metamorphic grade, the outcrop consists of sub-greenschist facies metabasalts with eroded interpillow materials and overall purplish veneer of physical weathering. There is no meshed network of veins on the pillow island, except for epidote veins tinged with iron oxides of sub-vertical orientations that are short (<10cm), straight, and occur commonly in parallel groupings of three or less.

 At the deformed zone, the protolith consists of volcanic breccias while the structures of lava flow have been obliterated by penetrative deformation and shear. The 184 few pillows identified dips steeply (60-65°) to the northeast. The deformed zone features scattered outcrops and small caves (vary from 1-10m long, 1-5m wide). Folds from compressional deformation (Suppl. Fig. 1e) result in obscured pillow outlines, variable paleohorizontal and obliterated features. Flattened and curved epidote veins are like those experienced by the ductile deformation of metavolcanics. These deformed outcrops are north of the headland and pillow island, separated by several hundred meters of modern beach. This outcrop is in contact with metasediments, where there is apparent soft sediment mixing towards the northern edge (Fig. 2), where long, straight,

macrocrystalline quartz veins ran on the microfaults.

Metabasalts

 The Taieri metabasalts are predominantly pillow lavas with common mineral veins and deformation associated with sub-greenschist metamorphism with the absence of prehnite bearing assemblages .The metabasalts are sparsely vesicular, aphyric tholeiites with on average over 50% in modal abundance the primary aphanitic groundmass of plagioclase and clinopyroxene, 25% epidotes, 20% quartz, 5% chlorite, and <1% trace and accessory minerals. Diabasic igneous texture, quartz amydgules and albite twinning of plagioclase are relicts of primitive igneous characteristics preserved in lava flow samples in the headland (Suppl. Fig. 2). Secondary minerals from low-temperature hydrothermal alteration such as epidote and chlorite occur within both the groundmass and crosscutting veins (Fig. 4a). Pumpellyite, iron oxides (hematite) and sulphides (sphalerite and pyrite) are present within the cataclastic, fine-grained matrix of the pillow groundmass (Table 1; Suppl. Fig. 2). There are no interstitial carbonate sediments incorporated in the basaltic flows and pillows.

Veins

 In the Taieri Mouth locality, the most prominent features of the metabasalt outcrops are well-defined veins consisting mainly of fine-grained epidote with subordinate chlorite, quartz and hematite. These crosscutting veins are flattened and deformed within the same plane of the pillow structures. The abundant epidote in the veins is distinctly different from the mineralogy of the metamorphic assemblage in surrounding metasediments, in which the secondary Ca-silicates are pumpellyite and actinolite (Fagereng and Cooper 2010a,b). These veins, and associated alteration of the adjacent rocks, are a principal focus of this study in which we differentiate their syn-metamorphic host origins and post-metamorphic alteration conditions.

218 Networks of veins $(≥0.5 \text{ cm width})$ and veinlets $(≤0.5 \text{ cm width})$ have distinct generations of epidote, quartz, chlorite and hematite (Fig. 4; Table 1). The shape of the epidote, quartz, and chlorite grains in veins ranges from anhedral to euhedral with sharp, well-formed faces (Suppl. Fig. 2). At the headland, veins commonly thin perpendicularly relative to the dip of pillows. For example, measured in 30 cm increments at the headland sample grid 4-6 m (Fig. 3a), an epidote vein thins upward

from 2.3 cm, to 1.4 cm, to 0.5 cm. Two-sided Wilcoxon rank sum tests for equal median

225 $(\alpha=0.05)$ shows no significant difference in the median vein widths between the

226 headland (geometric mean 0.6, median $0.5 \pm$ std 1.5 cm) and pillow island (geometric

227 mean 0.5, median $0.5 \pm$ std 0.4 cm) (p=0.857). However, the median vein width

228 (geometric mean 1.2, median $1.0 \pm$ std 5.0 cm) of the deformed zone is significantly

229 greater than at the headland and the pillow island, respectively $(p=0.040, 0.017)$, which

may suggest different mechanisms of fracture genesis at the deformed zone.

 The tilt-corrected vein orientations are dipping predominantly vertical to subvertical at the headland and pillow island (Fig, 3b), but horizontal to sub-horizontal at the deformed zone. Two-sided Wilcoxon rank sum tests for equal median shows no significant difference in the median vein orientations after rotation to the 235 paleohorizontal (p=0.804) between the headland (median $102 \pm$ std 36 degrees) and 236 pillow island (median $96 \pm$ std 26 degrees).

 There are three vein morphotypes in the Taieri metabasalt outcrops: straight (Fig. 4a), pillow margin (Fig. 4b), and radiating networks (Fig. 4c). Within a vein, distinctly bordered generations of minerals are commonly present. Straight veins (Fig. 4a) with epidote, quartz, chlorite and hematite are common in all three zones of the Taieri Mouth locality. At the headland, veins developed around pillow margins predominate with cataclastic epidote and quartz replacing the volcano glass and clay material (Fig. 4b). Most of these thin epidote veinlets are cross-cutting, but some extend off central bodies in fibrous patterns (Fig. 4c). Such networks of epidote veins are restricted to the basalt unit and absent from enclosing metasediments.

 Offset and asymmetrically folded veins are morphotypes that have been structurally deformed since genesis (Suppl. Fig. 1e). Offset veins are found only at the headland and pillow island while asymmetrically folded veins, associated with thrust faulting, are most prominent in the deformed zone. While the compression of s-fold veins are penetrative in the deformed zone, those in the headland and pillow island are non-penetrative, as no spaces are observed between fabric planes in thin section.

Cross-cutting relationships

 A concentrated zone of vertically dipping veins (Fig. 3a, b) at the headland outcrop fills a main normal fault structure with no offset. Cross-cutting relationships of fracture veins (Fig. 3c, 4c) and microfaults show sequences of genesis and structural changes.

 An example of a sequence is outlined in Fig. 3c, where at least three distinct events are present. Stage 1 records the sub-vertical vein and the network of veinlets surrounding it. Stage 2 records the low angle normal microfault that offsets and fractures the Stage 1 vein. Stage 3 shows sub-vertical epidote-quartz-chlorite vein that cross-cuts the main features of Stage 1 and 2. Although the duration and exact timing between events are not addressed here, the relative sequence of fracturing is well-preserved: fracture genesis, sub-horizontal normal faulting, compression, and modern erosion after emplacement. In the lava flow zone of the headland, slickensides on the underside of overhanging rock of a minor thrust fault (Fig.; 3a) with an estimated throw of 1m 265 suggest the direction of the fault slip motion is 212° while the dip is 20° NE relative to the modern tilt of the lava flow.

Analytical Results

Whole rock composition

 Whole rock compositions of the Taieri metabasalts were plotted in the N-MORB 270 thole ite field on the TiO₂/Yb vs Nb/Yb, and $Zr/(P_2O_5*10^4)$ vs TiO₂ tectonic discrimination diagram (Pearce and Cann, 1973; Fig. 5a). These data agree with previous analyses of the Taieri pillow basalts (Fagereng and Cooper 2010; Pitcairn et al. 2015). Silica content of pillows is within the 49-50% range with 274 Al₂O₃ around 14-15% (Table 2). There is an enrichment in the Na₂O and K₂O contents above normal tholeiitic basalt values at around 4-5%. Concentrations of major elements are plotted against the MgO concentration (Fig. 6), because it has been used as indicator for the extent of basalt/seawater interaction (Mottl 1983). CaO and Na2O concentrations correlate negatively to MgO concentration with the 279 majority of the samples, while the $TiO₂$ concentration correlate positively. Fe₂O₃ concentration correlate positively with LOI (i.e., loss on ignition, which records mass of moisture and volatile material present in sample).

 Relative to N-MORB, Taieri metabasalts exhibit strong enrichments in fluid- mobile alkali (K, Rb, Cs), and alkali earth elements (Ba, Sr) (Fig. 5b). Bulk samples exhibit enrichments in these fluid-mobile elements associate with low-temperature hydrothermal alteration at the headland and pillow island (Table 2), but not always at the deformed zone. The intensity and pattern of the enrichments of K, Rb, and Ba are lower for samples from the deformed zone, whereas Cs and Sr are the only elements

- that are enriched more than 20 times above N-MORB there. Although alkali element
- ratios are consistent between samples from the present study and Fagereng and Cooper
- (2010), Ba/Rb ratios (average 4.1) are less than half the primary igneous value of 11.3
- 291 published in Hofmann and White (1983), whereas Cs/Rb ratios (average 53.2 x 10^{-3}) are
- 292 about 4 times the published value of 12.6×10^{-3} . Strontium content is consistent for
- those observed in dredged and drilled weathered basalts (Kawahata et al. 1987), but
- ranges widely from 70 to 4015 ppm (Table 2) regardless of the zones.

Epidote chemistry

- 296 The variation in the ratio of Fe^{3+} to Al in epidote $Ca_2(Fe^{3+}, Al)_3(SiO_4)_3(OH)$, (Suppl.
- Table 2) is thought to be dependent on the coupling between the immediate
- geochemical environment (e.g., host rock composition), temperature, source rocks fluid
- 299 compositions (e.g., $f O_2$ and $f CO_2$) (Apted and Liou 1983; Caruso et al. 1988), volume
- of fluid flow (Hannington et al. 2003), and pressure (e.g. rate of crystallization [Arnason
- et al. 1993]). Epidote from each zone predominantly clusters within its own group in
- terms of Fe³⁺ content (Suppl. Fig. 3), but there are three outliers from the main trend, all
- from the deformed zone (Ps=25.3-33.6). The epidote from the headland is at the higher
- 304 end of the Fe³⁺ to Al ratio (Ps=31.3-39.1) while the epidote from pillow island is at the
- lower end (Ps=28.5-33.1) (Coombs et al. 1976).

δ ¹⁸O and ⁸⁷Sr / ⁸⁶ Sr stable isotopes

- 307 Data from the δ^{18} O and 87 Sr $/{}^{86}$ Sr stable isotopic analyses on four epidote and three
- metabasalt subsamples are listed in Table 3 and Table 4, respectively. In agreement with
- 309 the enrichments of K, Rb, and Cs, metabasalts have higher δ^{18} O values (from 9.0 to
- 310 13.1‰) than primary MORB ($\delta^{18}O = 5.7$ ‰ from Gregory and Taylor 1981;
- 311 Muehlenbachs and Clayton 1976) (Fig. 7). Initial ${}^{87}Sr/{}^{86}Sr$ ratio for the Triassic-Jurassic
- age (i.e., set at 200 ma inferred from background literature of the CBC) of the
- metabasalts vary from 0.704135 to 0.705302 and for veins, range from 0.706223 to
- 0.70624 (Fig. 7).

Discussion

Tectonic origin

Geochemical analyses indicate Taieri pillows are N-MORB tholeiites of spreading

centres (Fig. 5a; Pearce 2008). These results support prior work by Pitcairn et al.

(2015) and Fagereng and Cooper (2010) at Taieri and contrasts with the pillows of

seamount- or plume-affinities (i.e., E-MORB and/or OIB) from Akatore Creek and

Watsons Beach of the CBC.

Structural evidence of veins may be speculated to support a MOR-origin of the

metabasalts. The high concentration of vertical to sub-vertical veins in relation to the

orientation of lava flow (Fig. 3a, b) may be related to on- or near-axis hydrothermal

upflow. Abundant low-angle microfaults cross-cutting the vertical fractures may be

more permissive of an extensional environment rather than those related to an

accretionary wedge(MacLeod et al. 2002).

Alteration history

 Multiple fracturing morphotypes in the Taieri metabasalts represent episodes of fracture genesis and alteration (Fig. 3c): (1) repetitive vertical to subvertical fracture genesis during hydrothermal upwelling interspersed by normal faulting as shown by radiating vein networks and cross-cutting features, and (2) fractures and deformation produced by post-seafloor metamorphism near the subduction zone and/or accretionary wedge. Morphotypes of veins resemble two possible stages of genesis and fluid flow:

(1) crack initiation controlled by the crack-seal mechanism (Fig. 4a; Ramsay, 1980),

fluid ascension (Fig. 4a; Connolly 1997), and thermal cooling (Fig. 4b,c; Oliver and

Bons 2001), and (2) episodic fracturing and offset (Fagereng and Harris 2014) that

enhanced shearing, new genesis, and alteration of old veins as well as newly propagated

ones (Gillis and Sapp 1997).

Folds and faults present resulted from three separate events: (1) tectonic instability as

the mid-ocean ridge evolved and spread (Macdonald 1982), (2) subduction-related

metamorphism and faulting upon delamination and emplacement, and (3) normal and

subsequent reverse fault motion of the entire assemblage from the Akatore Fault nearby

in the late Cenozoic (Taylor-Silva et al. 2019). The major normal fault (Fig. 2, 3a) at the

headland may have resulted from the extensional environment, because the

 concentrated, flattened vein radiations on the bedding plane are continuous across and uncompressed (as opposed to offset). Radiating vein networks (Fig. 4c) are found only at the headland and may have a genesis limited to the seafloor through thermal cracking (Oliver and Bons 2001; Vearncombe 1993). The crosscutting relationships of microfaults cemented by the assemblage of mineral characteristic of seafloor hydrothermal alteration (Fig. 3c) suggest continued extensional faulting and tilting with the development of hydrothermal veins at decreasing temperatures (e.g., decrease in epidote grain size) and increased fluid/rock ratios (Alexander et al. 1993). Had radiating networks of fractures at the headland formed in a wedge, the structural sub-vertical relationship to the lava flow may have been absent and would not have been preserved due to deformation. In contrast, the deformed zone is representative of the compression and obliteration of structures during accretion-related metamorphism with thick, compressed S-fold epidote veins and coarse quartz veins.

Geochemical characteristics of hydrothermally altered basalt

 Taieri samples contain relict igneous minerals, and the metamorphic minerals albite, chlorite, quartz, epidote, pumpellyite and sulphide and oxide minerals. Bulk samples of altered basalt and veins from the headland and pillow island (Fig. 6) show elevated MgO varying from 4-8 wt.%. This may owe to the removal of Mg from solution and incorporation of Mg-rich secondary phases with a consistent prograde behaviour with increasing temperature (Mottl 1983; Seyfried 1987). The CaO and Na2O wt.% of samples correlate almost inversely with the MgO concentrations (Fig. 6a, d). This shows a net direction of Ca and Na transport into alteration fluids during seafloor hydrothermal alteration of MORB. The anomalies, mostly from the deformed zone, may be the result of temperature kinetics and varied fluid/rock ratios following multiple episodes of chemical changes. For example, Coogan et al. (2019) addresses the increase in Na₂O and K₂O content of pillows during surface weathering of the seafloor and exchange between seafloor lavas and heated seawater in fractures. Due to the presence of iron-rich epidote veins in the altered basalts, Fe₂O₃ concentration is higher than that of MORB and lies at 4-10 wt.% (Shikazono et al. 1995; Fig. 6c). Similarly, the enrichment in TiO₂ is related to the chlorite components from hydrothermal alteration (Fig. 6b; MacLean and Kranidiotis 1987). The transport of mobile elements during low-377 temperature hydrothermal alteration $(<,400^{\circ}$ C) is required for the formation of chlorite and epidote-quartz assemblages. The major oxides trends reported here are expected in

 upper breccias, interflow sediments and pillow basalts that have undergone seafloor alteration and secondary mineral precipitation (Alt and Teagle 2003).

381 Ratios of Fe^{3+} : Al in epidote samples analysed by the quantitative SEM are categorized as the early pistacitic (Ps=0.28-0.37) variety formed at lower temperatures 383 (i.e., $250-280$ °C from Shikazono et al. 1995). This contrasts with later clinozoisite varieties with rising temperatures up to the pumpellyite-actinolite facies. Within the narrow gradation of epidote chemical compositions, epidotes sampled from different 386 vein generations from the headland have higher Fe^{3+} :Al ratios (Suppl. Fig. 3), which may indicate short-range disequilibrium due to variably sourced episodic fluids even though the variability is small (Coombs et al. 1976). Alteration temperatures, depth and bulk and fluid compositions (e.g., *f*O2, amount of fluid-rock exchange, dissolution rate) determine the thermal stability curves for epidote and clinozoisite under oxidizing conditions (Bird and Spieler 2004). Because zoisites form under higher hydrostatic pressure, the formation process for epidotes here may resemble hydrothermal conditions without the presence of high shearing stress (Holdaway 1972). Reported ratios should be evaluated with caution, because measurements are not limited in single-grain epidotes as the spectra may have overlapped with compositions from the underlying basalt groundmass.

Seafloor source of fluids

398 Compilation of past δ^{18} O and δ^{7} Sr $/\delta^{6}$ Sr isotope studies on pillows and sheeted dikes sampled from DSDP Hole 504B (Kawahata et al. 1987), Troodos (Bickle and Teagle 1992; Turchyn et al. 2013), Semail (Gregory and Taylor 1981) and Jospehine (Alexander et al. 1993) ophiolites provide evidence for a fault-controlled, seafloor alteration history of the Taieri epidote and quartz veins at estimated temperatures from 403 220 to 405°C. Both isotope systems are co-utilized to provide constraints on fluid sources and approximate hydrothermal temperatures of alteration. Compilations suggest 405 slightly heavier compositions of $\delta^{18}O$ ranging from 10.7 to 12.7‰ for pillows on the oxic submarine weathering surface and from 4.9 to 11.3‰ for hydrothermally altered veined basalts to greenschist facies and sheeted dikes at greater depths. In this study, δ^{18} O values of 9.3 and 12.4‰ (Fig. 7; averaged for altered basalts and epidote grains, respectively, from Table 3) resemble hydrothermally altered basalt of the greenschist assemblage that has experienced subsequent surface weathering with seawater. In hydrothermal systems, the effects of isotopic fractionation between rock and heated

412 fluids under low and high temperature conditions are opposing: low-temperature 413 alteration (4 \degree C) with seawater would result in an 18 O enrichment compared to initial 414 value of unaltered basalt whereas hydrothermal fluids $(>200-300^{\circ}C)$ would result in an 115 ¹⁸O depletion (Muehlenbachs and Clayton 1976). The δ^{18} O values of the Taieri samples 416 (Table 3) are reflective of crustal rocks above the diabase-gabbro contact (McCulloch et 417 al. 1981) and exhibit enrichment relative to the initial MORB reservoir of $\delta^{18}O = 5.7\%$ 418 (Muehlenbachs and Clayton 1976), which suggests the surface seawater weathering 419 process. Epidote veins, secondary precipitates from low-temperature fluid interactions, 420 are consistently more enriched in δ^{18} O than those of pillow basalts by about 3‰,

421 reflecting low temperature alteration $(\sim 150^{\circ}C,$ Bickle and Teagle 1992).

 As described by the tracer transport fluid-rock interactions model (Bickle and Teagle 1992), ridge hydrothermal systems exhibit flow regimes and patterns that change in three dimensions with time. Vein alteration can thus occur by isotopic exchange with a mixture of seawater and hydrothermal fluids of shifting compositions. Interpretations 426 for ${}^{87}Sr/{}^{86}Sr$ compositions in Taieri rocks are based on two factors: (1) the ${}^{87}Sr/{}^{86}Sr$ ratio of seawater and derived hydrothermal fluid in rock at the time and site of alteration, and 428 (2) the amount of heat available for alteration and its duration. The average ${}^{87}Sr/{}^{86}Sr$ ratio of fluids at mid-ocean ridges is ~0.7035 (Palmer and Edmond 1989) as a result of 430 mixing between hydrothermal fluids $({}^{87}Sr/{}^{86}Sr=0.70285-0.70465)$, seawater $\frac{87}{5}$ r/ $\frac{86}{5}$ r=0.70916, but changes in geologic time), and the basaltic basement $^{87}Sr^{86}Sr=0.7022-0.7033$) in a compilation study of oceanic spreading centres around 433 the world (Bach and Humphris 1999). Jurassic-Triassic seawater ${}^{87}Sr/{}^{86}Sr$ ratio has been estimated at 0.7075 (Koepnick et al. 1990; McArthur et al. 2001), so hydrothermal fluid output after fluid-rock exchange and alteration would be at a lower composition (as 436 modelled by Antonelli et al. 2017; Bickle and Teagle 1992). In this study, ${}^{87}Sr/{}^{86}Sr$ compositions of epidote separates corrected to 200 Ma (Jurassic-Triassic boundary as a conservative age estimate for Taieri metabasalts based on Coombs et al. 1976; Mortimer 2000; Nelson 1982) are not homogeneous. Elevation in ${}^{87}Sr/{}^{86}Sr$ ratios of the epidote separates compared to altered basalts may have resulted from the infiltration of Triassic 441 seawater with an ${}^{87}Sr/{}^{86}Sr \sim 0.7075$ but are still rock-buffered. Further, the compositions of vein-forming fluids in the vertically dipping mesh network present in the headland are comparable to those of the s-folded veins at the deformed zone although the sample size is small in this study (Fig. 7). This attained fluid-rock equilibrium in which recharge was pervasive and not significantly channelled has been explained by Bickle

446 and Teagle (1992), where ${}^{87}Sr/{}^{86}Sr$ profile shows only small differences between the less mineralogically altered diabase and intensely metasomatized epidosite rocks. The $87\$ Sr/ $86\$ Sr ratios in this study once again fit in the 'uncertain' affinity when compared to

- 449 the Torelesse- and Caples- types in an isochrons study using $87\text{Sr}/86\text{Sr}$ ratios done by
- Adams and Graham (1997).

451 When the δ^{18} O and δ^{7} Sr $/86$ Sr data are cross plotted (Fig.7), a fracture flow trajectory is present as modelled by DePaulo (2006). There is a much larger shift in $453 \delta^{18}$ O in comparison to Sr, which suggests that the fluid oxygen is interacting with much more of the rock volume than is the fluid Sr. This fracture flow model on the effects of matrix diffusion on isotopic exchange between fluid and rocks are typical of mid-ocean ridge hydrothermal vent fluids in contrast to porous flow in other geo-hydrological 457 systems where the ${}^{87}Sr/{}^{86}Sr$ ratio changes rapidly longitudinally in the direction of flow 458 with almost no change in $\delta^{18}O$.

Conclusions

 In this study, we verified the MORB affinity for the Taieri metabasalts of the CBC accretionary wedge. The veins exposed at Taieri, first studied here in detail, pose important evidence for seafloor fluid flow. Preserved volcanic sections of oceanic crust show the flow structure of a seafloor hydrothermal system and the associated geochemical flux from seawater-fluid-rock interaction. We use a systematic approach based on structures, vein mineralogy as well as primary and secondary geochemistry to provide evidence for the igneous origin of the metabasalt and to differentiate between seafloor and subduction-related alteration history of the Taieri outcrops as part of the CBC:

- 470 1. The Taieri locale consists of MOR metabasalt pillows with seafloor hydrothermal alteration veins and later episodes of fractures, chemical alteration, and compressional deformation from post-seafloor metamorphism.
- 2. The fluid-rock alteration history and later metamorphism are recorded in veins, which filled the fractures, and pervasive amongst the metabasalts: (1) on the ridge-axis, crack initiation and propagation were controlled by structural extension and hydrothermal fluids, and (2) away from the ridge axis, alteration is dominated by compressional deformation, but minimal

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677 **Tables**

- 678 Table 1. Location (coordinate system of WGS1984), mineralogy, and estimated modal abundances (only for samples with thin sections made) of
- 679 bulk samples. Mineralogy determined by XRD and thin section studies (see Fig. 2, 3a for sample locations).

680 $\frac{1}{3}$ Field zones as we defined at the Taieri Mouth locality of the CBC: H=headland; PI=pillow island; DZ=deformed zone.
681 *Mineral abbreviations as follows in order of appearance: Otz=quartz, Chl=chlorite, Ep=e

681 *Mineral abbreviations as follows in order of appearance: Qtz=quartz, Chl=chlorite, Ep=epidote, Hem=hematite, Ab=albite, Pmp=pumpellyite $*$ ⁸² **Groundmass= fine-grained basalt groundmass of plagioclase, clinopyroxe

**Groundmass= fine-grained basalt groundmass of plagioclase, clinopyroxene, feldspar, epidote and vesicles of quartz

683 Table 2. Whole rock ICP-MS results for major, minor, and trace elements in weight percent. Samples were fused with lithium borate and
684 digested in nitric acid for complete dissolution. Data reduction was performed u digested in nitric acid for complete dissolution. Data reduction was performed using proprietary internal calibration and standardization with 685 propriety reference material SO-19 of Bureau Veritas Mineral Laboratories. LOI is loss on ignition. Mdl stands for method detection limit while 686 bdl stands for below detection limit. Sample names listed as 2018CBMF-##.

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Sample	Type	Location	$\delta^{18}O(960)$
$017-e$	epidote	H	12.2
			11.8
$019-e$	epidote	H	12.3
$025-e$	epidote	DZ	13.1
$031-e$	epidote	DZ	12.6
$023-p$	altered basalt	Η	9.2
			9.9
$024-p$	altered basalt	DZ	9.0
$L3-p$	altered basalt	PI	9.0
			9.7

Table 3. δ^{18} O stable isotope and alteration temperature results for epidote and pillow
690 basalt separates as subsamples 2018CBMF-0XX-e or 2018CBMF-0XX-p, respectively. basalt separates as subsamples 2018CBMF-0XX-e or 2018CBMF-0XX-p, respectively.

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694 subsamples 2018CBMF-0XX-e or 2018CBMF-0XX-p, respectively. ${}^{87}Sr/{}^{86}Sr$ measurements

695 were normalized to ${}^{86}Sr/{}^{88}Sr = 0.1194$. The long-term average ${}^{87}Sr/{}^{86}Sr$ for NIST

696 SRM987 on the instrument is 0.710245 ± 0.000025 (2 standard deviations) on 161 analyses.

analyses.

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Supplementary Tables and Figure

719 Supplementary Table 1. Vein orientations from mapping efforts in each field zone.
720 Locations are given as distance east (negative) or west (positive) from the baseline (

Locations are given as distance east (negative) or west (positive) from the baseline (Fig. 3).

*Dip is corrected with respect to the tilt of the presiding block (i.e., if dip direction is

W, + degree; if dip direction is E, 180 - degree; Table 1.)

** The CUZ (concentrated upflow zone) is referred to mapped cross-section of the lava

flowat the headland in Fig. 3a.

Sample	Oxide percent $(\%)$							Calculated formula stoichiometry based on oxygen									
2018CBMF-015	Ep1	Ep2	Ep3	Ep4	Ep5	Ep6	Ep7			Ep1	Ep2	Ep3	Ep4	Ep5	Ep6	Ep7	
Ca	9.64	9.38	9.56	9.53	9.53	9.44	9.72			1.98	1.92	1.96	1.95	1.95	1.93	1.99	
Fe	4.19	4.6	4.52	4.44	4.13	4.41	4.82			0.86	0.94	0.93	0.91	0.85	0.9	0.99	
AI	10.26	10.06	10.02	10.22	10.36	10.09	9.76			2.1	2.06	2.05	2.09	2.12	2.06	$\overline{2}$	
Si	14.77	14.71	14.76	14.67	14.77	14.89	14.63			3.03	3.01	3.02	3.01	3.03	3.05	3	
\mathbf{O}	61.01	61.03	61.02	61	60.99	61.08	60.98			12.5	12.5	12.5	12.5	12.5	12.5	12.5	
2018CBMF-017	Ep1	Ep2	Ep3	Ep4	Ep5	Ep6	Ep7	Ep8		Ep1	Ep2	Ep3	Ep4	Ep5	Ep6	Ep7	Ep8
Ca	9.36	9.74	9.05	9.56	9.4	9.48	9.69	9.17		1.92	$\overline{2}$	1.85	1.96	1.93	1.95	1.99	1.88
Fe	4.6	5.04	4.79	4.88	4.9	5.1	5.11	4.96		0.94	1.03	0.98	1	1	1.05	1.05	1.02
Al	10.09	9.48	10.05	9.88	9.77	9.67	9.54	9.78		2.06	1.94	2.05	2.02	2	1.99	1.96	$\overline{2}$
Si	14.71	14.65	14.81	14.58	14.67	14.48	14.61	14.74		3.01	$\overline{3}$	3.03	2.99	3.01	2.97	2.99	3.02
\overline{O}	61.08	61	61.14	60.99	60.98	60.88	60.98	61.04		12.5	12.5	12.5	12.5	12.5	12.5	12.5	12.5
2018CBMF-019	Ep1	Ep2	Ep3	Ep4						Ep1	Ep2	Ep3	Ep4				
Ca	9.66	9.63	9.89	9.71						1.98	1.97	2.03	1.99				
Fe	5.08	5.03	4.93	5.36						1.04	1.03	1.01	1.1				
AI	9.49	9.53	9.6	9.37						1.94	1.95	1.97	1.92				
Si	14.71	14.71	14.59	14.49						3.01	3.01	2.99	2.97				
Ω	61	61	60.94	60.94						12.5	12.5	12.5	12.5				

726 Supplementary Table 2. Quantitative SEM results for spot epidote chemical analysis organized by sample. The numbers represent the atomic 727 number of each element in the chemical formula of epidote $Ca_2(Fe^{3+}, Al)Al_2[SiO_4][Si_2O_7]O(OH)$.

Figure 1. The tectonic origin and alteration history of the Taieri Mouth volcanics were considered within the geologic context of the Otago Schist region. a Regional map of the Otago Schist and surrounding terranes. b Location of the field site Taieri Mouth along with the studied igneous regions of the Chrystalls Beach Complex (CBC) in South Island, New Zealand. Isograds and tectonic affinities after Coombs et al. (2000), Fagereng and Cooper (2010), and Pitcairn et al. (2006).

368x219mm (300 x 300 DPI)

Figure 2. Geological map of the three studied zones and unobserved area (i.e., recent sediment and foliage) within the Taieri Mouth locale. Sample locations are marked with associated identification numbers. Inset shows the studied locality with respect to local roads and the Akatore Fault.

380x224mm (300 x 300 DPI)

Figure 3. Structural features of pillows and veins at the headland. a Mapped cross-section of metabasalts and concentrated vein networks at the headland (24m wide outcrop; see Fig. 2) where the majority of dip orientations of veins are near perpendicular to those of pillows. b Vein dip orientation within the Headland and pillow island. The number of veins is denoted as n.c Relative sequence of fracture genesis, fluid-flow and alteration extrapolated from relict cross-cutting relationships. Restoration depicts episodic stages (1-3) of left-lateral faulting that produced the overlapping veins and microfaults. The extensional low angle normal fault of stage 2 is nearly perpendicular to the alteration veins.

261x233mm (300 x 300 DPI)

Figure 4. Vein morphotypes (left: field; right: photomicrograph) on the headland are indicative of on-axis fracture genesis: a tension gash of a straight vein, b vein around the pillow margins, and c radiating network of veins and veinlets.

276x357mm (300 x 300 DPI)

Let the set of the set Figure 5. Major oxides and trace element results: a Pillow samples of Taieri Mouth from our studyand Fagereng & Cooper (2010) plot as mid-ocean ridge basalt (MORB) while those of Akatore Creek and Watsons Beach from Fagereng & Cooper (2010) plots as others in the tectonic discrimination diagrams N-after after Pearce (2008). . See Fig. 1 for sample location of data from Fagereng & Cooper (2010). b Trace elements of bulk rock samples from Taieri Mouth show the elemental enrichments relative to N-MORB after Sun and McDonough (1989). Blue text and lines emphasize mobile large ion lithophile elements Cs, Rb, Ba, K, Sr.

358x150mm (300 x 300 DPI)

Figure 6. Major oxide relationships from bulk chemical analyses of metabasalts from the headland (green), pillow island (blue), and the deformed zone (red). These plots have been used in existing literature (Mottl 1983; Humphris and Thompson, 1978; Coogan et al., 2019) to express the extent of chemical exchange between seawater and basalt during hydrothermal alteration: a CaO v. MgO (wt. %), b TiO2 v. MgO (wt. %), c Fe2O3 v. LOI (wt. %), and d Na2O v. MgO (wt. %).

309x217mm (300 x 300 DPI)

Figure 7. New 87Sr/86Sr of altered basalt and epidote grain separates corrected to 200 Ma plotted against δ18O of the same samples.

139x257mm (300 x 300 DPI)

Supplementary Figure 1. Distinguishing structural features from each zone. a The headland consists of a concentrated zone of vertical veins. b The headland begins inland with a thrust fault and lava flow. c Pillows at the pillow island are surrounded by zones of weaknesses where interpillow hyaloclastites have been weathered away. d Rounded pillows on the horizontal cross-section of pillow island. e Veins in the deformed zone are compressed compared to those well-preserved at the headland.

449x202mm (300 x 300 DPI)

Supplementary Figure 2. Cataclastic fabrics and textures in sampled pillows are associated with low temperature (250-300oC) seafloor hydrothermal alteration. For example, reflected light microscopy shows a sulfides in the cataclastic texture of the basalt, b pyrite (yellow), and c sphalerite (red to orange). SEM shows secondary mineral replacement textures such as d an euhedral spear of epidote growth, and e the poikilitic texture of the albitization reaction in plagioclase to produce epidote. Microscopy shows f preserved quartz amydgules in basalt groundmass, g albite twinning in groundmass of plagioclase and pyroxene, h deformed grains with lack of prograde chemical changes, and the lack of carbonates.

460x370mm (300 x 300 DPI)

Supplementary Figure 3. Quantitative SEM data show the compositional variation in the Fe3+:Al ratio of epidote samples from the headland (green), pillow island (blue) and the deformed zone (red). Left y-axis show the pistacite number calculated by $[Fe] \wedge (3+)/(([Fe] \wedge (3+)+Al)) \times 100$. Grey line shows the slope governed by the stoichiometry of Fe3+ and Al atoms in epidote, which adds up to the sum of three. Green region shows the range for the early pistacitic (Ps=0.28-0.37) epidote variety.

317x244mm (300 x 300 DPI)