



Hydrothermal contributions to global biogeochemical cycles: Insights from the Macquarie Island ophiolite

Rosalind M. Coggon^{a,*}, Damon A.H. Teagle^a, Michelle Harris^{a,b}, Garry J. Davidson^c,
Jeffrey C. Alt^d, Timothy S. Brewer^{e,1}

^a Ocean and Earth Science, National Oceanography Centre Southampton, University of Southampton, European Way, Southampton SO14 3ZH, UK

^b School of Geography, Earth and Environmental Sciences, Plymouth University, Plymouth PL4 8AA, UK

^c ARC Centre for Excellence in Ore Deposit Research (CODES), School of Physical Sciences, University of Tasmania, Private Bag 79, Hobart 7001, Australia

^d Earth and Environmental Sciences, University of Michigan, 2534 C.C. Little Building, 1100 North University Ave, Ann Arbor, MI 48109-1005, USA

^e Department of Geology, University of Leicester, University Road, Leicester LE1 7RH, UK

ARTICLE INFO

Article history:

Received 2 December 2015

Accepted 17 August 2016

Available online 30 August 2016

Keywords:

Ocean crust

Hydrothermal alteration

Biogeochemical cycles

Macquarie Island

Ophiolite

ABSTRACT

Hydrothermal circulation is a fundamental process in the formation and aging of the ocean crust, with the resultant chemical exchange between the crust and oceans comprising a key component of global biogeochemical cycles. Sections of hydrothermally altered ocean crust provide time-integrated records of this chemical exchange. Unfortunately, our knowledge of the nature and extent of hydrothermal exchange is limited by the absence of complete oceanic crustal sections from either submarine exposures or drill core. Sub-Antarctic Macquarie Island comprises ~10 Ma ocean crust formed at a slow spreading ridge, and is the only sub-aerial exposure of a complete section of ocean crust in the ocean basin in which it formed. Hydrothermally altered rocks from Macquarie Island therefore provide a unique opportunity to evaluate the chemical changes due to fluid–rock exchange through a complete section of ocean crust. Here we exploit the immobile behavior of some elements during hydrothermal alteration to determine the precursor compositions to altered Macquarie whole rock samples, and evaluate the changes in bulk rock chemistry due to fluid–rock interaction throughout the Macquarie crust. The extent to which elements are enriched or depleted in each sample depends upon the secondary mineral assemblage developed, and hence the modal abundances of the primary minerals in the rocks and the alteration conditions, such as temperature, fluid composition, and water:rock ratios. Consequently the chemical changes vary with depth, most notably within the lava–dike transition zone where enrichments in K, S, Rb, Ba, and Zn are observed. Our results indicate that hydrothermal alteration of the Macquarie crust resulted in a net flux of Si, Ti, Al, and Ca to the oceans, whereas the crust was a net sink for H₂O, Mg, Na, K, and S. Our results also demonstrate the importance of including the contribution of elemental uptake by veins for some elements (e.g., Si, Fe, Mg, S). Extrapolation of our results, assuming a crustal production rate of 3 km²/yr, yields estimates of the hydrothermal contribution to global geochemical cycles. For example, the Mg flux to the crust is estimated to be $3.3 \pm 1.1 \times 10^{12}$ mol/year, sufficient to balance the riverine Mg input to the oceans given the uncertainties involved. However, the relationship between spreading rate and hydrothermal chemical exchange fluxes remains poorly understood, and the approach described here should be applied to crust produced at a range of spreading rates to refine the global hydrothermal flux estimates.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Hydrothermal circulation is an important component of global biogeochemical cycles. Chemical exchange between seawater and the

ocean crust influences the composition of the oceans, the ocean crust, and via subduction the composition and heterogeneity of the mantle. Despite nearly 50 years of scientific ocean drilling, the ultimate goal of drilling a continuous in situ section through the entire ocean crust has not yet been achieved (Teagle and Ildefonse, 2011). The absence of complete oceanic crustal sections makes full quantification of the ocean crust's primary compositions and its hydrothermal contributions to global geochemical cycles difficult. In particular, our knowledge of the nature and extent of fluid–rock interaction in the lower crust is limited by the absence of accessible submarine exposures or drill core. Ophiolites, sub-aerially exposed sections of crust formed via seafloor spreading and subsequently emplaced on continental margins, have

Abbreviations: LDTZ, lava–dike transition zone; DGTZ, dike–gabbro transition zone; Mg#, $100 \times \text{Mg}/[\text{Mg} + \text{Fe}^{2+}]$, calculated assuming that 90% of the total iron is Fe²⁺; LOI, loss on ignition; MORB, mid-ocean ridge basalt.

* Corresponding author.

E-mail addresses: R.M.Coggon@southampton.ac.uk (R.M. Coggon), Damon.Teagle@southampton.ac.uk (D.A.H. Teagle), michelle.harris@plymouth.ac.uk (M. Harris), Garry.Davidson@utas.edu.au (G.J. Davidson), jalt@umich.edu (J.C. Alt).

¹ Deceased.

been used to investigate chemical exchange between seawater and the ocean crust (e.g., [Bednarz and Schmincke, 1989](#); [Gregory and Taylor, 1981](#)). However, most intact ophiolites formed in supra-subduction settings and whether these outcrops are representative of normal mid-ocean ridge crust remains controversial ([Miyashiro, 1973](#); [Rautenschlein et al., 1985](#)). These ophiolites are more intensely recrystallized, and consistently record a greater extent of fluid–rock exchange than crust from mid-ocean ridges ([Alt and Teagle, 2000](#); [Bickle and Teagle, 1992](#)).

Sub-Antarctic Macquarie Island is the only sub-aerial exposure of a complete section of ocean crust in the open-ocean basin in which it formed ([Varne et al., 1969, 2000](#)). Macquarie Island provides a unique opportunity to investigate how the ocean crust is accreted, including the role of hydrothermal circulation in cooling the upper and lower crust and the resultant fluid–rock chemical exchange.

Chemical exchange between hydrothermal fluids and the crust is facilitated by mineral dissolution and the formation of secondary minerals, which replace igneous minerals and mesostasis, fill primary porosity (vugs and interstices) and form veins. Hydrothermally altered rocks therefore provide a time-integrated record of the effects of fluid–rock exchange on the composition of the crust. Here we evaluate the hydrothermal changes in bulk rock chemistry of Macquarie Island rocks, and compare our results with other independent estimates of seawater–ocean crust hydrothermal exchange.

2. Macquarie Island

Sub-Antarctic Macquarie Island (54°30'S, 158°56'E) in the Southern Ocean comprises ~10 Ma ocean crust formed during slow spreading (10 mm/yr half rate) along the Australian–Pacific plate boundary ([Armstrong et al., 2004](#); [Duncan and Varne, 1988](#); [Quilty et al., 2008](#); [Varne et al., 2000](#)). Spreading initiated along this boundary during the Eocene when the Tasman Sea rifted from the Campbell Plateau along a series of short ridge segments separated by fracture zones ([Sutherland, 1995](#)). Subsequent migration of the pole of Australian–Pacific relative plate motion caused progressive re-orientation of the spreading segments, producing the distinctive regional fracture zone curvature, with the system ultimately entering a dextral transpressional regime when extension was sub-parallel to the plate boundary ([Cande et al., 2000](#); [Lamarche et al., 1997](#); [Massell et al., 2000](#); [Sutherland, 1995](#)). Shortening along the boundary uplifted the Macquarie Ridge Complex, exposed at Macquarie Island since ~0.6 Ma ([Adamson et al., 1996](#)). The island comprises crust formed as the magmatism waned, with rocks from all crustal levels and the uppermost mantle exposed ([Fig. 1](#)) ([Varne et al., 2000](#); [Wertz et al., 2003](#)).

Basaltic lavas crop out across the southern three quarters of the island and on North Head ([Fig. 1](#)). To the northwest is an uplifted section of intrusive ocean crust comprising a sheeted dike complex, massive gabbros, layered gabbros, and a cumulate sequence of ultramafic rocks ([Fig. 1](#)), with the underlying residual mantle harzburgites exposed at Eagle Point. The extrusive portion of this block is not exposed, but a sequence of steeply dipping sheeted dikes that grade upwards into gently dipping lavas occurs within a 5 km wide fault-bounded block on the west coast near Double Point and Mount Waite, within which the original seafloor relationships are preserved and the lava–dike boundary is the original extrusive–intrusive crustal transition zone ([Davidson et al., 2004](#)).

Three major faults juxtapose rocks from different crustal levels or metamorphic grade ([Selkirk et al., 1990](#); [Varne et al., 2000](#)) ([Fig. 1](#)). The Finch–Langdon Fault separates the intrusive crustal section from lavas to the south. It is cemented by hydrothermal minerals, has talus breccias with clasts of basalt, dolerite and gabbro and is overlain by lava flows, consistent with it being a relict axial seafloor spreading fault ([Wertz et al., 2003](#)). The Isthmus fault emplaces greenschist facies dikes against the lower grade North Head lavas and the Major

Lake Fault Zone emplaces sheeted dikes and lavas against extrusives of a lower metamorphic grade ([Daczko et al., 2005](#); [Lewis, 2007](#); [Portner et al., 2010](#); [Rivizzigno and Karson, 2004](#)). There are numerous other minor faults throughout the island ([Goscombe and Everard, 2001](#)).

All levels of the Macquarie crust have been affected by fluid–rock interaction. O and C isotopic analyses reveal that the crust interacted with seawater-derived fluids, rather than meteoric water. The lavas interacted with cold seawater at high water:rock ratios, whereas the lower crust interacted with hotter (300–600 °C) hydrothermal fluids at low water:rock ratios ([Cocker et al., 1982](#)).

2.1. Macquarie Island sample transects and stratigraphic reconstruction

Using the published geological maps ([Goscombe and Everard, 1998a](#)), supplemented by our own field observations, we selected three transects through the Macquarie crust to develop a complete ocean crustal section: a parallel pair of transects through the upper crust near Mount Waite and Double Point (A and B, [Fig. 1](#)); and the coastal Isthmus to Eagle Point transect through the intrusive crust and uppermost mantle (C, [Fig. 1](#)).

2.1.1. Mount Waite and Double Point transects

The Mount Waite transect traverses a narrow (<50 m) zone of steeply dipping (~75° W) sheeted dikes and the overlying extrusive rocks ([Fig. 2a](#)). The extrusive sequence consists of variably (<5% to >30%) plagioclase-phyric pillow lavas, volcanoclastic breccias and turbiditic sediments, dipping 20–30° E. Pillow units are typically 50–100 m thick, and can be traced laterally for several kilometers. The lavas are pervasively altered. The upper lavas contain smectite, iron-oxides and carbonate, typical of low temperature 'ocean floor weathering' ([Alt et al., 1986](#)), whereas the underlying lavas were partially altered under zeolite or lower greenschist facies conditions and contain chlorite ± zeolites ± smectite ± calcite ± albite ± prehnite ± epidote. The inter-lava sediments include 1–10 m thick graded conglomerate, sandstone and red shale beds. Assuming the paleo-vertical is perpendicular to the lava flows, the extrusive section is ~850 m thick. A small volcanic cone of radially outward dipping elongate pillow lavas near Pyramid Peak, to the east of Mount Waite, indicates that the top of the Mount Waite extrusive sequence was at or near the paleo-seafloor ([Griffin and Varne, 1980](#)). The lava–dike transition (LDTZ) is therefore reconstructed to 850 m below seafloor, with sample depths assigned from this datum.

The Double Point transect is similar to the Mount Waite transect, but with a greater expanse of sheeted dikes exposed ([Fig. 2b](#)). The dikes are 1.5 to 3 m wide, with narrower cross-cutting dikes increasingly abundant up section ([Davidson et al., 2004](#)), and are partially altered under greenschist facies conditions (Table S1). The LDTZ is cut by minor faults with disseminated pyrite and chlorite halos ([Davidson et al., 2004](#)). Similar sulfide anomalies have been identified at the LDTZ in ocean crust from ODP Holes 504B and 1256D, and the Troodos ophiolite, Cyprus ([Alt, 1994, 1995b](#); [Alt et al., 2010](#)). A 40 m wide fault zone with epidote–actinolite–zoisite–quartz–chalcopyrite–pyrite veins is interpreted as a hydrothermal upwelling site ([Davidson et al., 2004](#)). The lavas at the western tip of Double Point were altered under greenschist to amphibolite facies conditions and were intruded by the dikes during spreading ([Davidson et al., 2004](#)), consequently the transect is treated as a continuous section. Sample depths are assigned assuming the paleo-vertical is perpendicular to the bedding, and the LDTZ was 850 m below seafloor.

2.1.2. The Isthmus–Eagle Point transect

Sheeted dikes are exposed in Hasselborough Bay. The dikes are typically 0.5–3 m wide and can be traced laterally <30 m along strike. They are sub-parallel, and their chilled margins dip ~60° SW on average ([Fig. 3](#)). Some dikes enclose and are chilled against gabbro screens that

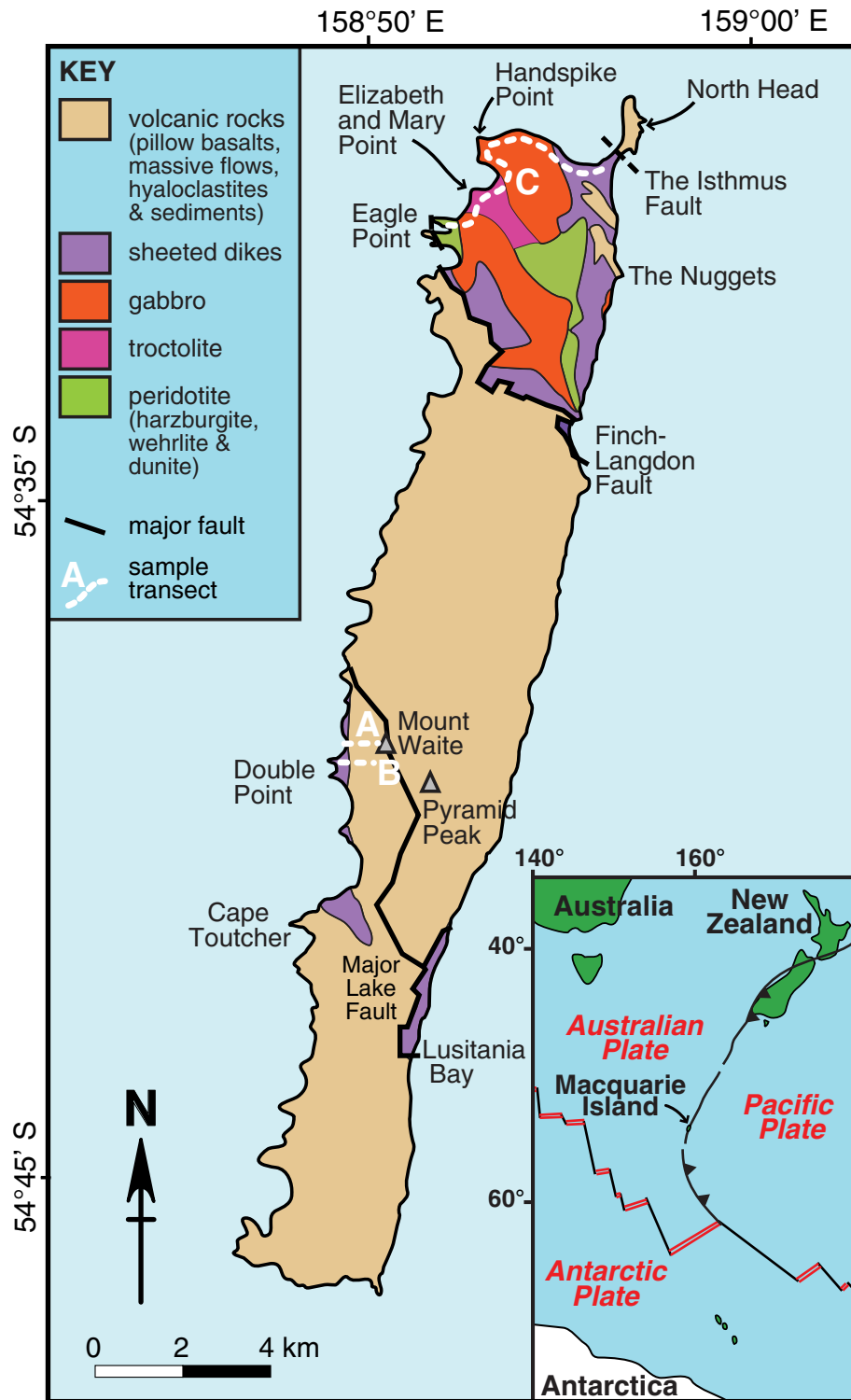


Fig. 1. Summary geological map of Macquarie Island, after Goscombe and Everard (1998a) and Varne et al. (2000). Major faults interpreted to be seafloor-spreading structures are distinguished, following Wertz et al. (2003) and Daczko et al. (2005). Inset map shows the main regional tectonic features, after Kamenetsky et al. (2000). (For interpretation of color in this figure, the reader is referred to the web version of this article.)

make up <5% of the outcrops. The dikes are aphyric to highly plagioclase phyr, with increasing phenocryst abundance and grain size of ground-mass and phenocrysts away from the well-defined chilled margins. Both porphyritic and aphyric dikes occur throughout the sheeted dike section, cross-cut by later stage narrow (~10 cm wide) aphyric dikes. The dike–gabbro transition (DGTZ) is characterized by an increase in size and abundance of gabbro screens and a decrease in the abundance

of dolerite dikes. The sheeted dikes were altered under greenschist facies conditions, with amphibolite grade dikes in the DGTZ. The most intense alteration typically occurs in ‘halos’ that flank veins.

The lower crust is predominantly massive gabbro with enclaves of anorthosite and olivine gabbro. Compositional layering is restricted to Handspike Point where felsic and mafic layering is oriented ~126/48°SW, sub-parallel to sheeted dike margins indicating

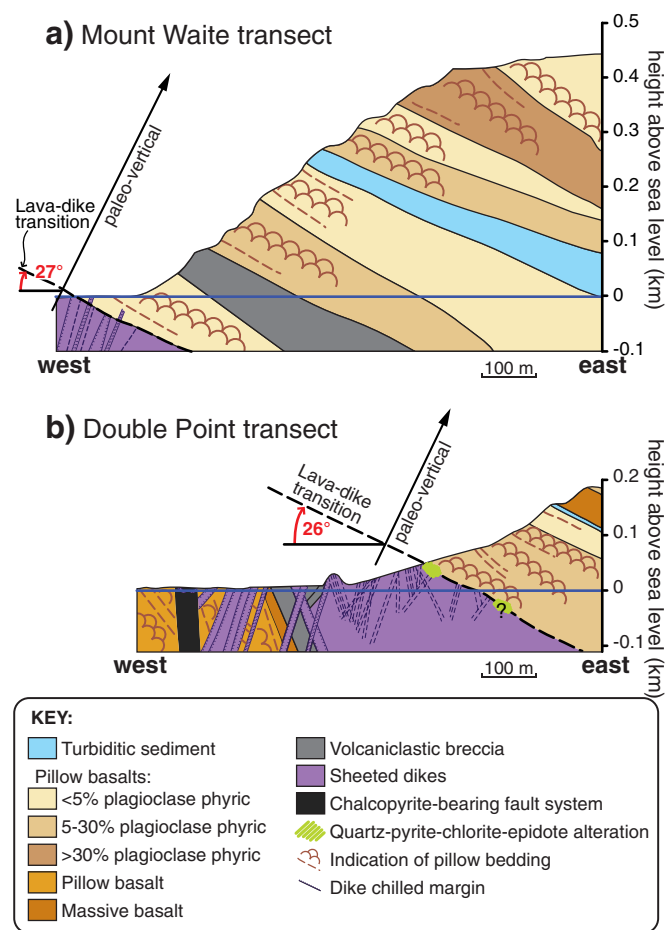


Fig. 2. Cross-sections parallel to: (a) the Mount Waite transect; and (b) the Double Point transect, after Davidson et al. (2004). Representative lava bedding and dike chilled margin orientations are indicated. (For interpretation of color in this figure, the reader is referred to the web version of this article.)

it was originally sub-vertical. The gabbros are typically fresher than the overlying sheeted dikes and were altered under greenschist to amphibolite facies conditions (Table S1). The alteration is highly heterogeneous and most intense adjacent to veins. Sub-parallel amphibole + chlorite veinlets impart a weak fabric and are cut by wider (<5 mm) epidote + prehnite veins and later-stage cataclastic prehnite + chlorite veins. Dolerite dikes similar to those of the sheeted dike complex occur throughout the gabbro, but were altered under similar conditions to the host gabbro. Narrower (<40 cm) microgabbro dikes and veins are common, with diffuse margins suggesting emplacement before the host gabbro had completely cooled. The transition between the gabbro and the underlying harzburgite comprises a complex association of highly to completely altered ultramafic rocks including dunite, plagioclase dunite, wehrlite, plagioclase wehrlite, olivine gabbro, troctolite and harzburgite. The contacts between the rock units are poorly constrained by limited exposure. Troctolite exposed at Elizabeth and Mary Point contains alternating mafic and felsic layers that dip ~30° east-northeast. The layers are sub-parallel and typically a few centimeters to tens of centimeters thick. Increasing plagioclase abundance upwards within layers indicates they are the correct way up (Goscombe and Everard, 2001). Dolerite sills intrude the troctolite at an oblique angle to the layering. The harzburgite exposed at Eagle Point is massive, serpentinized, and intruded by pegmatitic gabbro and rare <1 m wide plagioclase phryic dolerite dikes that are pervasively prehnitized or rodingitized. The paleo-vertical of this section is constrained to lie within the average plane of the dolerite dike chilled margins, which dips ~60° SW. The troctolite compositional layering is

orthogonal to the sheeted dikes' chilled margins, with the pseudo sedimentary structures indicating they are paleo-horizontal layers. Its pole is therefore taken as the paleo-vertical for this transect (Fig. 3b).

2.2. The proto-Macquarie Island ocean crust

Although slow-spread ocean crust is architecturally complex (e.g., Cannat et al., 2008; MacLeod et al., 2009), layered crust similar to that formed at fast spreading rates (Penrose Conference Participants, 1972) may be produced at the middle of relatively robust slow-spreading accretionary segments (Dick et al., 2003, 2006; Sinha et al., 1998). The proto-Macquarie Island crust includes all the components of normal layered ocean crust. Our sample transects are combined to give a complete section through this crust, with the LDTZ of the Mount Waite and Double Point transects aligned at 850 m below seafloor (mbsf), and the alteration assemblages of the sheeted dikes of the Eagle Point–Isthmus and Double Point transects correlated (Fig. 4). Our composite section is similar to previous Macquarie stratigraphies (Dijkstra and Cawood, 2004; Goscombe and Everard, 1998b), but with significantly different layer thicknesses. This in part reflects considerable lateral variability in crustal layer thicknesses across Macquarie Island, for example the maximum exposed thickness of lavas is 1.4 km. Goscombe and Everard (1998b) use the average thickness of gabbro in other ophiolites, which is approximately double the maximum gabbro thickness observed on Macquarie Island. The reconstructed thickness of the proto-Macquarie crust (3–4 km; Fig. 4) is consistent with its formation on a short segment of a slow spreading ridge in a waning magmatic system (Cannat, 1996; Chen, 1992; Dick et al., 2003).

The syn-volcanic tectonism along the Finch–Langdon Fault (Rivizzigno and Karson, 2004; Wertz et al., 2003) and the intrusion of dolerite dikes into relatively cool gabbros and harzburgite indicate that the Macquarie crust was generated during multiple magmatic episodes alternating with periods of tectonic extension, analogous to the 'tectono-magmatic cycles' observed at slow-spreading ridges (Sinha et al., 1998). The timing of the different magmatic events remains poorly constrained, and the co-genetic relationships between the different units unknown. For example, the majority of Macquarie basalts have highly enriched mid-ocean ridge basalt (MORB) compositions indicative of small-degrees of fractional melting (Kamenetsky et al., 2000) that are not consistent with their formation during the melting event that depleted the Macquarie upper mantle (Wertz, 2003). Despite its formation during multiple magmatic events, Macquarie Island represents the best available continuous section through the lower ocean crust produced at a slow-spreading ridge and complements lower crustal sections drilled at slow spreading ridges into gabbro (for example ODP Hole 735B and IODP Hole 1309D; (Blackman et al., 2006; Dick et al., 1999; Robinson et al., 1989)).

3. Analytical techniques

Representative samples (>1 kg) were taken every 20 m along transects orthogonal to bedding at Double Point and Mount Waite, with additional samples taken from fracture zones. Along the steep cliff sections of these transects the outcrop is nearly continuous, with soft sediment interbeds preserved in the walls of transecting gullies. Along the Isthmus–Eagle Point coastal transect outcrops are discontinuous, separated by cobble beaches and areas of marshland. Large samples (1–5 kg) representative of the rock types in each outcrop were taken.

Thin sections were prepared to include the variations in igneous, metamorphic, or tectonic features. Samples for whole rock geochemical analyses were cut, using a diamond saw, avoiding these heterogeneities with sub-samples of more intensely altered zones prepared for comparison. Exterior weathered surfaces were removed, and samples were ultrasonicated in deionized water, dried for 12 h at 70 °C, fragmented to <1 cm chips between sheets of clean paper in a hardened pure-iron

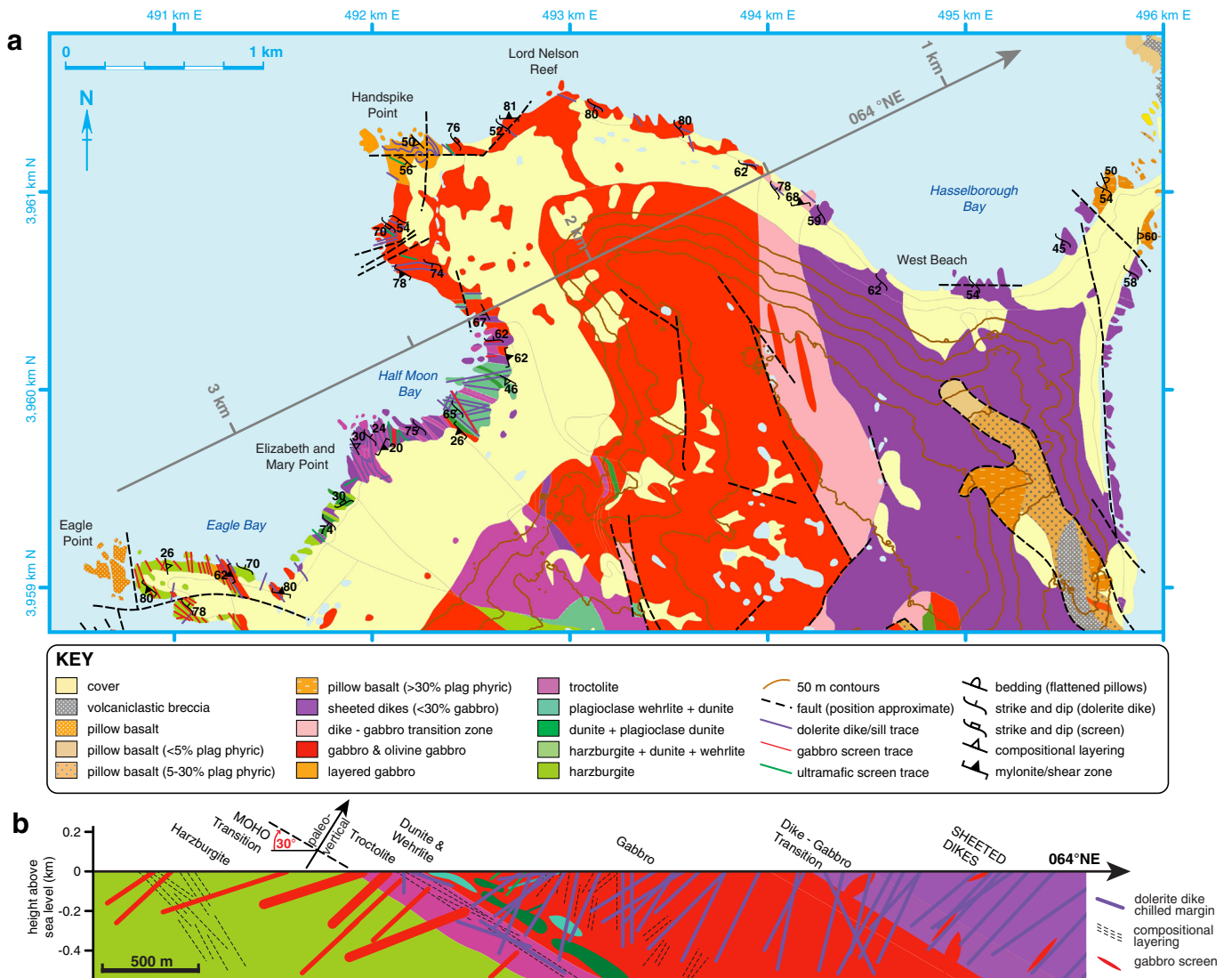


Fig. 3. (a). Geological map of the Isthmus–Eagle Point transect area, after Goscombe and Everard (1998a), supplemented with our own structural measurements. Lithological and structural data are projected onto a line perpendicular to the paleo-vertical to construct a cross-section (b), with reconstructed proto-Macquarie Island crustal depths indicated along this line. (For interpretation of color in this figure, the reader is referred to the web version of this article.)

fly press, and powdered using a hardened pure-iron terna. Lithologies were determined from the modal mineralogy. The key petrographic features of each rock type are summarized in Table S1.

Geochemical analyses of 236 Macquarie Island whole rock samples are presented in Table S2. Major and trace elements were analyzed by X-ray fluorescence (XRF), following the methods of Brewer et al. (1998), using a PW1400 X-Ray Spectrometer at the University of Leicester. Geochemical reference materials were used to construct calibrations for individual elements and to evaluate precision and accuracy (Table S3). A subset of samples were analyzed at the University of Tasmania School of Earth Sciences using a PW1410XRF, following the methods of Norrish and Hutton (1969). Carbon and sulfur concentrations were analyzed using a LECO Carbon/Sulfur Analyzer by high-temperature combustion, at the University of Leicester. The lower limit of detection was 10 ppm, with a precision of $\pm 5\%$ and $\pm 8\%$ for C and S, respectively.

Trace element concentrations were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) at the University of Southampton using a VG PlasmaQuad PQ2+. Precision and accuracy were better than $\pm 5\%$ RSD and $\pm 8\%$ RMSD, respectively, for the majority of elements (Table S4).

4. Primary magmatic diversity of Macquarie Island igneous rocks

Published analyses of fresh glasses from Macquarie Island hyaloclastites and pillow margins reveal they are basaltic in composition, with 47.4–51.1 wt.% SiO_2 and 5.65–8.75 wt.% MgO , but range from depleted N-MORB to compositions more enriched than typical E-MORB (Kamenetsky et al., 2000; Wertz, 2003). They span a wider range in K_2O content (0.1–0.8 wt.%) than usual for a single MORB suite (Kamenetsky et al., 2000) and span most of the range in Zr/Y ratios of other MORB suites combined (Fig. 5a). This diversity reflects a complex melting history. Glass compositions have been divided into two groups on the basis of their Mg-numbers ($\text{Mg\#} = 100 \times \text{Mg}/[\text{Mg} + \text{Fe}^{2+}]$) and K_2O contents, Group 1 being those with the highest Mg-number at a given K_2O content (Kamenetsky et al., 2000). Group 1 glasses, which have the lowest Y concentrations at a given Zr concentration, are interpreted to be near-primitive 'parental' melts from which Group 2 glasses fractionated (Kamenetsky et al. (2000); Fig. 5a). The seriate variation in parental melt compositions is attributed to an increasing degree of partial melting of a mantle source that is homogeneous on a large scale (Kamenetsky and Maas, 2002). This interpretation is supported by a progressive decrease in the degree of incompatible

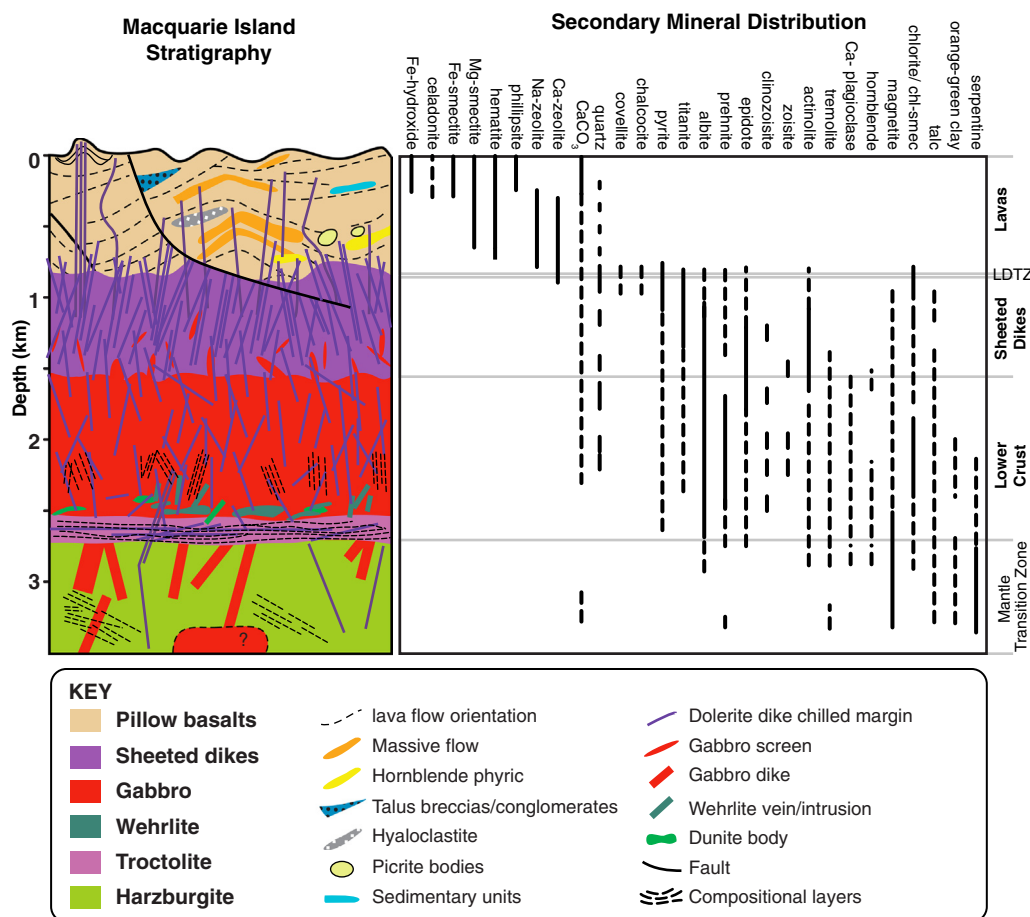


Fig. 4. Stratigraphic reconstruction of the proto-Macquarie Island ocean crust and depth distribution of secondary minerals. Details within the extrusive section after Goscombe and Everard (1998a). Secondary mineral distribution in upper crust after Griffin (1982), supplemented by our own observations. (For interpretation of color in this figure, the reader is referred to the web version of this article.)

element enrichment up through several extrusive sequences on the island (Wert, 2003). Aphyric lavas and dikes have Zr/Y ratios consistent with fractionation from parental melts with Group 1 glass compositions (Fig. 5b). The anorthosites and gabbros have similar Zr/Y ratios to the dikes and lavas produced by higher degrees of partial melting.

All whole rock samples are altered to some extent and alteration effects are superimposed on and may obscure primary magmatic compositional variations. However, there are variations in whole rock chemistry that correspond to changes in rock type, reflecting differences in primary mineral modal proportions, and hence are of magmatic origin. Consequently there are broad trends with depth; for example decreasing concentrations of Ti, Fe, Na, P, K, Sr, Zr, and Nb and increasing Cr and Ca contents and magnesium number (Fig. 6).

Since Zr, Y, and the REEs are relatively immobile during hydrothermal alteration the Zr/Y and La/Sm ratios should record primary magmatic variations through the crust. In general the La/Sm ratio decreases with depth, despite significant variability at a given depth. Gabbros, dikes and lavas with similar Zr/Y and La/Sm ratios may be co-magmatic. Systematic variations in melt composition through the gabbro section due to cyclic magma chamber processes, such as fractionation and magma replenishment, cannot be distinguished given the sampling scale.

5. Calculating the chemical changes due to hydrothermal alteration

The impact of hydrothermal circulation on ocean chemistry depends on the changes in bulk rock chemistry due to seawater–rock interaction. As hydrothermal alteration of the ocean crust is pervasive the fresh igneous precursors to altered rocks are rarely preserved, and their

compositions are difficult to determine if the altered rocks comprise a fractionated suite. However, the behavior of elements that remain immobile during hydrothermal alteration can be used to account for: (i) passive changes in elemental concentrations in response to net changes in mass; and (ii) the primary magmatic variation in precursor suites (Grant, 1982; Gresens, 1967; MacLean, 1990; MacLean and Barrett, 1993). During alteration, immobile element concentrations change only in passive response to net mass changes, being concentrated by bulk rock mass loss or diluted by mass gains (Fig. 7a). If one immobile element is incompatible (e.g. Zr, Y or Nb) and another is compatible, their fractionation trend is distinct to the alteration trends, which radiate from the origin. Their concentrations in the precursor to a given altered rock can therefore be determined from the intersection of its alteration trend and the fractionation trend, established using fresh samples from the same fractionated suite (MacLean, 1990) (Fig. 7b). Similarly the precursor's mobile compatible element concentrations can be determined from their fractionation trends with the immobile incompatible element, also defined using the fresh samples, and the calculated precursor immobile incompatible monitor element concentration.

Determining fresh precursor compositions for Macquarie Island rocks is challenging given the complex melting history of the ophiolite. For each immobile element pair the variable degree of partial melting produced a series of primitive parental melt compositions from which fractional crystallization yielded a large array of potential fresh precursor compositions (Fig. 7c–d). Consequently, precursor immobile element concentrations are difficult to determine, unless the net mass change due to alteration is known. There is a weak correlation between the samples' specific gravity and LOI (Table S2; $R^2 = 0.3$, $n = 128$)

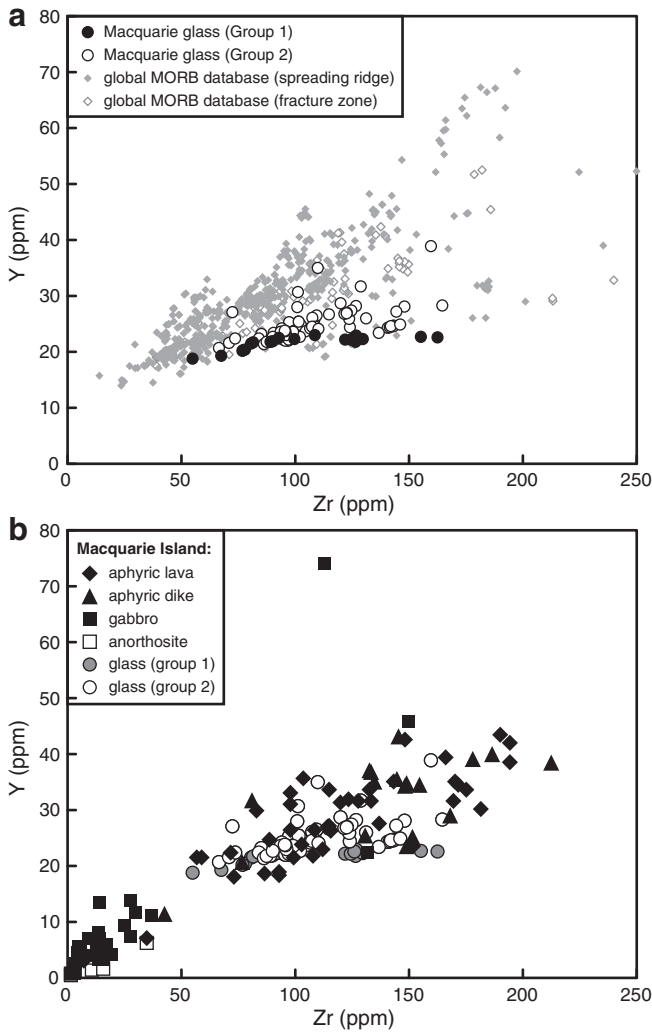


Fig. 5. (a) Y and Zr concentrations of Macquarie Island glasses, after Kamenetsky et al. (2000) and Wertz (2003). Group 1 glasses (black circles) comprise a suite of primitive parental magmas from which Group 2 melts (open circles) evolved as a result of fractional crystallization. MORB glasses from a global database of spreading ridges (gray diamonds) and fracture zones (open diamonds) are shown for comparison (Jenner and O'Neill, 2012). (b) Comparison of Y and Zr concentrations of Macquarie Island glasses (Kamenetsky et al., 2000; Wertz, 2003) and whole rock samples.

indicating a slight decrease in density associated with hydration during alteration, which equates to less than a 5% decrease in mass assuming constant volume. In the following calculations we therefore assume that there is no net mass change during alteration, i.e. $M^A/M^0 = 1$, where M^A and M^0 are the total masses of an altered rock and its fresh precursor, respectively, but allow for 5% uncertainty in this ratio.

We also assume that: (i) Zr, Y, and Nb were immobile during alteration, and can be used as 'monitors' of magmatic fractionation to estimate precursor mobile element concentrations; and (ii) fresh glasses and the least altered whole rock samples are representative precursors for the altered rocks. The Macquarie samples include eight pairs, each cut from variably altered portions of the same protolith. The more altered portions have the same Zr/Y and Nb/Y ratios as their less altered counterparts (Fig. 8) indicating that Y, Zr, and Nb were immobile during alteration. The least altered whole rock samples were identified petrographically and from their LOI, with low LOI indicating minimal addition of hydrous secondary minerals. The assumption that they represent fresh precursor compositions despite their slight alteration may result in the underestimation of some hydrothermal chemical changes.

The methods used to determine precursor compositions for different sample types are summarized in Fig. 9. The precursors to samples

crystallized from fractionated magmas (aphyric lavas and dikes, and non-cumulate plutonic rocks) are determined from the magmatic fractionation trends of compatible elements (e.g., Ti, Fe, Mn, Mg, Ca, Na and K) against immobile incompatible 'monitor' elements (Zr and Nb) defined by Macquarie glasses supplemented with the least altered dike, anorthosite, and gabbro samples to extend the range of precursor compositions. The interplay of varying degree of partial melting and extent of subsequent fractional crystallization produced a diverse range in Macquarie magma compositions (Fig. 7). However, for each compatible element the extent to which the partial melting and fractional crystallization trends diverge against the immobile monitor elements varies. We have exploited this effect, selecting the immobile monitor element (Nb or Zr) that best constrains the primary magmatic trend for each compatible element (Table S5). Several elements (Si, Al, S, Zn and Lu) show no significant variation with Zr or Nb, and the precursor concentrations adopted for each rock type are the average concentrations of the glasses and least altered samples (Table S5). Phenocryst accumulation in phyric samples causes deviations from primary magmatic fractionation trends. To determine precursor compositions for such rocks we must account for: (i) the types, abundances and primary compositions of phenocrysts; and (ii) primary magmatic variation of the groundmass. The former could be achieved by comparing samples to the least altered samples with similar phenocryst abundances, but this does not compensate for primary variation in groundmass composition. Here, we attempt to account for the variation in phyric sample precursor composition using the average compositions of the least altered samples of similar Nb content (Table S6). We make a first order estimate of the hydrothermal chemical changes to cumulate olivine gabbros through comparison with the average composition of the least altered cumulate olivine gabbro samples (Table S6). All troctolite, dunite and harzburgite samples are significantly altered, and do not represent precursor compositions. Consequently we have not calculated the chemical changes associated with alteration of these rocks.

The change in mass of component i during alteration (Δm_i) is the difference between the mass of component i before (m_i^0) and after (m_i^A) alteration:

$$\Delta m_i = m_i^A - m_i^0 \quad (1)$$

where $m_i^A = c_i^A M^A$ and $m_i^0 = c_i^0 M^0$ (M^A and M^0 are the total masses of the altered rock and its precursor, respectively, and c_i^A and c_i^0 are their concentrations of component i). The mass of the rock after alteration can be determined from the change in concentration of an immobile element, c_x

$$M^A = \frac{c_x^0}{c_x^A} M^0 \quad (2)$$

So Eq. (1) can be rewritten:

$$\Delta m_i = M^0 \left[\left(\frac{c_x^0}{c_x^A} \right) c_i^A - c_i^0 \right] \quad (3)$$

Here we present changes in mass of each element during hydrothermal alteration, calculated from the analyzed whole rock compositions and their estimated precursor compositions using Eq. (3), for an arbitrary initial sample mass (M^0) of 100 g (Fig. 10) and assuming the net mass change is less than 5% (i.e. $c_x^0/c_x^A = 1 \pm 0.05$). The errors in the calculated values of Δm_i are propagated on a sample-by-sample basis (Fig. 10) to include (i) analytical uncertainty, (ii) the uncertainty in the net change in mass; and (iii) the uncertainty in estimated precursor compositions (see Supplementary material).

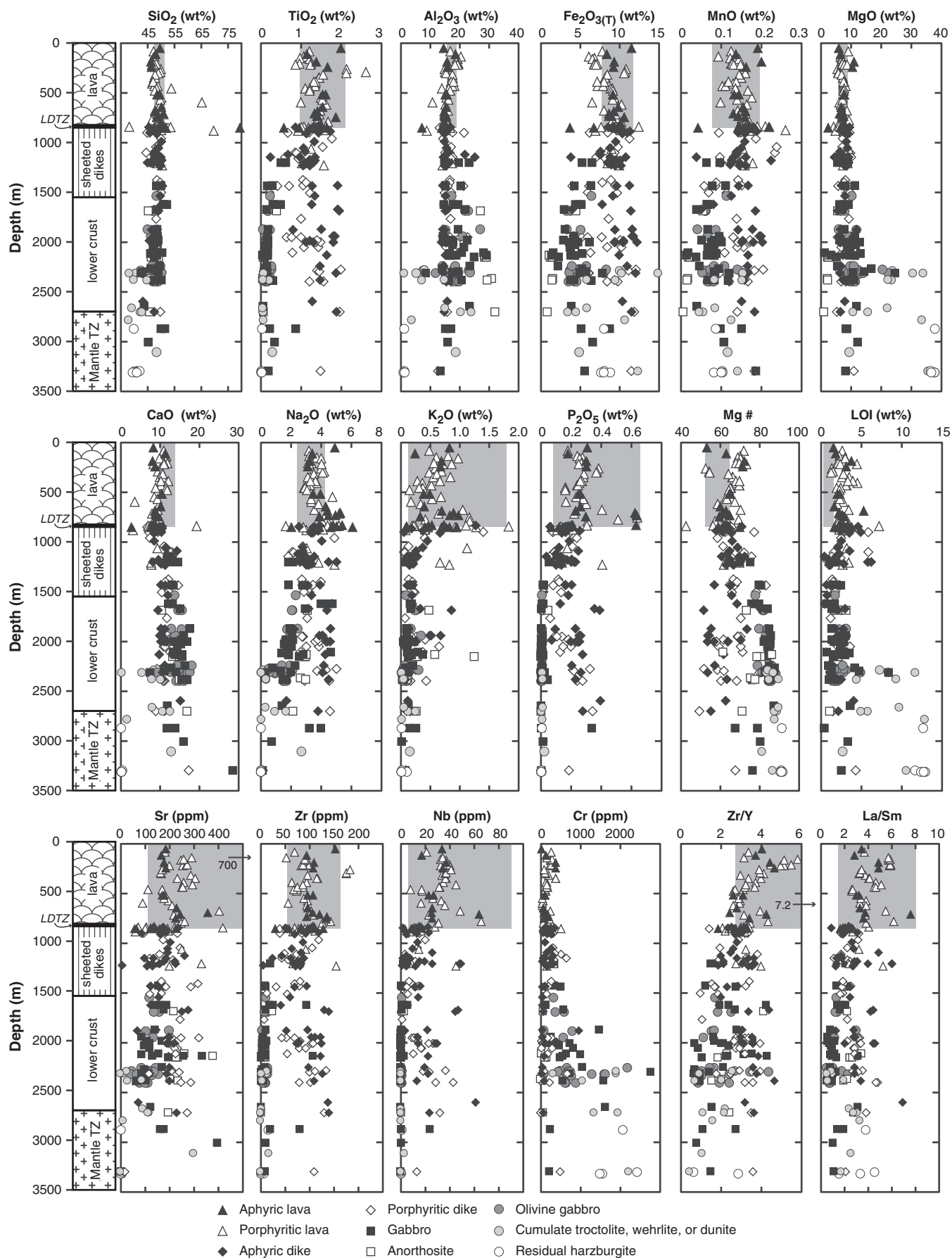


Fig. 6. Whole rock chemistry of the proto-Macquarie Island crust. Shaded area indicates the range of fresh Macquarie glass compositions, after Kamenetsky et al. (2000) and Wertz (2003).

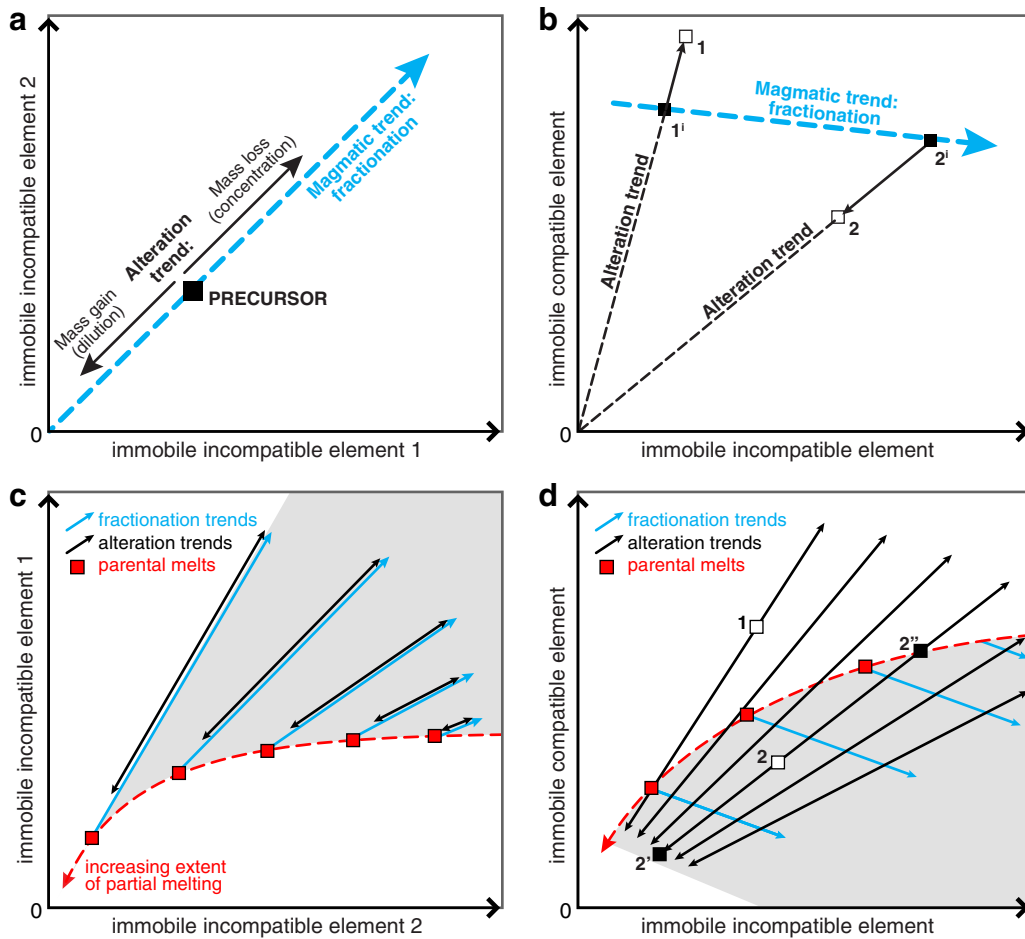


Fig. 7. Immobile element behavior during alteration. During alteration, immobile element concentrations change only in passive response to net mass loss or gain (black arrows). (a) If two immobile elements are similarly incompatible the magmatic fractionation crystallization trend (blue arrow) parallels the alteration trend. (b) If one element is compatible the magmatic and alteration trends are distinct, and the precursor composition to an altered rock is given by their intersection (e.g. altered rocks 1 and 2 have precursor compositions 1' and 2', respectively). The variation of immobile elements in Macquarie magmas is more complex: (c) if both elements are incompatible the fractional crystallization of a series of primitive parental melts (produced by differing extents of partial melting) yields an array of precursor compositions (shaded region). (d) A similar 'precursor array' is produced if one element is compatible. Here altered rock 1 must have lost mass to concentrate the immobile elements, but rock 2 could be fresh or may have altered from a wide range of precursors spanning from 2' to 2". (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6. Hydrothermal changes in Macquarie Island whole rock chemistry

In the following discussion depths (m) refer to the crustal depth within the proto Macquarie Island crust (Fig. 4). The calculated hydrothermal changes in whole rock chemistry (Δm_i) are presented as

absolute values (per 100 g of initial sample; Fig. 10), to enable comparison between lithologies and evaluation of hydrothermal exchanges within the crust. The crust is divided into 25–400 m thick intervals and the mean Δm_i within each interval are calculated assuming the samples are representative of the lithologies and their proportions in that interval.

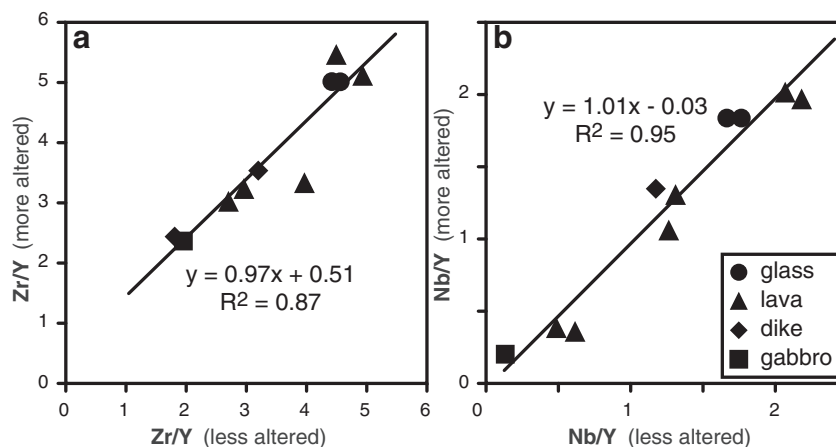


Fig. 8. Comparison of (a) Zr/Y and (b) Nb/Y ratios for pairs of more- and less-altered rocks from the same precursor; glass compositions after Wertz (2003).

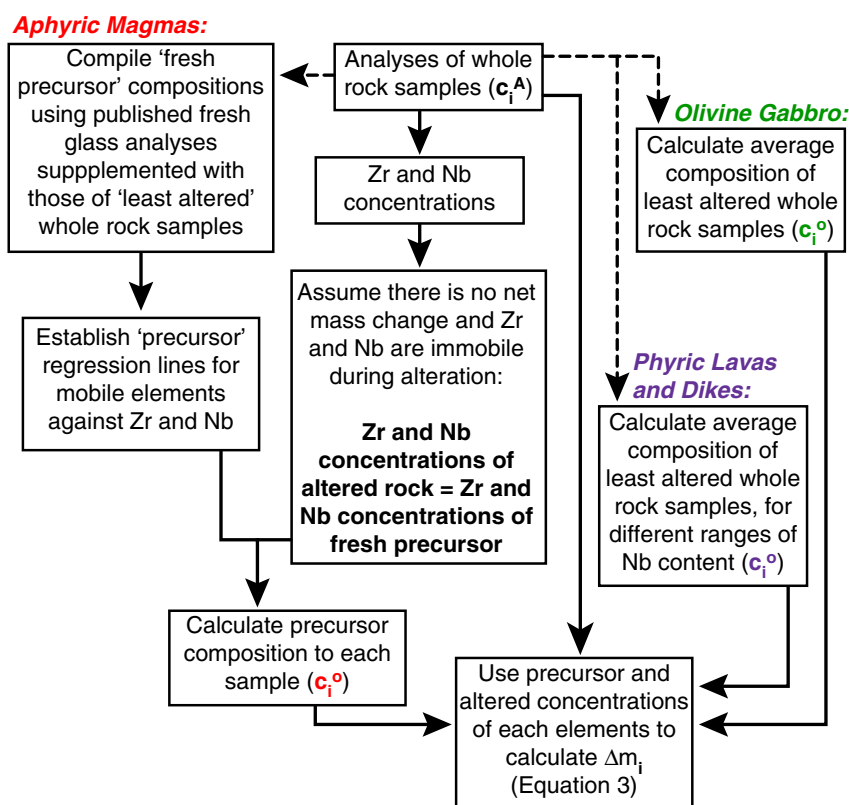


Fig. 9. Flow chart showing the methods used to calculate precursor compositions for the different types of altered whole rock samples: (i) aphyric lavas and dikes, and plutonic rocks with fractionated magma compositions; (ii) phyric lavas and dikes; and (iii) cumulate plutonic rocks.

The results (termed 'depth-averaged' data) are presented in Fig. 11. The thicknesses of the selected intervals reflect stratigraphic horizons in the section (e.g. the 25 m LDTZ) and the sampling frequency versus depth, with depth intervals containing 2–27 samples. The average relative changes in composition of each rock type are summarized in Table 1.

The most significant change in Macquarie Island whole rock chemistry is the increase in volatile content, which we have determined from altered samples' loss on ignition (LOI) and their estimated precursor H_2O contents. A sample's LOI gives an indication of its volatile content, offset by the increase in mass due to oxidation of ferrous iron during combustion. Provided the Fe^{2+}/Fe^{3+} ratio is known and there was complete oxidation of the ferrous iron, this effect can be corrected for using $LOI_{actual} = LOI_{measured} + 0.11 \text{ FeO (wt.\%)} (Lechler \text{ and } Desilets, 1987)$. Assuming that 90% of the total iron is Fe^{2+} the average Fe contents of the Macquarie lavas, dikes and gabbros correspond to an additional LOI of 0.79, 0.82 and 0.41 wt.% respectively. Consequently the hydrothermal increases in volatile content of Macquarie samples are likely underestimated here by ~0.4–0.8 g/100 g. The increase in volatile content primarily reflects hydration and CO_2 -uptake during fluid–rock interaction. Given limited sample material the C content was determined for only 55% of samples and LOI data are not corrected for CO_2 content. However, assuming that all C present in the analyzed samples occurs as CO_2 , the CO_2 content of the majority of samples is less than 0.5 wt.%, with CO_2 contents greater than 1 wt.% only observed in five $CaCO_3$ bearing dike samples. The calculated increases in volatile content (up to 8.3 g/100 g) therefore primarily reflect the formation of hydrous secondary phases, including clay minerals, zeolites, chlorite, amphiboles, epidote, talc and serpentine. On average all lithologies are moderately to highly enriched in volatiles, but the calculated enrichment is typically lower for porphyritic lava and dike samples compared to the aphyric samples (Table 1) because the least altered whole rock samples chosen to represent precursor compositions are themselves partially hydrated (LOI < 2 wt.%) relative to the fresh Macquarie glasses (0.25–1.49 wt.% H_2O (Kamenetsky

et al., 2000; Wertz, 2003)). Samples from throughout the Macquarie crust are hydrated, with harzburgite-hosted dike and gabbro samples from the base of the section (3300 m) enriched in volatiles by 3.1 and 2.3 g/100 g but CO_2 contents of <0.1 wt.%, indicating that hydrous fluids penetrated through the entire crustal section and into the uppermost mantle (Fig. 10). The greatest average enrichment (~2.5 g/100 g) occurs in the uppermost sheeted dikes, between 850 and 950 m, decreasing with depth through the sheeted dikes to ~0.4 g/100 g at 1550 m (Fig. 11).

6.1. Major elements

The changes in mass of the major element oxides are variable both within and between lithologies reflecting differences in secondary mineral assemblages, variations in the extent of fluid–rock interactions, and the thermal structure of the crust. SiO_2 was variably enriched or depleted throughout the crust, with ΔSiO_2 within error of zero for many samples due to the uncertainty in precursor compositions (Fig. 10). SiO_2 is on average depleted through most of the crust, but enrichments occur in the lavas (500–600 m), LDTZ, uppermost dikes (825–1050 m), and the DGTZ (1550–1650 m), where SiO_2 enrichment is associated with secondary quartz formation.

Titanium is usually assumed to be immobile during hydrothermal processes (Bednarz and Schmincke, 1991; MacLean and Barrett, 1993; Teagle et al., 1996), consistent with many Macquarie whole rock samples recording enrichments or depletions in TiO_2 within error of zero change (Fig. 10). Depth-averaged changes in TiO_2 reveal that the upper 200 m of gabbros gained on average ~0.2 g/100 g TiO_2 , but Ti was immobile through the rest of the lower crust (Fig. 11). Ti was also enriched within the upper-sheeted dikes (between 950 and 1050 m), but depleted or immobile through the lavas and lower sheeted dikes (Fig. 11). Enrichments likely reflect secondary titanite formation.

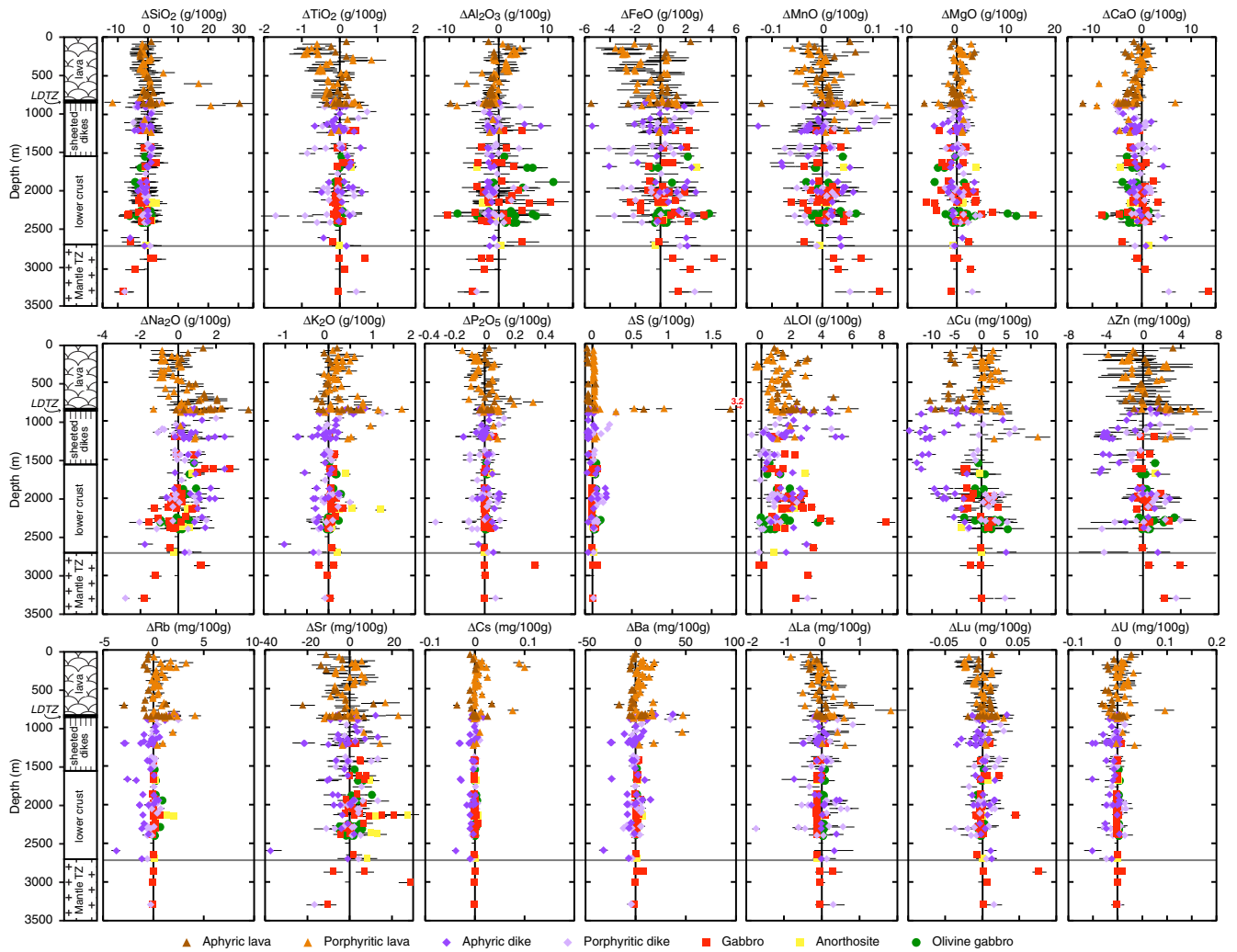


Fig. 10. Calculated hydrothermal changes in mass of major element oxides and trace elements through the proto-Macquarie Island crust, for 100 g of precursor. Errors propagated on a sample-by-sample basis (see Supplementary material).

Each Macquarie lithology includes samples that were enriched and samples that were depleted in Al_2O_3 , CaO and Na_2O due to hydrothermal alteration (Fig. 10). The depth-averaged data indicate that whole rock samples were on average depleted in CaO and Al_2O_3 and enriched in Na_2O or experienced changes in these elements within error of zero throughout the majority of the Macquarie crust (Fig. 11). Depletions in Al_2O_3 and CaO associated with Na_2O enrichments reflect the replacement of calcic plagioclase by secondary albite, although the loss of CaO due to albitisation is partially compensated by the uptake of Ca in calcium carbonate minerals and prehnite. The plagioclase-phyric lavas are depleted in Al and Ca and enriched in Na , but to a lesser extent than the aphyric lavas and dikes (Fig. 10). This may be because the large plagioclase phenocrysts are relatively fresh in the porphyritic samples, except where they are intersected by veins. Alternatively, this difference could be an artifact of using ‘least altered’ whole rock samples to define the precursor compositions of porphyritic samples.

Changes in K_2O are variable throughout the Macquarie section (Fig. 10), but K_2O is on average enriched in all rock types except the aphyric dikes (Table 1). K_2O enrichment of the lavas (~ 0.2 g/100 g on average) reflects potassium uptake from seawater-derived fluids into secondary celadonite and zeolite (phillipsite). The greatest average K_2O enrichment (~ 0.5 g/100 g) occurs at the LDTZ, with the extent of K_2O enrichment decreasing down through the sheeted dikes. The greatest average K_2O enrichment in the lower crust (0.25 g/100 g)

occurs between 2100 and 2200 m due to K_2O enrichment of anorthosites, in which plagioclase has been seritized.

Magnesium, iron and manganese were variably enriched or depleted throughout the Macquarie crust due to hydrothermal exchange, with changes reflecting the development of saponite, celadonite, Fe-oxyhydroxide and chlorite in the upper crust, and chlorite, amphibole (actinolite, tremolite and hornblende), talc and serpentine in the lower crust. There are significant enrichments in MgO , FeO , and MnO in the gabbros and olivine gabbros at ~ 2300 m of up to ~ 15 , 3.5 and 0.07 g/100 g, respectively (Fig. 10). These calculated enrichments should be treated with caution as they may be artifacts of estimated precursor compositions that do not adequately account for the primary mineral modal variation of these samples. However, they are associated with hydration of up to 8.3 g/100 g, consistent with significant fluid–rock interaction that resulted in the replacement of olivine by talc + amphibole + chlorite + clay \pm serpentine. The depth-averaged ΔMgO data indicate that MgO was enriched or within error of zero change throughout the crustal section, with the exception of the uppermost lower crust, which lost on average ~ 0.9 g/100 g MgO (Fig. 11). In contrast FeO was on average depleted or within error of zero change throughout, with the only significant enrichments (< 1.2 g/100 g) occurring between 950 and 1050 m and below 2200 m. Depth averaged ΔMnO reveal variable enrichments or depletions within error of zero change through much of the Macquarie crust. However, MnO is on average

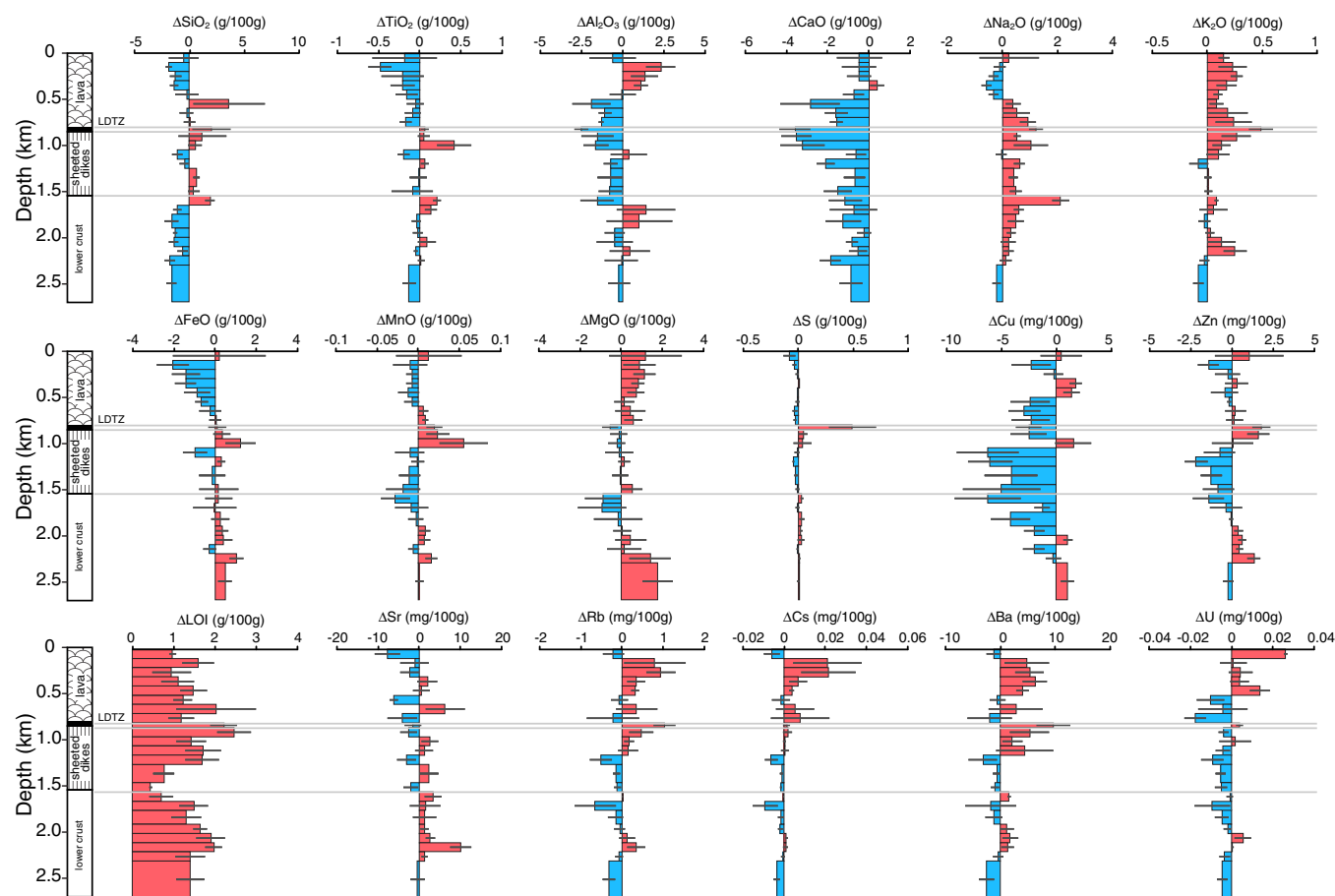


Fig. 11. Average hydrothermal changes in mass of major element oxides (g per 100 g precursor) and trace elements (mg per 100 g precursor), through the proto-Macquarie Island crust. Error bars show the standard error of the mean change in mass in each depth interval.

enriched in the lowermost lavas and upper sheeted dikes, with the extent of enrichment increasing with depth to ~0.05 g/100 g at 1050 m, but depleted in the uppermost lower crust (Fig. 11).

Changes in the sulfur content are typically small (<0.1 g/100 g) through the Macquarie crustal section and dominated by S-enrichment at the LDTZ (<3.2 g/100 g) where secondary sulfides are most abundant

(Davidson et al., 2004). Above the LDTZ, the majority of aphyric lavas have lost ~0.08 g/100 g S, whereas porphyritic lavas show no change (Fig. 10). This difference likely reflects a very early stage of alteration resulting in S-depletion that is not observed when comparing to 'least altered' porphyritic precursors that also experienced S-depletion. The average changes in S content due to hydrothermal alteration may therefore be underestimated here by 0.04 to 0.08 g/100 g, depending on the relative proportion of the lavas that are porphyritic in each depth interval (50–100%). Similarly, aphyric dikes show greater S-depletions compared to porphyritic dikes. The LDTZ and upper sheeted dikes are on average enriched in S by ~0.5 and 0.05 g/100 g, respectively, whereas the lower sheeted dikes are on average depleted in S. This is consistent with leaching of sulfur from the lower sheeted dikes by high temperature hydrothermal fluids (Alt, 1994, 1995b). In contrast the lower crust is on average enriched in S (Fig. 11).

Phosphorous is variably enriched or depleted throughout the Macquarie crustal section (Fig. 10). On average the gabbros, olivine gabbros and anorthosites are enriched in P_2O_5 (Table 1), but their absolute calculated ΔP_2O_5 values are small (<0.01 g/100 g) and generally within error of no change (Fig. 10) given the uncertainty in precursor P_2O_5 concentrations.

6.2. Trace elements

The base metals Cu and Zn were highly mobile during alteration of the Macquarie Island crust (Fig. 10). Cu is accommodated in fresh rocks by primary sulfides that typically occur as 'blebs' in the ground-mass (Doe, 1994). The estimated precursor Cu contents of the porphyritic lavas and dikes (25 ± 7) is lower than that of the aphyric

Table 1
Summary of chemical changes for each Macquarie lithology.

	Lavas		Dikes		Gabbro	Anorthosite	Olivine Gabbro
	Aphyric	Porphyritic	Aphyric	Porphyritic			
SiO ₂	(+)		(-)	(-)	(-)	(+)	(-)
TiO ₂		-	(+)	(-)	+	+++	(-)
Al ₂ O ₃	-		(-)	(-)		(-)	+
FeO _T		(-)	(+)		+	+	+
MnO	(+)	(+)			(+)	++	
MgO		(+)		(+)	(+)	++	
CaO	-	-	-			(-)	-
Na ₂ O	+		+			+	
K ₂ O	+	+++	-	+	+++	+++	+
P ₂ O ₅	+				+++	+++	+++
S	+++	+++	-	+++	-		++
LOI	+++	++	+++	++	+++	+++	++
Cu	--	++	--	++	-	-	+
Zn	+	+	-	+	+	+	+
Rb	-	+++	--		++	+++	+++
Sr	-				+	+++	+
Cs	-	+++	--	-	+	+++	-
Ba	(-)	++			+	+++	+++
La			(-)		-	---	+
Lu	+				+	+++	-
U	-	+	-	-	+	++	++

Blank = variable behavior; (+) <10% enriched; + slightly (10–50%) enriched; ++ moderately (50–100%) enriched; +++ highly (>100%) enriched; (-) <10% depleted; - slightly (10–50%) depleted; -- moderately (50–100%) depleted.

rocks ($\sim 100 \pm 20$ ppm), which may reflect the lower proportion of groundmass in porphyritic rocks. Alternatively it could be an artifact of using 'least altered samples' as precursors to these rocks if they were depleted in sulfur and consequently Cu during early hydrothermal alteration. Cu is on average moderately depleted in the aphyric lavas and dikes (Table 1). Cu-depletion of the aphyric rocks is less pronounced at the LDTZ (Fig. 10) coincident with the zone where secondary sulfides including chalcopyrite are most abundant, indicating that the depletion is partially compensated by secondary mineralization. Aphyric dikes from the sheeted dike complex experienced a greater extent of Cu-depletion (<15 mg/100 g) than those from below the DGTZ (<10 mg/100 g; Fig. 10). Consequently the greatest depth-averaged Cu depletions occur within the sheeted dikes (Fig. 11).

Zn is mildly incompatible during magmatic fractionation and is concentrated in the glass phase, but can be incorporated into olivine, spinel, magnetite, titanomagnetite and, to a lesser extent, pyroxene (Doe, 1994). Zn behaves more variably than Cu, and absolute changes in Zn content are smaller (<6 mg/100 g). The lavas are variably enriched or depleted in Zn, with no systematic difference in Δ Zn of aphyric and porphyritic lava samples (Fig. 10). Within the LDTZ there is variable Zn-enrichment (<5 mg/100 g) consistent with quartz-sphalerite-chalcopyrite mineralization in this zone (Davidson et al., 2004). Aphyric dikes record increasing Zn depletion with depth through the sheeted dike complex, to ~ 5 mg/100 g at the DGTZ, whereas Zn is variably enriched or depleted in porphyritic dikes and gabbros in this interval (Fig. 10). Although there are no correlations between Δ S and either Δ Cu or Δ Zn within the Macquarie crust, Δ Cu and Δ Zn are weakly correlated in dike samples ($R^2 = 0.44$, $n = 59$). The depletion of Cu and Zn from the aphyric dikes is consistent with previously observed base-metal losses from the lower sheeted dikes of ODP Holes 504B and 1256D due to the breakdown of sulfide minerals and titanomagnetite under greenschist facies conditions (Alt et al., 1996a, 2010).

The alkali elements Cs and Rb are incorporated into minerals by cation-substitution, with preferential substitution for ions of similar ionic potential. They therefore have an affinity for K-rich phases including clays and feldspars (Hart, 1969). Consequently Δ Rb and Δ K₂O of Macquarie samples are correlated ($R^2 = 0.82$, $n = 203$). Rb

and Cs display similar average behavior in most Macquarie lithologies except olivine gabbros, which are on average highly enriched in Rb but slightly depleted in Cs (Table 1). The anorthosites are highly enriched in Cs and Rb, which may reflect the seritization of plagioclase. The Cs and Rb enrichment of porphyritic samples relative to aphyric samples at a given depth may reflect the greater proportion of plagioclase feldspar in the phyric samples. The observed average enrichments of K, Rb and Cs in the extrusive section are consistent with uptake from seawater during low-temperature hydrothermal alteration of in-situ upper crust (Staudigel and Hart, 1983; Teagle et al., 1996). The depletion of Rb and Cs in the lower sheeted dikes and upper gabbros (Fig. 10) is consistent with their enrichment in hydrothermal fluids relative to both MORB and seawater (Palmer and Edmond, 1989; Von Damm, 1995).

The alkali earth elements Sr and Ba have an affinity for Ca, and Sr is therefore predominantly incorporated into Ca-rich phases such as feldspar, calcium carbonate, prehnite, and epidote. Sr is variably enriched or depleted throughout the Macquarie crust (Fig. 10). This variability reflects differences in the secondary mineral assemblages, with samples that contain significant volumes of calcium carbonate or epidote having gained Sr. On average Sr is slightly depleted in the aphyric lavas and dikes, but slightly to highly enriched in gabbro, olivine gabbro and anorthosite. Consequently, Sr is on average depleted or within error of zero change through the extrusive section and sheeted dikes, but enriched or within error of zero change through the lower crust (Fig. 11). This indicates that hydrothermal circulation caused a net transfer of Sr downward within the crust. Ba displays similar behavior to Sr on average in most Macquarie lithologies (Table 1) but unlike Sr, Ba is moderately enriched in porphyritic lavas and is therefore on average enriched through the upper 500 m of the crust (Fig. 11).

Uranium is variably enriched or depleted throughout the Macquarie crust (Fig. 10), and the depth-averaged changes in U content are within error of zero throughout most of the crustal section, with significant U-enrichment (<0.025 mg/100 g) occurring only in the lavas (0–100 m and 400–500 m) as a result of U-uptake from cold seawater. U is depleted on average in the Macquarie lower lavas and upper sheet dikes, by up to 0.02 mg/100 g, indicating U-loss during higher

Table 2
Summary of average vein mineral abundances and compositions in drill core.

Vein mineral	Specific gravity	Vein mineral abundance (vol.%)				Vein mineral composition (wt.%)											
		Lavas ^a	LDTZ ^b	Sheeted dikes ^b	Gabbro ^c	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	Total	Reference
Mg-saponite	2.27	0.85	0.6	0.01	0.14	47.71	0.04	5.64	15.43		0.05	16.07	0.82	0.11	0.44	86.31	^e
Celadonite	3.00	0.12				51.24	0.05	3.57	23.56		0.02	4.93	0.50	0.01	7.19	91.06	^e
Prehnite	2.88	0.01 ^d	0.01	0.01	0.01 ^d	42.67	0.01	22.83		2.07	0.07	0.78	24.87	0.03	0.03	93.35	^f
Epidote	3.45			0.01	0.008	37.95	0.08	23.47		11.74	0.11	0.27	23.07	0.02	0.01	96.73	^f
Chlorite	2.95		0.3	0.44	0.007	28.52	0.02	17.59	21.89		0.26	14.45	0.20	0.01	0.01	82.94	^e
Amphibole	3.00			0.01	0.12	51.19	0.46	4.07	14.38		0.22	14.51	11.01	0.67	0.02	96.52	^g
Feldspar	2.63				0.11	63.44	0.01	22.85		0.15			4.15	8.95	0.10	99.64	^h
Na-zeolite	2.20	0.01	0.05			59.70		18.58	0.65			0.69	1.66	4.69	5.81	91.77	ⁱ
Serpentine					0.005 ^d	40.32	0.01	0.56	5.18			37.33	0.26			96.01	^j
Calcite	2.85	0.01	0.01	0.01	0.02	Mineral formulae											
Fe(O,OH)x	2.71	0.01			0.01 ^d	CaCO ₃											
Quartz/SiO ₂	2.65	0.15	0.03	0.13	0.02	Fe(O,OH)											
Ca-zeolite	2.29		0.05	0.01	0.009	SiO ₂											
Pyrite	5.05	0.02	0.01	0.1		CaAl ₂ Si ₄ O ₁₀ (OH) ₂											
Talc	2.75			0.1	0.01 ^d	Fe ₂ S											
TOTAL:		1.17	1.06	0.83	0.47	Mg ₃ Si ₄ O ₁₀ (OH) ₂											

^a Average vol.% of Hole 1256D inflated flows and sheet and massive flows (Wilson et al., 2003).

^b vol.% in Hole 1256D (Teagle et al., 2006).

^c vol.% in Hole 735B (Dick et al., 1999).

^d vol.% estimated from Macquarie Island sample petrographic observations.

^e Median Hole 1256D vein mineral composition (Alt et al., 2010).

^f Mean Hole 504B secondary mineral composition (Laverne et al., 1995).

^g Mean Hole 504B vein and halo amphibole composition (Vanko et al., 1996).

^h Mean Hole 735B vein feldspar composition (Robinson et al., 2002).

ⁱ Mean Hole 896A secondary Na-zeolite composition (Laverne et al., 1996).

^j Mean of Holes 1274A, 1268A and 1272A vein serpentine compositions (Moll et al., 2007).

temperature fluid–rock reaction. In contrast, the lower lavas and upper sheeted dikes of ODP Hole 504B were enriched in U under greenschist facies conditions (Bach et al., 2003). Calculated values of ΔLa and ΔLu are typically small relative to the computational uncertainty for the majority of samples (Fig. 10), consistent with previous observations that the rare earth elements are generally immobile during hydrothermal alteration of in-situ ocean crust (Bach et al., 2003; Teagle et al., 1996).

7. Elemental exchange fluxes for Macquarie Island

To assess the contribution hydrothermal alteration of the Macquarie crust made to global geochemical cycles the calculated changes in composition of the Macquarie crust due to hydrothermal alteration are converted into net fluxes to or from the crust, following:

$$F_i = \sum_t \Delta \bar{m}_{i-t} z_{tp} \rho_c \quad (4)$$

where F_i is the mass flux of component i through 1 m^2 of seafloor due to alteration of a section of crust of thickness T and $\Delta \bar{m}_{i-t}$ is the average change in mass of component i per unit mass of rock in each sub-interval t , z_t is the thickness of each sub-interval t and ρ_c is the density of the crust (2900 kg/m^3). The net fluxes due to hydrothermal alteration of the Macquarie lavas, LDTZ, sheeted dikes and gabbros, are determined from the depth-averaged Δm_i (Table S7), with uncertainty propagated from the standard error of the mean chemical change of each sub-interval (Supplementary material). However, to fully account for the fluxes associated with hydrothermal alteration we also need to include the contribution from the veins that formed from fluids circulating through fractures in the crust.

Veins were deliberately excluded from the whole rock samples, as they need to be included in a manner representative of their true proportion within the crust, rather than individual samples. Unfortunately it is not possible to accurately estimate the proportion of the Macquarie crust that veins make up without drill core. However the volume and mineralogy of hydrothermal veins have been quantitatively logged in sections of ocean crust recovered by scientific ocean drilling. We therefore estimate the volume proportions of the various secondary vein-filling minerals through the Macquarie crust from their occurrence in representative drilled sections of ocean crust (Table 2). These data are combined with published major element analyses of secondary mineral compositions (Table 2) to estimate the net effect of hydrothermal vein formation in the Macquarie crust on global geochemical cycles. Assuming that the veins formed in open fractures, the net mass flux of component i through 1 m^2 of seafloor due to hydrothermal vein formation in crustal interval T is given by:

$$F_{i-v} = z_T \sum_x V_x \rho_x M_{i-x} \quad (5)$$

where z_T is the thickness of interval T , V_x is the volume proportion of the rock filled with vein mineral x , ρ_x is the specific gravity of mineral x , and M_{i-x} is the mass proportion of component i in vein mineral x . The net uptake of major elements as a result of vein formation in the Macquarie lavas, LDTZ, sheeted dikes and gabbro is calculated using Eq. (5). The net mass flux of component i through 1 m^2 of seafloor due to hydrothermal alteration of crustal interval T is given by combining Eqs. (4) and (5):

$$F_{i-\text{TOTAL}} = F_{i-v} + (1-V).F_i \quad (6)$$

where V is the total volume proportion of veins in interval T . The hydrothermal fluxes due to alteration of the Macquarie Island lavas, LDTZ, sheeted dikes and gabbros calculated using Eq. (6) (Table S7) are extrapolated to global annual fluxes (Table 3), assuming a global ocean crustal production rate of $\sim 3 \text{ km}^2/\text{yr}$ (Müller et al., 2008).

Table 3
Hydrothermal fluxes.

	Unit factor (mol/year)	Lavas		Lava-dike TZ		Sheeted dikes		Lower crust		Full crust		Total flux ^a % of Macquarie crustal budget	
		WR	WR + Veins	WR	WR + Veins	WR	WR + Veins	WR	WR + Veins	WR	WR + Veins		
Si	$\times 10^{11}$	–8.1 to 3.2	–1.8 to 9.5	0.1 to 1.4	0.2 to 1.5	–0.8 to 6.6	2.5 to 9.9	–22 to –16	–18 to –12	–25 to –10	–12 to 3.3	–0.6 to 0.2	
Ti	$\times 10^{10}$	–23 to –11	–23 to –11	0.04 to 0.3	0.04 to 0.3	–2.0 to 6.9	–2.1 to 6.9	–5.9 to 1.7	–5.8 to 1.8	–25 to –8.4	–25 to –8.1	–3 to –8	
Al	$\times 10^{11}$	–4.9 to 3.4	–4.3 to 4.1	–1.3 to –0.9	–1.2 to –0.8	–1.4 to –5.7	–12.9 to –4.6	–8.4 to 8.2	–7.6 to 9.0	–22 to –1.6	–19 to 1.0	–2 to 0.1	
Fe	$\times 10^{11}$	–11 to –4.5	–9.5 to –2.9	–0.1 to 0.2	–0.1 to 0.2	–1.4 to 3.2	0.3 to 5.0	2.3 to 7.2	2.9 to 7.8	–7.0 to 2.5	–2.8 to 6.6	–1 to 3	
Mn	$\times 10^9$	–7.9 to 4.3	–7.5 to 4.7	0.3 to 0.9	0.3 to 0.9	–2.7 to 9.7	–1.7 to 10	–5.8 to 3.8	–5.2 to 4.3	–8.5 to 11	–6.6 to 13	–2 to 3	
Mg	$\times 10^{11}$	8.2 to 18	10 to 20	–0.5 to –0.1	–0.4 to 0	–2.5 to 3.3	–1.1 to 4.8	6.7 to 24	7.7 to 25	18 to 39	23 to 44	5 to 10	
Ca	$\times 10^{12}$	–1.6 to –0.9	–1.6 to –0.9	–0.2 to –0.1	–0.2 to –0.1	–2.2 to –1.6	–2.2 to –1.6	–2.1 to –1.2	–2.0 to –1.1	–5.6 to –4.3	–5.5 to –4.2	–8 to –10	
Na	$\times 10^{11}$	–1.2 to 6.4	–1.2 to 6.3	0.7 to 1.0	0.7 to 1.0	7.4 to 12	7.3 to 12	7.1 to 12	7.3 to 13	18 to 28	18 to 28	8 to 13	
K	$\times 10^{10}$	21 to 34	23 to 35	1.8 to 2.8	1.8 to 2.8	4.1 to 12	4.1 to 12	–2.4 to 8.6	–2.3 to 8.7	32 to 50	36 to 52	27 to 42	
S	$\times 10^{10}$	–3.5 to –7.4	–3.2 to 0.7	1.9 to 4.8	1.9 to 4.8	–3.3 to 2.0	1.4 to 20	1.8 to 5.1	1.7 to 5.1	–3.3 to 4.7	19 to 27	76 to 108	
H ₂ O	$\times 10^{12}$	4.6 to 5.9	4.9 to 6.2	0.23 to 0.31	0.24 to 0.32	4.0 to 4.9	4.3 to 5.2	7.3 to 8.8	7.4 to 8.9	17 to 19	18 to 20	195 to 220	
Cu	$\times 10^8$	–16 to –4.0		–1.3 to –0.4		–4.6 to –2.6		–25 to –11		–78 to –51		–25 to –38	
Zn	$\times 10^8$	–4.3 to 2.8		0.4 to 0.8		–9.4 to –2.9		–2.8 to 2.5		–12 to –1.0		–1 to –9	
Rb	$\times 10^8$	0.9 to 3.6		0.2 to 0.3		–0.6 to 0.4		–2.8 to –1.0		–1.2 to 2.2		–8 to 15	
Sr	$\times 10^8$	–22 to –4.5		–0.9 to 0.1		–5.5 to 7.5		11 to 30		–7.1 to 22		–2 to 5	
Cs	$\times 10^6$	2.0 to 5.9		–0.01 to 0.05		–0.8 to –0.2		–2.4 to –1.2		–0.5 to 3.7		–5 to 42	
Ba	$\times 10^8$	6.4 to 18		1.0 to 2.0		–0.5 to 8.7		–10 to –0.2		3.8 to 22		3 to 17	
U	$\times 10^6$	–0.3 to 1.1		0.02 to 0.05		–1.6 to –0.7		–1.8 to –0.7		–3.0 to –1.0		–12 to –4	

^a as % of Macquarie crustal budget, with the total crustal budget calculated from the mean estimated precursor composition of each interval (Lavas, LDTZ, sheeted dikes, and lower crust) and the interval thicknesses.

8. Global hydrothermal fluxes

The ultimate goal of this and similar studies is to quantify the hydrothermal contributions from seawater–ocean crust exchange to global biogeochemical cycles, and assess how they have varied in the past. Hydrothermal fluxes between a given section of crust and the overlying ocean depend on the crust's age, architectural and thermal history, and the spreading rate. Consequently hydrothermal contributions to global geochemical cycles depend on the global length of slow, intermediate and fast spreading ridges and the age–area distribution of the ridge flanks, all of which have varied significantly throughout the Phanerozoic (Müller et al., 2008). To achieve this goal we therefore require complete sections of altered ocean crust produced at different spreading rates and at different times.

Several studies have quantified the chemical changes associated with hydrothermal alteration from sections of ocean crust, recovered through scientific ocean drilling of in-situ crust or tectonically uplifted lower crust, and sampling of crust tectonically exposed on the seafloor or sub-aerially exposed in ophiolites (for example, Bach et al., 2003; Bednarz and Schmincke, 1989; Coogan and Dosso, 2012; Gillis and Robinson, 1990; Staudigel, 2014). These studies vary in many ways, including: (i) the properties of the section studied, including: spreading rate, age, depth interval, and its thermal, architectural, and hydrogeologic evolution; (ii) the elements investigated; (iii) the assumptions and numerical approaches used to compute chemical changes; (iv) the parameters used to extrapolate calculated chemical changes to global hydrothermal fluxes; and (v) their assessment of the uncertainties involved. Unfortunately our current sampling of in-situ ocean crust is too sparse to make a detailed assessment of the variations in hydrothermal fluxes with respect to spreading rate and crustal age, and a full comparison of the results of the sections sampled to date is beyond the scope of this investigation.

Here we compare the global hydrothermal fluxes extrapolated from chemical changes through the Macquarie crust with: (i) fluxes determined from hydrothermal chemical changes through a composite section of ocean crust recovered by scientific ocean drilling (Staudigel, 2014); and (ii) fluxes extrapolated from element/heat ratios of sampled hydrothermal fluids and estimates of the total convective heat loss (Elderfield and Schultz, 1996) (Table 4). The altered sections of ocean crust provide time-integrated records of hydrothermal alteration, and hence should be comparable to the net axial and ridge flank fluxes (Fig. 12).

The chemical changes for the composite section of ocean crust are primarily based on analyses of in-situ lavas from DSDP Holes 417D and 418A (120 Ma, slow-spread crust; Donnelly et al., 1979) and tectonically uplifted gabbros from ODP Hole 735B; (9 Ma, ultraslow-spread crust (Dick et al., 1999)). Although in-situ sheeted dikes were recovered from in-situ crust at ODP Site 504 (6.9 Ma, intermediate-spread crust (Alt et al., 1996b)), the chemical changes at intermediate depths in the composite section were in most cases extrapolated from analyses of Site 417/418 lavas and 735B gabbros because Site 504 was considered to be too young to represent hydrothermally mature ocean crust (Staudigel, 2014). Such an approach ignores the significant differences between the hydrothermal processes and hence chemical reactions occurring in the dikes compared to both the lavas and the lower crust. The composite section was therefore produced at a similar (slow) spreading rate to the Macquarie crust. Uncertainties in the estimated chemical changes are only quoted for the upper 600 m of lavas in the composite section (Staudigel, 2014), hence the uncertainties in the extrapolated annual hydrothermal fluxes (Table 4; Fig. 12) are not known.

Differences between the average chemical changes recorded by the two crustal sections likely reflect (i) differences in their stratigraphy, predominantly due to the greater thickness of gabbro in the composite section (5000 m; (Staudigel, 2014)) compared to the Macquarie crust (1150 m; Fig. 4); (ii) the longer duration of hydrothermal exchange

Table 4

Comparison of estimated hydrothermal chemical changes and fluxes.

Average bulk crustal chemical changes (Δm_i): gains (+) and losses (–)			Extrapolated global hydrothermal element fluxes: (+ve, net flux to crust; –ve net flux to the oceans)			
	ODP ^a	MQ ^b	ODP ^c	MQ ^d	Axial fluids ^e	Flank fluids ^e
Major elements						
	g/100 g	g/100 g	10 ¹² mol/year	10 ¹² mol/year	10 ¹² mol/year	10 ¹² mol/year
SiO ₂	0.237	–0.30 to 0.08	Si	2.78	–0.66 to –0.43	–1.8 to –1.3
TiO ₂	[O] ^f	–0.08 to –0.03	Ti	[O] ^f	–	–
Al ₂ O ₃	–	–0.42 to 0.02	Al	1.89	–0.0006 to –0.0001	–
FeO _T	–	–0.09 to 0.20	Fe	–	–0.19 to –0.02	–
MnO	–	–0.002 to 0.004	Mn	–	–0.01 to 0.01	–
MgO	–0.157	0.39 to 0.75	Mg	–2.75	1.6	0.7 to 1.1
CaO	0.134	–1.3 to –1.0	Ca	1.68	–1.3 to –0.009	–0.55 to –0.20
Na ₂ O	0.0655	0.24 to 0.37	Na	1.49	–	–
K ₂ O	0.0485	0.07 to 0.1	K	0.36	–0.69 to –0.23	0.1 to 0.64
H ₂ O	0.449	1.35 to 1.52	H ₂ O	17.6	–	–
S	–0.004	0.03 to 0.04	S	–0.08	–0.12 to 0.76	–8.0
Trace elements						
	mg/kg	mg/kg	10 ⁸ mol/year	10 ⁸ mol/year	10 ⁸ mol/year	10 ⁸ mol/year
Cu	–	–21 to –14	–	–78 to –51	–13 to –3	–
Zn	–	–3.3 to –0.3	–	–12 to –1.0	–32 to –12	–
Rb	0.927	–0.4 to 0.8	0.77	–1.2 to 2.2	–9.5 to –2.6	1.9 to 2.8
Cs	0.0172	–0.003 to 0.02	0.01	–0.005 to 0.04	–0.06 to –0.03	0.020 to 0.023
Sr	1.4	–2.6 to 8.3	11	–7.1 to 22	0	–
Ba	–	2.2 to 13	–	3.8 to 22	–13 to –2.4	2
U	0.0375	–0.03 to –0.01	0.11	–0.03 to –0.01	–	0.1

^a Average bulk chemical changes for a composite drilled ocean crustal section (Staudigel, 2014).

^b Average bulk chemical changes through the Macquarie crust, including vein-contributions for major elements.

^c After Staudigel (2014), total crustal thickness = 7000 m.

^d Total crustal thickness = 2700 m.

^e After Elderfield and Schultz (1996).

^f Ti assumed to be immobile; – not determined.

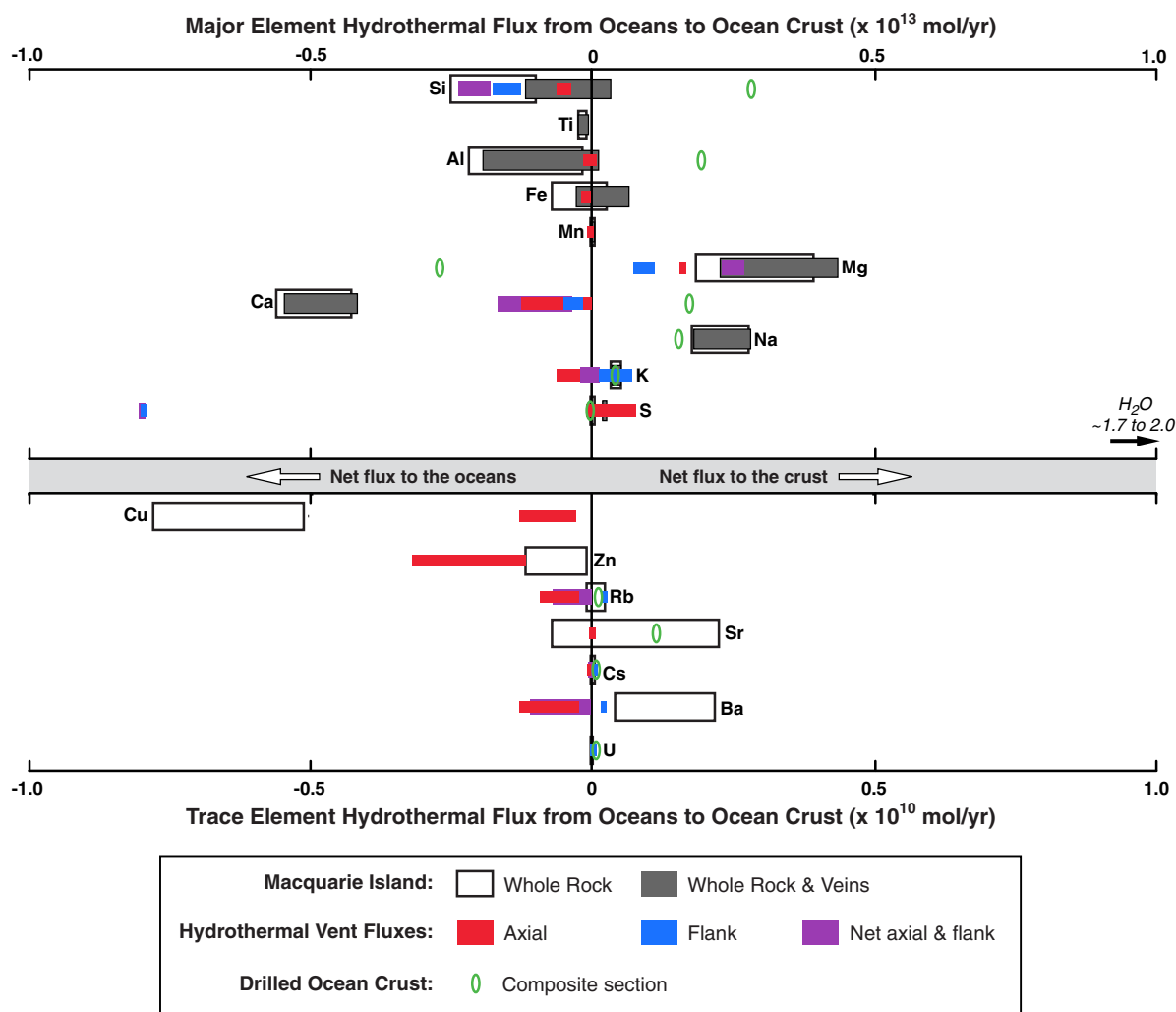


Fig. 12. Global hydrothermal fluxes (mol/year) extrapolated from calculated hydrothermal changes in Macquarie crustal whole rock composition, excluding (white bars) and including (gray bars) estimated contributions from veins. Results are compared to: global hydrothermal fluxes extrapolated from chemical changes within a composite crustal section recovered by scientific ocean drilling (green ovals; Staudigel, 2014); and global fluxes through axial vents (red bars), ridge flanks (blue bars), and both combined (purple bars), after Elderfield and Schultz, 1996). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

within the lavas of the composite section, given their greater age (120 vs 10 Ma); (iii) their differing geologic histories; and (iv) the approaches used to calculate the chemical changes. In contrast to the Macquarie crust and sampled vent fluids, the composite crust records net fluxes of Si, Al and Ca to the crust and a net flux of Mg to the oceans (Fig. 12). The discrepancies between the two studies of slow-spread crust emphasize the need for more thorough sampling of in-situ ocean crust, a consistent approach to calculating chemical changes, and full consideration of the associated uncertainties.

Assuming that hydration is the primary cause of volatile enrichment, Macquarie-style alteration results in uptake of 1.9×10^{13} mol/year of water. In contrast hydrothermal alteration of the Macquarie crust resulted in a net flux of Si to the oceans, consistent with the observed Si-enrichment of black smoker and ridge flank vent fluids relative to seawater (Butterfield et al., 2003; Wheat and Mottl, 2000). Macquarie whole rock alteration extrapolates to a Si flux to the oceans of 9.7 to 25×10^{11} mol/year but a large proportion is compensated by vein formation, resulting in a net flux to the oceans of $3.7 \pm 7.3 \times 10^{11}$ mol/year. This is less than the estimated combined Si flux from axial vents and ridge flank exchange (Elderfield and Schultz (1996); Fig. 12).

Ti was assumed to be immobile during hydrothermal alteration of the composite crustal section ((Staudigel, 2014) Table 4). However, our results indicate that hydrothermal alteration causes a net Ti flux to

the oceans of $0.8\text{--}2.5 \times 10^{11}$ mol/year, equivalent to 3–8% loss of Ti from the full crustal section (Table 3). Similar Ti losses (15%) from upper crustal samples from ODP Hole 504B cannot solely be attributed to dilution through secondary mineral infilling and require Ti mobility during hydrothermal alteration (Bach et al., 2003). However, titanite is common in small amounts in chlorite veins in ODP Holes 504B and 1256D (Alt et al., 1996a; Teagle et al., 2006) and the Macquarie crust, indicating that some of the mobilized Ti is re-incorporated into veins. The titanite abundance in the drilled crustal sections is not quantified and titanite-uptake is not included in our hydrothermal flux estimates. Consequently the estimated Ti-loss from the Macquarie crust is a maximum estimate.

The hydrothermal changes in Macquarie crustal composition extrapolate to a global Mg flux of $3.3 \pm 1.1 \times 10^{12}$ mol/year into the crust, but indicate that there is no net flux of Fe or Mn into or out of the crust (Fig. 12). Our extrapolated Mg flux is comparable to the combined estimates of the axial and ridge flank Mg flux ($2.5 \pm 0.2 \times 10^{12}$ mol/year; Elderfield and Schultz (1996)). Approximately half the Macquarie Mg-uptake occurs in the lower crust (Table 3). Most likely due to tectonic exposure of the lower crust to seawater with the greatest Mg-enrichment observed 1 m from a chloritic fault zone. The timing of this alteration is uncertain, and could have occurred on axis, off axis, or during uplift. Significant Mg-enrichment of the lower

crust may therefore be restricted to crust produced at slow spreading ridges, where amagmatic extension results in uplift and exposure of the lower crust (MacLeod et al., 2009). However, our results contrast with those from ODP Hole 735B, where low-temperature alteration of uplifted lower crust acts as a source of Mg to the oceans, rather than a sink (Bach et al., 2001).

The behavior of Mg during uplift of the lower crust may depend on the timing and rate of exhumation, which affect the thermal and chemical conditions of fluid–rock interaction as indicated by differing clay mineral distributions in Holes 735B and U1309D (Nozaka et al., 2008). Penetration of cold seawater causes oxidation and Mg removal but reaction with warmer fluids leads to chlorite and smectite precipitation and Mg uptake.

The modern oceans contain $\sim 75 \times 10^{18}$ mol Mg, but the Mg concentration of seawater has increased from ~ 35 to 55 mmol/kg since the Neogene (Horita et al., 2002). Such an increase requires an average net Mg flux of $\sim 1 \times 10^{12}$ mol/year to the oceans since 35 Ma. Global hydrothermal Mg-uptake at the upper end of our estimated range (4.3×10^{12} mol/year) is consistent with the observed increase in Mg in seawater since the Neogene, given an estimated riverine Mg input from the continents of 5.2×10^{12} mol/year (Edmond et al., 1979). If the Mg-uptake in the Macquarie lower crust is globally representative, our results therefore indicate that Mg uptake during axial and ridge flank hydrothermal alteration is sufficient to balance the Mg-budget of the oceans, given the uncertainties involved.

Hydrothermal alteration of the Macquarie crust supplied Ca to the oceans, but provided a net sink for Na. Given our estimated Ca flux to the oceans (4.2 – 5.5×10^{12} mol/year) and a maximum axial Ca flux of 1.3×10^{12} mol/year (Elderfield and Schultz, 1996) at least two thirds of the Ca removal must occur on the ridge flanks. We estimate that hydrothermal exchange removes 3.3 – 5.2×10^{11} mol/year of K from the oceans, but it is neither a net sink nor source for Cs and Rb because their removal during high temperature reactions is compensated by uptake during low temperature alteration.

Our extrapolated flux of S to the crust (1.9 – 2.7×10^{11} mol/year) is sensitive to the volume of vein pyrite, which accounts for three quarters of this uptake (Table 3). Bulk rock S contents combined with pyrite and anhydrite vein abundances in crust from ODP Holes 504B and 735B indicate that the S flux from the volcanic crust to the oceans (2.5×10^{12} g/year) is approximately compensated by S uptake in the lower crust (2.1×10^{12} g/year) (Alt, 1995b). Elderfield and Schultz (1996) estimate axial fluxes of 0.85 – 9.6×10^{11} mol/year H_2S to the oceans and 8.4×10^{11} mol/year SO_4 to the crust, resulting in a net axial S flux of $3.2 \pm 4.4 \times 10^{11}$ mol/year of S to the crust. The discrepancy between the estimated axial and time integrated hydrothermal S fluxes indicates that much of the anhydrite is either dissolved at lower temperatures on the ridge flanks, or that the paucity of anhydrite in drilled crust reflects a sampling bias due to incomplete core recovery (Alt, 1995b). Although anhydrite was not recovered from the sampled Macquarie section, gypsum (formerly anhydrite) is locally present elsewhere in the Macquarie crust (Alt et al., 2003).

For the majority of the trace elements (Zn, Sr, Rb and Cs) we find no conclusive evidence that the hydrothermal alteration crust results in a net flux either to or from the oceans. The Macquarie-based estimates of global Si and S fluxes discussed above confirm the importance of determining the contribution of hydrothermal veins (Alt, 1995a; Alt and Teagle, 2000; Alt et al., 1986). Unfortunately we do not have trace element analyses of all the hydrothermal vein minerals, so the extent to which any trace element loss from the whole rock samples is compensated by uptake in veins is not determined. In the absence of uptake by veins our results indicate a net flux of $\sim 6.5 \times 10^9$ mol/year of Cu to the oceans and $\sim 1.3 \times 10^9$ mol/year of Ba to the crust. However, given the occurrence of minor chalcopyrite (CuFeS_2) veins at least some of the Cu lost from the bulk rock is re-incorporated into veins.

9. Conclusions

Most elements were variably enriched or depleted through the Macquarie crust during hydrothermal alteration. The changes in bulk rock composition (enrichment or depletion) depend upon the secondary mineral assemblages developed, and are controlled by: (i) the modal abundances of the primary minerals in the rocks; (ii) the alteration conditions such as temperature, fluid composition, or water:rock ratios; and (iii) the chemical behavior of the elements, such as their mobility in fluid. Consequently there are variations with depth, most notably an interval of greater fluid–rock reaction at the lava–dike transition zone where lavas and dikes are enriched in K, S, Rb, Ba, and Zn. Since the rocks provide a time-integrated record of alteration, the behavior of some elements appears complex, and initial changes during high temperature alteration may be partially or completely compensated for during later, low-temperature alteration.

The hydrothermal changes in Macquarie crustal composition are used to estimate net elemental fluxes to and from the crust. Our results indicate that hydrothermal alteration results in a net flux of Si, Ti, Al, and Ca, to the oceans, whereas the crust is a net sink for H_2O , Mg, Na, K, and S. Our results also demonstrate the importance of accounting for hydrothermal uptake in veins, which affects the seawater–ocean crust exchange budgets of Si, Fe, Mg and S. The extrapolation of the hydrothermal changes through a section of ocean crust to global hydrothermal fluxes is limited by how representative that section of crust is. The relationship between spreading rate and hydrothermal flux remains poorly known. Consequently, the approach described here needs to be applied to ocean crustal sections produced at a range of spreading rates to refine global hydrothermal flux estimates.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.lithos.2016.08.024>.

Acknowledgments

This research was funded by: Australian Antarctic Division Project 2327–55th ANARE, Royal Society grant 24177, and Nuffield Foundation grant NAL/00392/G to DAHT; Natural Environmental Research (NERC) – Natural History Museum CASE studentship NER/S/A/2001/063 and a Royal Society Dorothy Hodgkin Fellowship (DH100131) to RMC; NERC studentship NER/S/A/2005/1347A to MH; and US National Science Foundation grant OCE-9911901 to JCA. GJD acknowledges support of an Australian Research Council postdoctoral fellowship (D0008755) and large grant (D0009364), and logistical and financial support from ANARE grant 2122, Mineral Resources Tasmania. We thank the crew of the Aurora Australis and especially the Macquarie Island base staff, for their hospitable logistical support in the field. Sincere thanks are due to Robert Connell, who volunteered to companion GJD to collect Mount Waite and Double Point transect samples, and gave unflagging support under often miserable conditions. Matt Cooper and Andy Milton are thanked for their support with geochemical analyses. DAHT acknowledges a Royal Society Wolfson Foundation Merit Award (WM130051) that also supported this research.

References

- Adamson, D.A., Selkirk, P.M., Price, D.M., Selkirk, J.M., 1996. Pleistocene uplift and palaeoenvironments of Macquarie Island: evidence from palaeobeaches and sedimentary deposits. *Papers and Proceedings of the Royal Society of Tasmania* 130, 25–32.
- Alt, J.C., 1994. A sulphur isotopic profile through the Troodos ophiolite, Cyprus: primary composition and the effects of seawater hydrothermal alteration. *Geochimica et Cosmochimica Acta* 58, 1825–1840.
- Alt, J.C., 1995a. Subseafloor processes in mid-ocean ridge hydrothermal systems. In: Humphris, S.E., Zierenberg, R., Mullineaux, L., Thomson, R. (Eds.), *Seafloor Hydrothermal Systems* Geophysical Monograph 91. American Geophysical Union, Washington, D.C., pp. 85–114.
- Alt, J.C., 1995b. Sulphur isotopic profile through the oceanic crust: sulphur mobility and seawater–crustal sulphur exchange during hydrothermal alteration. *Geology* 23, 585–588.

- Alt, J.C., Teagle, D.A.H., 2000. Hydrothermal alteration and fluid fluxes in ophiolites and oceanic crust. In: Dilek, Y., Moores, E.M., Elthon, D., Nicolas, A. (Eds.), *Ophiolites and Oceanic Crust: New Insights From Field Studies and the Ocean Drilling Program*. Spec. Pap.—Geol. Soc. Am., pp. 273–282.
- Alt, J.C., Honnorez, J., Laverne, C., Emmermann, R., 1986. Hydrothermal alteration of a 1 km section through the upper oceanic crust, Deep Sea Drilling Project Hole 504B: mineralogy, chemistry and evolution of seawater–basalt interactions. *Journal of Geophysical Research* 91, 10309–10335.
- Alt, J.C., Laverne, C., Vanko, D.A., Tartarotti, P., Teagle, D.A.H., Bach, W., Zuleger, E., Erzinger, J., Honnorez, J., Pezard, P.A., Becker, K., Salisbury, M.H., Wilkens, R.H., 1996a. Hydrothermal alteration of a section of upper oceanic crust in the Eastern Equatorial Pacific: a synthesis of results from site 504 (DSDP legs 69, 70 and 83, and ODP legs 111, 137, 140 and 148). In: Alt, J.C., Kinoshita, H., Stokking, L.B., Michael, P.J. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 148*, pp. 417–434.
- Alt, J.C., Teagle, D.A.H., Laverne, C., Vanko, D.A., Bach, W., Honnorez, J., Becker, K., Ayadi, M., Pezard, P.A., 1996b. Ridge flank alteration of upper oceanic crust in the eastern Pacific: synthesis of results for volcanic rocks of Holes 504B and 896A. *Proceeding of the Ocean Drilling Program, Scientific Results* 148, 435–450.
- Alt, J.C., Davidson, G.J., Teagle, D.A.H., Karson, J.A., 2003. Isotopic composition of gypsum in the Macquarie Island ophiolite: implications for the sulfur cycle and the subsurface biosphere in oceanic crust. *Geology* 31, 549–552.
- Alt, J.C., Laverne, C., Coggon, R.M., Teagle, D.A.H., Banerjee, N.R., Morgan, S., Smith-Duque, C.E., Harris, M., Galli, L., 2010. The subsurface structure of a submarine hydrothermal system in ocean crust formed at the East Pacific Rise, ODP/IODP Site 1256. *Geochemistry, Geophysics, Geosystems*.
- Armstrong, R.A., Kohn, B., Goscombe, B.D., Everard, J.L., 2004. U–Pb and fission track ages from oceanic crust at Macquarie Island. 17th Australian Geological Convention Abstracts Volume. Geological Society of Australia.
- Bach, W., Alt, J.C., Niu, Y., Humphris, S.E., Erzinger, J., Dick, H.J.B., 2001. The geochemical consequences of late-stage low-grade alteration of lower oceanic crust at the SW Indian Ridge: results from ODP Hole 735B (Leg 176). *Geochimica et Cosmochimica Acta* 65, 3267–3287.
- Bach, W., Peucker-Ehrenbrink, B., Hart, S.R., Blusztajn, J., 2003. Geochemistry of hydrothermally altered oceanic crust: DSDP/ODP Hole 504B — implications for seawater–crust exchange budgets and Sr- and Pb-isotopic evolution of the mantle. *Geochemistry, Geophysics, Geosystems* 4. <http://dx.doi.org/10.1029/2002GC000419>.
- Bednarz, U., Schmincke, H.U., 1989. Mass transfer during sub-seafloor alteration of the upper Troodos crust (Cyprus). *Contributions to Mineralogy and Petrology* 102, 93–101.
- Bednarz, U., Schmincke, H.U., 1991. Chemical patterns of seawater and hydrothermal alteration in the northeastern Troodos extrusive series and sheeted dyke complex (Cyprus). In: Gibson, I.L., Malpas, J., Robinson, P.T., Xenophontos, C. (Eds.), *Cyprus Crustal Study Project: Initial Report, Holes CY-1 and 1a*. Geological Survey of Canada, pp. 639–653.
- Bickle, M.J., Teagle, D.A.H., 1992. Strontium alteration in the Troodos ophiolite: implications for fluid fluxes and geochemical transport in mid-ocean ridge hydrothermal systems. *Earth and Planetary Science Letters* 113, 219–237.
- Blackman, D.K., Ildefonse, B., John, B.E., Ohara, Y., Miller, D.J., MacLeod, C.J., the Expedition 304/305 Scientists, 2006. *Proceedings of the Integrated Ocean Drilling Program, 304/305*. Integrated Ocean Drilling Program Management International, Inc., College Station, TX.
- Brewer, T.S., Daly, J.S., Åhäll, K.-I., 1998. Contrasting magmatic arcs in the Palaeoproterozoic of the south-western Baltic Shield. *Precambrian Research* 92, 297–315.
- Butterfield, D.A., Seyfried, W.E., Lilley, M.D., 2003. Composition and evolution of hydrothermal fluids. In: Halbeck, P.E., Tunnicliffe, V., Hein, J.R. (Eds.), *Energy and Mass Transfer in Marine Hydrothermal Systems*. Dahlem University Press, Berlin, pp. 123–161.
- Cande, S.C., Stock, J.M., Muller, R.D., Ishihara, T., 2000. Cenozoic motion between East and West Antarctica. *Nature* 404, 145–150.
- Cannat, M., 1996. How thick is the magmatic crust at slow spreading oceanic ridges? *Journal of Geophysical Research* 101, 2847–2857.
- Cannat, M., Sauter, D., Bezos, A., Meyzen, C., Humler, E., Le Rigoleur, M., 2008. Spreading rate, spreading obliquity, and melt supply at the ultraslow spreading Southwest Indian Ridge. *Geochemistry, Geophysics, Geosystems* 9.
- Chen, Y.J., 1992. Oceanic crustal thickness versus spreading rate. *Geophysical Research Letters* 19, 753–756.
- Cocker, J.D., Griffin, B.J., Muehlenbachs, K., 1982. Oxygen and carbon isotope evidence for seawater hydrothermal alteration of the Macquarie-Island ophiolite. *Earth and Planetary Science Letters* 61, 112–122.
- Coogan, L.A., Dosso, S., 2012. An internally consistent, probabilistic, determination of ridge-axis hydrothermal fluxes from basalt-hosted systems. *Earth and Planetary Science Letters* 323–324, 92–101.
- Daczko, N.R., Mosher, S., Coffin, M.F., Meckel, T.A., 2005. Tectonic implications of fault-scarp-derived volcanoclastic deposits on Macquarie Island: sedimentation at a fossil ridge-transform intersection? *Bulletin of the Geological Society of America* 117, 18–31.
- Davidson, G.J., Varne, R., Brown, A.V., Connell, R., 2004. Structural controls on sulphide deposition at the dyke-lava boundary, slow-spreading ocean crust, Macquarie Island. *Terra Nova* 16, 9–15.
- Dick, H.J.B., Natland, J.H., Miller, D.J., the ODP Leg 176 Shipboard Party, 1999. *Proceedings of the Ocean Drilling Program, Initial Report vol. 176*. Ocean Drilling Program, College Station, TX.
- Dick, H.J.B., Lin, J., Schouten, H., 2003. An ultraslow-spreading class of ocean ridge. *Nature* 426, 405–412.
- Dick, H.J.B., Natland, J.H., Ildefonse, B., 2006. Past and Future Impact of Deep Drilling in the Oceanic Crust and Mantle. *Oceanography* 19, 72–80.
- Dijkstra, A., Cawood, P.A., 2004. Base-up growth of ocean crust by multiple phases of magmatism: field evidence from Macquarie Island. *Journal of the Geological Society, London* 161, 739–742.
- Doe, B.R., 1994. Zinc, copper, and lead in mid-ocean ridge basalts and the source rock control on Zn/Pb in ocean-ridge hydrothermal deposits. *Geochimica et Cosmochimica Acta* 58, 2215–2223.
- Donnelly, T., Francheteau, J., Bryan, W., Robinson, P.T., Flower, M., Salisbury, M., 1979. *Init. Rept. DSDP*, Washington, DC.
- Duncan, R.A., Varne, R., 1988. The age and distribution of the igneous rocks of Macquarie Island. *Papers and Proceedings of the Royal Society of Tasmania* 122, 45–50.
- Edmond, J.M., Measures, C.I., McDuff, R.E., Chan, L.H., Collier, R., et al., 1979. Ridge crest hydrothermal activity and the balance of the major and minor elements in the ocean: the Galapagos data. *Earth and Planetary Science Letters* 46, 1–18.
- Elderfield, H., Schultz, A., 1996. Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean. *Annual Review of Earth and Planetary Sciences* 24, 191–224.
- Gillis, K.M., Robinson, P.T., 1990. Patterns and processes of alteration in the lavas and dikes of the Troodos ophiolite, Cyprus. *Journal of Geophysical Research* 95, 21523–21548.
- Goscombe, B.D., Everard, J.L., 1998a. *Geology of Macquarie Island*. Mineral Resources Tasmania, Hobart, Australia.
- Goscombe, B.D., Everard, J.L., 1998b. Macquarie Island mapping reveals three tectonic phases. *Eos, Transactions of the American Geophysical Union* 80, 50–55.
- Goscombe, B.D., Everard, J.L., 2001. Tectonic evolution of Macquarie Island: extensional structures and block rotations in oceanic crust. *Journal of Structural Geology* 23, 639–673.
- Grant, J.A., 1982. The isocon diagram — a simple solution to Gresens' Equation for metasomatic alteration. *Economic Geology* 81, 1976–1982.
- Gregory, R.T., Taylor, H.P., 1981. An oxygen isotope profile in a section of cretaceous oceanic crust, Semail Ophiolite, Oman: evidence for d¹⁸O buffering of the oceans by deep (>5 km) seawater-hydrothermal circulation at mid-ocean ridges. *Journal of Geophysical Research - Solid Earth* 86, 2737–2755.
- Gresens, R.L., 1967. Composition–volume relationships of metasomatism. *Chemical Geology* 2, 47–65.
- Griffin, B.J., 1982. *Igneous and Metamorphic Petrology of Lavas and Dykes of the Macquarie Island Ophiolite Complex*. Ph.D. thesis University of Tasmania, Hobart.
- Griffin, B.J., Varne, R., 1980. The Macquarie Island ophiolite complex: mid-Tertiary oceanic lithosphere from a major ocean basin. *Chemical Geology* 30, 258–308.
- Hart, S.R., 1969. K, Rb, Cs contents and K/Rb, K/Cs ratios of fresh and altered submarine basalts. *Earth and Planetary Science Letters* 6, 295–303.
- Horita, J., Zimmerman, H., Holland, H.D., 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. *Geochimica et Cosmochimica Acta* 66, 3733–3756.
- Jenner, F.E., O'Neill, H.S.C., 2012. Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochemistry, Geophysics, Geosystems* 13.
- Kamenetsky, V.S., Maas, R., 2002. Mantle-melt evolution (dynamic source) in the origin of a single MORB suite: a perspective from magnesian glasses of Macquarie Island. *Journal of Petrology* 43, 1909–1922.
- Kamenetsky, V.S., Everard, J.L., Crawford, A.J., Varne, R., Eggins, S.M., Lanyon, R., 2000. Enriched end-member of primitive MORB melts: petrology and geochemistry of glasses from Macquarie Island (SW Pacific). *Journal of Petrology* 41, 411–430.
- Lamarche, G., Collot, J.Y., Wood, R.A., Sosson, M., Sutherland, R., Delteil, J., 1997. The Oligocene–Miocene Pacific–Australia plate boundary, south of New Zealand: evolution from oceanic spreading to strike-slip faulting. *Earth and Planetary Science Letters* 148, 129–139.
- Laverne, C., Vanko, D.A., Tartarotti, P., Alt, J.C., 1995. Chemistry and geothermometry of secondary minerals from the deep sheeted dike complex, Hole 504B. In: Erzinger, J., Becker, K., Dick, H.J.B., Stokking, L.B. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 148*. Ocean Drilling Program, College Station, TX, pp. 167–189.
- Laverne, C., Belarouchi, A., Honnorez, J., 1996. Alteration mineralogy and chemistry of the upper oceanic crust from Hole 896A, Costa Rica Rift. In: Alt, J.C., Kinoshita, H., Stokking, L.B., Michael, P.J. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 148*, pp. 151–169.
- Lechler, P.J., Desilets, M.O., 1987. A review of the use of loss on ignition as a measurement of total volatiles in whole-rock analysis. *Chemical Geology* 63, 341–344.
- Lewis, S.J., 2007. *Focused Hydrothermal Alteration in Upper Crustal Oceanic Faults on Macquarie Island*. PhD thesis University of Tasmania.
- MacLean, W.H., 1990. Mass change calculations in altered rock series. *Mineralium Deposita* 25, 44–49.
- MacLean, W.H., Barrett, T.J., 1993. Lithogeochemical techniques using immobile elements. *Journal of Geochemical Exploration* 48, 109–133.
- MacLeod, C.J., Searle, R.C., Murton, B.J., Casey, J.F., Mallows, C., Unsworth, C.S., Achenbach, K.L., Harris, M., 2009. Life cycle of oceanic core complexes. *Earth and Planetary Science Letters* 287, 333–344.
- Massell, C., Coffin, M.F., Mann, P., Mosher, S., Frohlich, C., Duncan, C.S., Karner, G., Ramsay, D., Lebrun, J.F., 2000. Neotectonics of the Macquarie Ridge Complex, Australia–Pacific plate boundary. *Journal of Geophysical Research - Solid Earth* 105, 13457–13480.
- Miyashiro, A., 1973. The Troodos ophiolite complex was probably formed in an island arc. *Earth and Planetary Science Letters* 19, 218–224.
- Moll, M., Paulick, H., Suhr, G., Bach, W., 2007. Data report: microprobe analyses of primary phases (olivine, pyroxene, and spinel) and alteration products (serpentine, iowaite, talc, magnetite, and sulfides) in Holes 1268A, 1272A, and 1274A. In: Kelemen, P.B., Kikawa, E., Miller, D.J. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results, Vol 209*. Ocean Drilling Program, College Station, TX.
- Müller, R.D., Sdrolias, M., Gaina, C., Steinberger, B., Heine, C., 2008. Long-term sea level fluctuations driven by ocean basin dynamics. *Science* 319, 1357–1362.

- Norrish, K., Hutton, J.T., 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochimica et Cosmochimica Acta* 33 (431), 453.
- Nozaka, T., Fryer, P., Andreani, M., 2008. Formation of clay minerals and exhumation of lower-crustal rocks at Atlantis Massif, Mid-Atlantic Ridge. *Geochemistry, Geophysics, Geosystems* 9, Q11005.
- Palmer, M.R., Edmond, J.M., 1989. Cesium and rubidium in submarine hydrothermal fluids: evidence for recycling of alkali elements. *Earth and Planetary Science Letters* 95, 8–14.
- Penrose Conference Participants, 1972. Report of the Penrose field conference on ophiolites. *Geotimes* 17, 24–25.
- Portner, R.A., Murphy, M.J., Daczko, N.R., 2010. A detrital record of lower oceanic crust exhumation within a Miocene slow-spreading ridge: Macquarie Island, Southern Ocean. *Geological Society of America Bulletin* 123, 255–273.
- Quilty, P.G., Crundwell, M.P., Wise Jr., S.W., 2008. Microplankton provide 9 Ma age for sediment in the Macquarie Island ophiolite complex. *Australian Journal of Earth Sciences* 55, 1119–1125.
- Rautenschlein, M., Jenner, G.A., Hertogen, J., Hofmann, A.W., Kerrich, R., Schmincke, H.U., White, W.M., 1985. Isotopic and trace element composition of volcanic glasses from the Akaki Canyon, Cyprus: implications for the origin of the Troodos ophiolite. *Earth and Planetary Science Letters* 75, 369–383.
- Rivizzigno, P.A., Karson, J.A., 2004. Structural expression of oblique seafloor spreading in the Macquarie Island Ophiolite, Southern Ocean. *Geology* 32, 125–128.
- Robinson, P.T., Von Herzen, R., the ODP Leg 118 Shipboard Party, 1989. *Proceedings of the Ocean Drilling Program, Initial Reports vol. 118*. Ocean Drilling Program, College Station, TX.
- Robinson, P.T., Erzinger, J., Emmermann, R., 2002. The composition and origin of igneous and hydrothermal veins in the lower ocean crust—ODP Hole 735B, Southwest Indian Ridge. In: Natland, J.H., Dick, H.J.B., Miller, D.J., Von Herzen, R.P. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 176*. Ocean Drilling Program, College Station (TX).
- Selkirk, P.M., Seppelt, R.D., Selkirk, D.R., 1990. *Subantarctic Macquarie Island: Environment and Biology*. Cambridge University Press, Cambridge.
- Sinha, M.C., Constable, S., Peirce, C., White, A., Heinson, G., MacGregor, L.M., Navin, D.A., 1998. Magmatic processes at slow spreading ridges: implications of the RAMESSES experiment, Mid-Atlantic Ridge at 57° N. *Geophysical Journal International* 135, 731–745.
- Staudigel, H., 2014. Chemical fluxes from hydrothermal alteration of the oceanic crust. In: Rudnick, R.L. (Ed.), *Treatise on Geochemistry, 2nd edition The Crust vol. 4*. Elsevier, Oxford, pp. 583–606.
- Staudigel, H., Hart, S.R., 1983. Alteration of basaltic glass: mechanisms and significance for the oceanic crust budget. *Geochimica et Cosmochimica Acta* 47, 337–350.
- Sutherland, R., 1995. The Australian–Pacific boundary and Cenozoic plate motions in the SW Pacific: some constraints from Geosat data. *Tectonics* 14, 819–831.
- Teagle, D., Ildefonse, B., 2011. Journey to the mantle of the Earth. *Nature* 471, 437–439.
- Teagle, D.A.H., Alt, J.C., Bach, W., Halliday, A.N., Erzinger, J., 1996. Alteration of upper ocean crust in a ridge-flank hydrothermal upflow zone: mineral, chemical, and isotopic constraints from Hole 896A. In: Alt, J.C., Kinoshita, H., Stokking, L.B., Michael, P.J. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 148*. Ocean Drilling Program, College Station (TX), pp. 119–150.
- Teagle, D.A.H., Alt, J.C., Umino, S., Miyashita, S., Banerjee, N.R., Wilson, D.S., the Expedition 309/312 Scientists, 2006. Superfast Spreading Rate Crust 2 and 3. Integrated Ocean Drilling Program Management International, Inc, Washington DC. <http://dx.doi.org/10.2204/iodp.proc.309312.2006>.
- Vanko, D.A., Laverne, C., Tartarotti, P., Alt, J.C., 1996. Chemistry and origin of secondary minerals from the deep sheeted dikes cored during Leg 148 (Hole 504B). In: Alt, J.C., Kinoshita, H., Stokking, L.B., Michael, P.J. (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results vol. 148*. Ocean Drilling Program, College Station, TX, pp. 71–86.
- Varne, R., Gee, R.D., Quilty, P.G.J., 1969. Macquarie Island and the cause of oceanic linear magnetic anomalies. *Science* 166, 230–233.
- Varne, R., Brown, A.V., Falloon, T., 2000. Macquarie Island: its geology, structural history, and the timing and tectonic setting of its N-MORB to E-MORB magmatism. *Geological Society of America, Special Paper* 349.
- Von Damm, K.L., 1995. Controls on the chemistry and temporal variability of seafloor hydrothermal fluids. In: Humphris, S.E., Zierenberg, R.A., Mullineaux, L.S., Thompson, R.E. (Eds.), *Seafloor Hydrothermal Systems, Geophysical Monograph* 91. American Geophysical Union, Washington, DC, pp. 222–247.
- Wertz, K.L., 2003. From Seafloor Spreading to Uplift: the Structural and Geochemical Evolution of Macquarie Island on the Australian–Pacific Plate Boundary. University of Texas, Austin, p. 169.
- Wertz, K.L., Mosher, S., Daczko, N.R., Coffin, M.F., 2003. Macquarie Island's Finch-Langdon fault: a ridge-transform inside-corner structure. *Geology* 31, 661–664.
- Wheat, C.G., Mottl, M.J., 2000. Compositions of pore and spring waters from Baby Bare: global implications of geochemical fluxes from a ridge flank hydrothermal system. *Geochimica et Cosmochimica Acta* 64, 629–642.
- Wilson, D.S., Teagle, D.A.H., Acton, G.D., the ODP Leg 206 Shipboard Party, 2003. *Proceedings of the Ocean Drilling Program, Initial Reports*. Ocean Drilling Program, College Station, TX.