Chapter 9

Halogens in seawater, marine sediments and the altered oceanic crust and lithosphere

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Abstract. This chapter aims to provide a framework for understanding the distribution of halogens in the oceanic lithosphere. It reviews the concentration of F, Cl, Br and I in seawater, marine sediment pore waters, hydrothermal vent fluids, fluid inclusions from deeper in the crust, and the complementary solid-phase reservoirs of organic matter and minerals present in sediments and crustal rocks from varying depths.

Seawater (3.4-3.5 wt. % salt) is depleted in F, weakly enriched in I and strongly enriched in Br and Cl compared to the primitive mantle. Sequestration of I and Br by phytoplankton lead to the storage of these elements in marine sediments which are the Earths dominant I reservoir. Regeneration of organic matter during diagenesis releases I and Br to marine sediment pore waters which can be advected into the underlying crust and lithosphere. In contrast, Cl is assumed to behave conservatively in pore waters and F is precipitated in sedimentary minerals meaning it is not significantly advected into the underlying basement.

Vent fluids have salinities of 0.1-6 wt. % salts, which provide evidence for phase separation and segregation of vapours and brines in hydrothermal systems. The majority of vent fluids have Br/Cl ratios within 10% of the seawater value. However, elevated Br/Cl and I/Cl ratios indicate that some vent fluids interact with sediments, and depressed Br/Cl ratios suggest some vent fluids leach Cl from glassy volcanic rocks or halite. Vent fluids have F/Cl ratios scattered around the seawater value which reflects the generally low mobility of F during diagenesis and hydrothermal alteration. In comparison to vent fluids, fluid inclusions also provide evidence for phase separation but preserve a much greater range of salinity including brines with salinities as high as ~50 wt. % salt in many parts of the crust.

The altered ocean crust has a F concentration of close to its initial value. In contrast, Cl is mobilised within layer 2 pillows and dykes and strongly enriched in layer 3 gabbros subjected to high temperature alteration. Amphibole is the dominant Cl host in the oceanic crust, with Cl concentrations of <500 ppm under greenschist conditions and up to wt. % levels under amphibolite conditions. The increasing Cl content of amphibole as a function of metamorphic grade most likely reflects a decreasing water/rock ratio and a general increase in fluid salinity as a function of depth in the crust. Amphibole preferentially incorporates Cl relative to Br and I; however, it is possible that I is enriched in absolute terms, and relative to Cl, in clay-rich alteration and biogenic alteration of glassy rocks in the upper crust.

Serpentinites formed in the oceanic lithosphere can contain thousands of ppm Cl and some serpentinites preserve Br/Cl and I/Cl signatures very similar to sedimentary pore waters, indicating that all halogens have high compatibilities in serpentine. Fluorine is slightly enriched in serpentinites compared to peridotites which may indicate mobilisation of F from igneous lithologies in the crust. Overall, the altered oceanic lithosphere reaching subduction zones is estimated to have a maximum median Cl content of ~400 ppm, and it is estimated to have a F/Cl ratio of ~0.25 compared to ~2 in pristine crust. It is therefore estimated that approximately 90% of the Cl present in altered oceanic lithosphere is introduced during seawater alteration.

57 **9.1 Introduction**

58 As a chemical group, the halogens (F, Cl, Br, I) are united by the ability to form
59 negatively charged anions; however, Cl is uniquely important within this group because it is
60 the dominant ligand that enables metal transport in the majority of hydrothermal solutions
61 (Bischoff and Dickson, 1975; Seyfried and Bischoff, 1981; Yardley, 2005). Fluid salinity is
62 consequently of profound importance to the mass transfer processes operating during
63 hydrothermal alteration of the oceanic lithosphere. There is wide interest in the scale of
64 seafloor alteration processes and metasomatism because alteration of the oceanic lithosphere
65 moderates the composition of seawater (Bischoff and Dickson, 1975; Edmond et al., 1979) and
66 determines the chemical composition of the slab that is subducted into the mantle at convergent
67 plate margins meaning that seafloor alteration is critical to the geological cycles of all elements
68 (Spandler and Pirard, 2013).

69 In comparison to Cl, the other halogens exhibit systematically different behaviours in
70 the oceanic lithosphere that are related to their ionic sizes or elemental abundances. Fluorine
71 and Cl are similarly abundant on Earth with primitive mantle concentrations on the order of
72 ~15-25 ppm (Table 1; Pyle and Mather, 2009). However, the F^- anion is significantly smaller
73 than the heavier halogens and F is strongly electronegative, being the only element in the
74 periodic table that is more electronegative than oxygen. These properties result in F having a
75 much higher compatibility than Cl in many hydrous and nominally anhydrous minerals
76 (Bernini et al., 2013; Carpenter, 1969; Dalou et al., 2012; Frohlich et al., 1983; Ichikuni, 1979;
77 Seyfried and Ding, 1995). In addition, F is distinguished from the heavier halogens by a low
78 solubility in aqueous fluids (Seyfried and Ding, 1995).

79 Bromine and I have even higher solubilities in aqueous fluids than Cl, but they are trace
80 constituents on Earth with primitive mantle concentrations of less than ~60 ppb for Br and less
81 than ~10 ppb for I (Table 1). Iodine is a weakly electronegative redox sensitive element that

82 is important in a number of biochemical pathways, which together with its low abundance
83 mean it is regarded as an essential element for life (Elderfield and Truesdale, 1980; Fuge and
84 Johnson, 1986; Leblanc et al., 2006).

85 The contrasting solubilities of F, Cl, Br and I in aqueous fluids mean that their relative
86 abundances, or the F/Cl, Br/Cl and I/Cl, ratios of a fluid, can provide useful information about
87 a number of hydrogeochemical processes relevant to alteration of the oceanic lithosphere.
88 These include the roles of phase separation, crustal-hydration, dissolution of evaporites, or
89 precipitation of hydrothermal-halite in controlling vent fluid salinity (Campbell and Edmond,
90 1989; Oosting and Von Damm, 1996; Seyfried et al., 2003; You et al., 1994). In addition, the
91 presence of organic matter can be inferred from high I abundances (Campbell and Edmond,
92 1989; Gieskes et al., 2002; Kawagucci et al., 2011). This information is of considerable
93 importance to investigating the role of fluids in alteration of the oceanic lithosphere and the
94 depth of the biosphere (Campbell and Edmond, 1989; Mottl et al., 2011; Oosting and Von
95 Damm, 1996; Reeves et al., 2011; Wu et al., 2012; You et al., 1994).

96 The current chapter aims to show how the different geochemical behaviours of the
97 halogens control their abundances in both hydrothermal fluids and the complementary
98 reservoirs of the oceanic lithosphere and how salts, and acids generated by hydrolysis of salts,
99 facilitate transport of metals in solution (Seyfried and Bischoff, 1981). The majority of data
100 for both altered oceanic rocks and fluids are for Cl, with more limited data available for F and
101 Br, and very limited data for I. Therefore while the aim is to provide a framework for
102 understanding the distribution of halogens in the oceanic lithosphere, an important role of this
103 chapter is also to identify current gaps in our knowledge. Improving constraints on the absolute
104 and relative abundances of F, Cl, Br, and I in different lithospheric reservoirs (e.g. sediments,
105 altered basalt, serpentinites) is critical for optimal use of halogen abundance ratios in tracking
106 halogens through the subduction cycle (Kendrick et al., 2012b; Straub and Layne, 2003) and

will further contribute to our understanding of marine halogen cycling (Frohlich et al., 1983; Leblanc et al., 2006; Seyfried et al., 1986; Seyfried and Ding, 1995).

9.2 Halogen chemistry in seawater and marine sediments

The halogen composition of seawater and the more evolved fluids that have interacted with sediments and could be advected into the mafic portions of the oceanic lithosphere is controlled by the unique chemical properties of each halogen and their abundances on Earth.

The concentrations of F, Cl and Br in seawater, present as the fluoride (F^-), chloride (Cl^-), and bromide (Br^-) anions, is fairly constant over thousand-year timescales with minor variations related to salinity which fluctuates around ~3.4-3.5 wt. % salts (Drever, 1997; Pinet, 1992). In contrast, I is unique among the halogens because its predominant species in seawater is iodate (IO_3^-) and iodide (I^-) is only important in surface waters and small anoxic basins (Elderfield and Truesdale, 1980; Huang et al., 2005; Wong and Brewer, 1977). The concentration of iodate, which is taken up by a number of marine organisms, is correlated with other nutrients such as nitrate and phosphate and varies as a function of water depth and latitude (Elderfield and Truesdale, 1980; Huang et al., 2005). In addition to iodate and iodide, dissolved organic I is significant at shallow and intermediate depths accounting for up to ~5 ppb of the total I at depths of 400 m in the north Pacific (Huang et al., 2005). The total I concentration of seawater varies from about 44 ppb up to 76 ppb with a mean of ~58 ppb (Elderfield and Truesdale, 1980; Huang et al., 2005; Nakayama et al., 1989; Zheng et al., 2012).

The average abundances of halogens in seawater (Drever, 1997; Elderfield and Truesdale, 1980; Huang et al., 2005) and estimated abundances of halogens in the primitive mantle (McDonough and Sun, 1995; Palme and O'Neill, 2003; Sharp and Draper, 2013) are given in Table 1. Recent estimates for primitive mantle Cl, Br and I still vary by a factor of

131 ten (e.g. Pyle and Mather, 2009); however, the representative values in Table 1 illustrate that
132 F is unique among the halogens because it is depleted in seawater relative to the primitive
133 mantle (Table 1). In comparison, I exhibits a modest enrichment in seawater and Cl and Br are
134 both enriched by ~1000 times in seawater compared to the primitive mantle (Table 1).

135

136 ***9.2.1 Fluorine's low solubility***

137 The low solubility of F in aqueous fluids means that in contrast to the heavy halogens
138 (Cl, Br and I), F is inefficiently transported by rivers, and is removed from solution once in the
139 ocean (Carpenter, 1969). Important F sinks in the oceanic environment include marine
140 carbonates, phosphates, and alumina-silicate clay minerals (cf. Carpenter, 1969; Frohlich et al.,
141 1983; Matthies and Troll, 1990; Rude and Aller, 1994). Calcite can contain hundreds of ppm
142 of F (Fig 1). Magnesium-calcite and aragonite have maximum F concentrations in excess of
143 1000 ppm that represent a 1000-fold enrichment over seawater and demonstrate the high
144 compatibility of F in carbonate (Fig 1; Ohde and Kitano, 1980; Okumura et al., 1983; Opdyke
145 et al., 1993; Rude and Aller, 1991; Tanaka et al., 2013). An exchange reaction has been
146 proposed in which two F^- anions substitute for CO_3^{2-} (Ichikuni, 1979):

147 $$CaCO_3 + 2F^- = CaF_2 + CO_3^2 \quad (1)$$

148 Given the conservative nature of F^- in seawater, the implication of this reaction is that the F
149 content of aragonite can be used to monitor the CO_2 content of seawater, which exhibits
150 significant spatial and temporal variation (e.g. Ichikuni, 1979; Ramos et al., 2005; Tanaka et
151 al., 2013).

152 Carbonate fluorapatite (CFA) in marine phosphates with concentrations of 1-3 wt. % F
153 contains an order of magnitude more F than carbonate (Li and Schoonmaker, 2003; Rude and

154 Aller, 1991). However, because phosphorite deposits are restricted to zones of nutrient rich
155 water upwelling they are estimated to account for only ~20% of F uptake from the ocean
156 (Frohlich et al., 1983). Fluorine also substitutes for the hydroxyl group in alumina-silicate
157 clay minerals; however, the relative importance of this sink is disputed (cf. Carpenter, 1969;
158 Matthies and Troll, 1990; Rude and Aller, 1994).

159 Fluorine is mobilised during diagenesis of marine carbonates but it is fixed into newly
160 formed carbonates, apatite, or clay minerals, meaning the fluids occupying sediment pore
161 spaces have low ppm levels of F and F/Cl ratios similar to seawater (Frohlich et al., 1983;
162 Mahn and Gieskes, 2001; Rude and Aller, 1994).

163 Fluorine is further distinguished from the heavier halogens by its relative compatibility
164 in the mantle. Fluorine has a compatibility comparable to moderately incompatible elements
165 like Nd (Workman et al., 2006), whereas the heavy halogens (Cl, Br and I) have
166 incompatibilities comparable to more strongly incompatible elements such as K, La or Nb
167 (Kendrick et al., 2012a; le Roux et al., 2006; Schilling et al., 1980). This difference cannot
168 explain the F depletion of seawater but it does imply the surface reservoirs of seawater and
169 sediments are less enriched in F than the heavy halogens (cf. Table 1).

170

171 ***9.2.2 Chlorine in halite***

172 In contrast to F, Cl is often regarded as a conservative element in sedimentary marine pore
173 waters, meaning its concentration is not easily altered. Chlorine and Br have very low
174 compatibilities in marine carbonate (Kitano et al., 1975; Okumura et al., 1986) and low
175 concentrations in other sedimentary minerals such as carbonate fluorapatite. As a result,
176 evaporites formed by evaporation of seawater beyond the point of halite saturation (30-35 wt.

177 % salt; McCaffrey et al., 1987; Zherebtsova and Volkova, 1966), commonly represent the only
178 significant mineral reservoir of Cl in sedimentary settings (Hanor, 1994; Worden, 1996).
179 Evaporite deposits are important sedimentary units in some ocean basins and dissolution of
180 evaporites is indicated as an important source of salinity for hydrothermal fluids in Red Sea
181 brine pools (e.g. Pierret et al., 2001; Shanks and Bischoff, 1977; Zierenberg and Shanks III,
182 1986). In addition, halite could be important in some hydrothermal settings where precipitation
183 of hydrothermal halite is possible (Butterfield et al., 1997; Foustoukos and Seyfried, 2007).

184 Evaporitic salt deposits are characterised by very low Br/Cl and I/Cl ratios (Bein et al.,
185 1991; Fontes and Matray, 1993; McCaffrey et al., 1987). Halite has partition coefficients (D
186 = R_{salt}/R_{fluid}) of ~0.03 for Br/Cl and <0.003 for I/Cl, whereas Br can be accommodated more
187 easily in sylvite (D ~0.2), carnalite, and other potash salts (Fontes and Matray, 1993; Hermann,
188 1980; Holser, 1979; Siemann and Schramm, 2000). As a result, the actual concentrations of
189 Br and I in evaporite deposits vary depending on the salts present; on the presence of organic
190 material and fluid inclusions which contain significant Br and I; and on the diagenetic history
191 of the deposit (Bein et al., 1991; Fontes and Matray, 1993). Experimental studies suggest Br
192 is excluded from the halite lattice under hydrothermal conditions (Berndt and Seyfried, 1997;
193 Foustoukos and Seyfried, 2007). This means that fluid interaction with either sedimentary or
194 hydrothermal halite has the potential to strongly alter Cl concentrations and fluid Br/Cl and
195 I/Cl ratios.

196

197 ***9.2.3 Iodine and bromine in organic matter***

198 The marine I cycle is dominated by accumulation of I in algae: Kelp (a type of seaweed, which
199 is multicellular macroalgae) is the main I accumulator in coastal environments, whereas

200 phytoplankton is the main I accumulator at sea (Iwamoto and Shiraiwa, 2012; Leblanc et al.,
201 2006).

202 Iodine is seasonally variable and heterogeneously distributed in Kelp (Gall et al., 2004).
203 Maximum concentrations of ~6 wt.% I have been reported in parts of a Kelp plant (Laminaria
204 Digitalis; Kuepper et al., 2013), but an average I content of 1 wt. % has been suggested (Gall
205 et al., 2004). Other seaweeds contain ~1-500 ppm I (Muramatsu and Wedepohl, 1998; Yang
206 et al., 2014). Several species of coral have skeletons in which organic components can have
207 very high halogen concentrations of 5-6 wt. % I, 1-2 wt. % Br, and <1000 ppm Cl (Collins,
208 1969; Goldberg et al., 1994). The Br/I weight ratios of seaweeds and corals range from ~0.1
209 to 2.5 (Collins, 1969; Kuepper et al., 2013). In comparison, plankton has variable halogen
210 contents ranging from sub-ppm to typical values of ~200 to 300 ppm I and 1000 to 4000 ppm
211 Br. Plankton have Br/I weight ratios of 3-24 and $I/C_{organic}$ of 0.0002-0.002 (Bobrov et al., 2005;
212 Iwamoto and Shiraiwa, 2012; Martin et al., 1993; Price and Calvert, 1977).

213 Iodine accumulated by algae is either emitted to the atmosphere as I_2 gas (or volatile
214 iodocarbon compounds) or buried in marine sediment, which has previously been estimated to
215 contain ~70% of the I present in the crust and seawater (Leblanc et al., 2006; Muramatsu and
216 Wedepohl, 1998). Regeneration of organic matter releases iodide (I^-), bromide (Br^-), and CH_4
217 into sedimentary pore waters in the subsurface (Kennedy and Elderfield, 1987a, b; Muramatsu
218 et al., 2007; Price and Calvert, 1973, 1977). Studies of cosmosgenic ^{129}I indicate pore waters
219 can migrate laterally over many km (e.g. Fehn et al., 2006; Muramatsu et al., 2001; 2007).
220 However on average, pore waters seep gradually upwards toward the seafloor (Wong and
221 Brewer, 1977). In typical oxic basins, iodide in escaping pore waters is oxidised and, together
222 with seawater iodate, is then adsorbed back onto organic detritus close to the sediment surface
223 (Fig 2; Price and Calvert, 1973, 1977). If present, additional adsorption may also occur on Fe-
224 hydroxides (Ullman and Aller, 1985) and clay minerals (Montavon et al., 2014). As a result

225 sediment profiles in oxic basins can have very high I concentrations of 100-2000 ppm close to
226 the surface (Fig 2a; Price and Calvert, 1977), along with elevated $I/C_{organic}$ and I/Br ratios, but
227 at depths of more than a metre below the surface sediments have more typical concentrations
228 of ~5-50 ppm I, along with $I/C_{organic}$ and I/Br ratios similar to plankton (Kennedy and
229 Elderfield, 1987a, b; Price and Calvert, 1973, 1977; Upstillgoddard and Elderfield, 1988).

230 Halogen regeneration processes result in pore water Br and I concentrations which tend
231 to increase with depth and solid phase Br and I concentrations which tend to decrease with
232 depth and sediment maturity (Fig. 2). Pelagic sediments have typical I concentrations of ~5-
233 50 ppm I in the solid phase (Kennedy and Elderfield, 1987b; Muramatsu et al., 2007).
234 However, Murumatsu et al (2007) reported that sediments from the Nankai Trough contain 3-
235 4 times more Br and I in pore waters than in the solid phase. In contrast to unconsolidated
236 sediment, lithified marine sediments have much lower halogen concentrations. For example,
237 the median I concentration of twenty limestones and shales analysed by Muramatsu and
238 Wedepohl (1998) is 2^{+2}_{-1} ppm. The Callovian-Oxfordian clay of France contains 1 to 7 ppm I
239 and 0.4 to 1.2 wt. % organic C (Claret et al., 2010). The organic rich Kimmeridge clay of
240 England contains 6 to 34 ppm I and 16 to 55 wt. % organic C (Cosgrove, 1970). Taken together,
241 these data give a combined average of 4 ± 3 ppm I in lithified marine sediments (Table 2) and
242 suggest that variable depletion of I occurs relative to C in lithified sediments, compared with
243 organic I/C ratios.

244 A large database is now available for Cl, Br and I in sedimentary marine pore waters
245 (Fig 3; Fehn et al., 2000; 2003; 2006; 2007ab; Gieskes and Mahn, 2007; Mahn and Gieskes,
246 2001; Martin et al., 1993; Muramatsu et al., 2001; 2007; Tomaru et al., 2007abc; 2009). These
247 studies have shown that sedimentary pore waters have a relatively narrow range in salinity (~1-
248 5 wt. % salt), which reflects the modification of seawater salinity (3.5 wt. % salts) by formation
249 and destruction of gas hydrate (Fig 3b). Plotting pore fluid Cl, Br, and I data as ratios in a three

element plot, which removes the effects of salinity variation, enables the sediment-derived halogen component to be fully resolved from seawater (Fig 3a). The slopes in Fig 3a indicate that the sediment-derived halogen component has a fairly constant seawater-corrected Br/I weight ratio of ~0.3-1.6 (Fig 3a; Kendrick et al., 2011a). The low seawater-corrected Br/I ratio of sedimentary pore waters (0.3-1.6), compared to plankton (3-24; Bobrov et al., 2005; Collins, 1969; Martin et al., 1993), reflects preferential mobilisation of I compared to Br during diagenesis, with the excess I representing the surface-adsorbed I component acquired under oxic conditions (Francois, 1987; Martin et al., 1993; Upstillgoddard and Elderfield, 1988). In comparison, the solid sedimentary phase preserves higher Br/I ratios, which are similar to planktonic values (Fig 3; Muramatsu et al., 2007).

9.2.4 Iodine adsorption and substitution in carbonate

In addition to I sorption onto organic detritus at the sediment-seawater interface (Price and Calvert, 1973, 1977), I is significantly adsorbed onto the surfaces of a number of reactive minerals (Ullman and Aller, 1985). Available data indicate that hydrogenetic Fe-Mn crusts formed on igneous substrates, and nodules formed in sedimentary environments, contain up to 390 ppm F, 1.1 wt. % Cl, 200 ppm Br and 900 ppm I which represent a factor of ~2 depletion of Cl, a factor of ~3 enrichment of Br, a factor of ~300 enrichment of F and a factor of ~2000 enrichment of I compared to seawater (Table 2; Glasby, 1973; Glasby et al., 1978; Hein and Koschinsky, 2014; Rude and Aller, 1991). Hydrogenetic Fe-Mn crusts and nodules include detrital minerals such as fluorapatite and a mixture of MnO_2 and FeOOH precipitated from cold seawater (with a varying hydrothermal component in some cases; Baturin and Dubinchuk, 2011; Hein and Koschinsky, 2014). The crusts have slow growth rates, very high porosities, and large reactive surface areas that enable efficient scavenging of reactive trace elements from

seawater (Hein and Koschinsky, 2014). The experiments of Ullman and Aller (1985) confirm iodate, but not iodide, is strongly adsorbed onto Fe-oxyhydroxides and the same may be true for Mn oxide crusts.

Clay minerals such as montmorillonite [$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2.nH_2O$] have reactive surfaces that adsorb variable quantities of water (e.g. nH_2O) and other substances. Due to the environmental significance of radioactive iodide, which is one of the most mobile radioisotopes present in nuclear waste, a number of investigations have been conducted to evaluate the sorption of I to clay. Experimental results showing significant I sorption have been controversial because of uncertainties regarding the speciation of I in the experiments (Glaus et al., 2008), and the potential of I to be irreversibly bound in carbonate formed during the experiment (Claret et al., 2010). However, a recent study that controlled for these factors reported reversible sorption of iodide onto clay minerals under controlled PCO_2 (Montavon et al., 2014).

Claret et al. (2010) suggested carbonate within Callovian-Oxfordian clay rock (France) contains ~2 ppm I. Recent experimental data suggest that IO_3^- but not I^- can substitute for CO_3^{2-} in calcite (Lu et al., 2010) and the iodate mineral lautarite [$Ca(IO_3)_2$] is known from I-rich nitrate deposits (Jackson and Ericksen, 1997). In contrast, $2F^-$ can readily substitute for CO_3^{2-}, but Br^- and Cl^- (like I^-) have low compatibilities in carbonate (Kitano et al., 1975; Okumura et al., 1986). It should however, be noted that while the maximum I concentration of 2 ppm reported for carbonate represents a considerable enrichment over seawater I concentration of ~58 ppb, it is 100 times less than the maximum I concentration of ~220 ppm in sedimentary pore waters (Table 2). Further work is clearly required to understand the interactions of I species, clay minerals and carbonates.

9.2.5 Summary

Two distinct fluids that could be advected into the mafic portions of the oceanic crust have been identified and are relatively well defined: i) seawater and ii) sedimentary marine pore water. Sedimentary marine pore waters comprise seawater modified by the addition of organic components and adsorbed I present in marine sediments. The majority of pore waters preserve salinities close to seawater, but salinities of 1-5 wt. % salts can be explained by fluid interaction with gas hydrate (Fig 3). Fluorine has a low solubility in aqueous fluids and is retained by or incorporated into several marine minerals during diagenesis. In contrast, diagenesis releases considerable Br and I from the solid phase in organic-rich sediments to the fluid phase. It is usually assumed that Cl has a negligible concentration in the solid phase of marine sediment (Martin et al., 1993; Muramatsu et al., 2007; Gieskes and Mahn, 2007). However, the few data available for Cl in lithified sedimentary rock indicate surprisingly high Cl concentrations ranging up to ~1000's of ppm, which might be partly explained by the variable presence of salt derived from seawater or sedimentary pore waters (Table 2; John et al., 2011; Turekian and Wedepohl, 1961). Further data are therefore required to evaluate the significance of water soluble halogens in marine sediment and to improve the constraint on the Cl content of the solid phase. Water soluble halogens might be included in estimates of bulk silicate Earth concentrations, but removal of pore waters by sediment compaction suggests that sedimentary pore waters (and therefore salt in dry sediments) are not relevant for estimation of deep subduction budgets (Peacock, 1990).

9.3 The oceanic crust-lithosphere and the scale of fluid infiltration

As a first step toward evaluating the behaviour of halogens during alteration and metasomatism of the oceanic crust, it is desirable to review current knowledge concerning the structure of the oceanic crust and the scale of fluid infiltration.

It is now recognised that the character of the oceanic crust generated along the Earth's 67,000 km long system of oceanic spreading centres varies as a function of spreading rate (Bird, 2003; Dick et al., 2006; Snow and Edmonds, 2007). The classic 'Penrose' style of oceanic crust, as defined by the participants of the 1972 Penrose conference (Conference Participants, 1972), which has a homogenous layered structure where sediments are underlain by pillow basalts, sheeted dykes, and layered intrusives, is only generated at fast spreading centres (>60 mm/yr; Dick et al., 2006). In these cases, the rate of magma supply exceeds the rate of plate divergence and the seismic Moho at depths of 6-7 km represents a petrological transition from layered gabbro to peridotite (Fig 4; Dick et al., 2006).

In contrast, extremely heterogenous crust is generated at ultra-slow spreading centres, which have rates of divergence of <20 mm/yr, and account for more than 20,000 km of the global ridge system (Bird, 2003; Dick et al., 2003). In some cases, ultra-slow spreading centres are completely amagmatic and characterised by tectonic extension with hydrated ultramafic rocks (serpentinites) exposed on the seafloor (Dick et al., 2006; Snow and Edmonds, 2007). In other cases, a thin and/or patchy carapace of volcanic rock lies directly on top of layered intrusives or mantle peridotites (Fig 4; Dick et al., 2006) and the seismic Moho at depths of only 1-4 km could represent a hydration front between serpentine and mantle peridotite, as originally suggested by Hess (1962).

Finally, slow spreading ridges, such as the Mid-Atlantic Ridge, with rates of divergence of between 20 mm/yr and 60 mm/yr, are characterised by alternating segments of the two

crustal styles implying the Penrose model is inadequate for a large portion of the oceanic crust (Dick et al., 2006; Larsen et al., 2009; Snow and Edmonds, 2007).

9.3.1 Crustal permeability

Pillow lavas and hyaloclastite breccias in seismic layer 2a of the oceanic crust have relatively high permeability (~10^{-13} m^2), meaning that the upper 500 m of the crustal basement enjoys good connectivity with cold seawater and is subject to low-temperature 'brownstone' facies weathering at very high water/rock ratios (e.g. w/r > 100; Anderson et al., 1985; Fisher, 1998). In situ borehole permeability measurements indicate permeability decreases to 10^{-18}-10^{-15} m^2 at greater depths, but numerical heat flow models imply that localised fracture generated permeabilities of up to 10^{-9} m^2 control the effective permeability in the deeper crust (Fig 4; Anderson et al., 2012; Fisher, 1998; Fisher and Becker, 2000; Nehlig, 1994). Unlithified sediments represent a low permeability barrier to vertical fluid flow (Fig 4) and hydrothermal systems on the ridge flanks are therefore connected to seawater, and each other, through fractures exposed on basement outcrops (Anderson et al., 2012; Hutnak et al., 2008).

9.3.2 High temperature hydrothermal vent systems

High temperature (350-400 °C) black smoker vent systems, where precipitation of Fe, Cu, and Zn sulphides generate vent chimneys and sulphide mounds, are found along mid-ocean ridges, back arc basin spreading centres and at intra-plate submarine volcanoes (Baker and German, 2004; Edmond et al., 1979; Hannington et al., 2011; Staudigel et al., 2004; Von Damm et al., 1985). The majority of high temperature hydrothermal fields at spreading centres occur on the ridge axes, but off-axis systems linked to crustal fractures are known at distances of up

366 to several km from the axis (Melchert et al., 2008; Rona et al., 1990; Zierenberg et al., 1995).
367 The circulation of hydrothermal fluids is responsible for up to 80 % of the geothermal heat lost
368 in these settings, meaning it is the major mechanism by which the oceanic crust cools (e.g.
369 Williams et al., 1974).

370 Heat flow calculations and the distribution of hydrothermal plumes in the water column
371 indicate that independent vent fields and associated ore deposits (e.g. hydrothermal outflow
372 zones) occur at intervals of as little as 25 km along fast spreading centre ridge axes and as far
373 apart as 200 km on slow spreading centre ridge axes (Baker, 2007; Hannington et al., 2011).
374 Seawater is drawn into the oceanic crust to feed these systems through fractures, gaps between
375 pillow lavas or dykes, and breccia zones over wide but poorly defined areas between the vent
376 fields and on the ridge flanks (Anderson et al., 2012; Hutnak et al., 2008).

377 Seismic evidence for brittle deformation suggests that hydrothermal fluids penetrate to
378 maximum depths of ~10 km on parts of the Mid-Atlantic Ridge (Glasby, 1998). The TAG
379 hydrothermal field at 26° N on the Mid-Atlantic Ridge is situated above a 15 km long
380 detachment fault that penetrates >7 km into the crust to near Moho depths (deMartin et al.,
381 2007). Periodic reactivation of the fault has supplied heat to the overlying hydrothermal
382 system and enabled sporadic hydrothermal activity over tens to hundreds of thousands of years
383 in this area (Humphris and Cann, 2000; Kleinrock and Humphris, 1996; Tivey et al., 2003).

384 In comparison, seismic evidence suggests that hydrothermal fluids penetrate only ~3
385 km into the fast spreading East Pacific Rise (Glasby, 1998). Melt lenses at depths of 1-3 km
386 on the East Pacific Rise supply heat to the overlying hydrothermal system but represent a
387 barrier to deeper fluid flow. The duration of hydrothermal activity is difficult to constrain but
388 is commonly related to magmatism on fast spreading ridges, and individual vent fields are
389 probably sustained over periods of only ten's to hundred's of years (Stakes and Moore, 1991).

390

391 ***9.3.3 Serpentinite hosted systems***

392 The Lost City Hydrothermal Field on the Atlantis Facture Zone occurs 15 km from the
393 Mid-Atlantic ridge axis at 30° N (Kelley et al., 2001). This system is hosted by ultramafic
394 rocks and is characterised by carbonate vent chimneys and low temperature (40-90° C) alkaline
395 fluids (pH 9-10) (Kelley et al., 2001; 2007). The alkalinity of the fluids and the presence of
396 hydrogen, methane and abiogenic hydrocarbons are characteristics of fluids produced by
397 serpentinisation of ultramafic lithologies (Kelley et al., 2007; Proskurowski et al., 2008). The
398 discovery of this system was significant because it is driven by heat generated by exothermic
399 serpentinisation reactions, rather than magmatism, and similar reactions could potentially drive
400 numerous hydrothermal systems distal to ridge axes, implying a much higher level of seafloor
401 hydrothermal activity than previously recognised (Kelley et al., 2001). Serpentinites are
402 commonly exposed along transform faults and low angle detachments related to oceanic core
403 complexes, providing evidence for widespread fluid activity at varying distance from oceanic
404 spreading axes (Fryer, 2002).

405 The slab bend formed immediately before subduction is now recognised as an
406 additional site of important hydrothermal alteration (Fig 5). Seismic evidence suggests faults
407 cut at least 20 km below the seafloor in this location, with the potential for large scale
408 serpentinisation of the lithospheric mantle (Fig 5; Ranero et al., 2003). Heat flow
409 measurements off shore Nicaragua and Central Chile indicate these areas are characterised by
410 unexpectedly low heat flow consistent with heat loss by hydrothermal activity (Grevemeyer et
411 al., 2005).

412

413 **9.4 Black smoker vent fluid chemistry and halogens**

414 In comparison to seawater, high temperature black smoker vent fluids contain negligible Mg
415 or SO_4^{2-} (dissolved sulphur is S^{2-}), and are often depleted in U, P and F (Fig 6). In contrast,
416 they are enriched in trace elements, dissolved SiO_2 and contain 5-10 times more K and Ca
417 relative to Na, than seawater (Fig 7). Typical vent fluids have pH of 3-4, maximum
418 temperatures of close to 400 °C and salinities that range from 0.1 to 6 wt. % salts (Fig 8).

419 The composition of hydrothermal vent fluids results partly from chemical reaction of
420 seawater with the oceanic crust and the mobilisation of trace elements and silica made possible
421 by the high temperature of the fluid, acidity, and presence of the chloride ligand (Bischoff and
422 Dickson, 1975; Humphris and Thompson, 1978; Seyfried and Bischoff, 1981). The take up of
423 Mg into Mg-rich hydrous-silicate minerals, including smectite, chlorite, amphibole, and talc,
424 is important because Mg-metasomatism is the primary source of vent fluid acidity and leads to
425 extensive hydration of the crust (reaction 2; Bischoff and Dickson, 1975; Seyfried and Mottl,
426 1982).

427 $$3MgCl_{2(aq)} + 4SiO_{2(aq)} + 4H_2O_{(l)} = Mg_3Si_4O_{10}(OH)_{2(s)} + 6HCl_{(aq)} \quad (2)$$

428 SO_4^{2-} is removed from solution by reduction to sulphide and precipitation with Ca as anhydrite;
429 Ca is released to the fluid by albitisation of plagioclase and the Ca/Na ratio of the fluid is
430 subsequently controlled by plagioclase and epidote solid solution (Berndt et al., 1989).
431 Potassium is incorporated into K-minerals at low temperature but it is released to the fluid at
432 temperatures of >150 °C, which means most high temperature vent fluids have K/Cl ratios
433 higher than seawater. The K/Cl ratio of the vent fluid is usually limited by the low K content
434 of the basaltic crust, but high K/Cl ratios occur in the Manus basin vent fluids where more
435 evolved K-rich rocks are present on the seafloor (Fig 7; Reeves et al., 2011).

436 The growth of Mg-rich hydrous minerals causes a finite increase in the salinity of
437 hydrothermal fluids; however, this is only detectable at low water-rock ratios of <1 (e.g. Kelley
438 and Robinson, 1990; Seyfried et al., 1986; Seyfried and Mottl, 1982). Therefore, the
439 occurrence of vent fluids with salinities of less than seawater, and in some cases the dominance
440 of vent fluids with lower than seawater salinity over many years of observation (Campbell et
441 al., 1988), has been interpreted as strong evidence for phase separation and segregation of
442 brines and vapours in submarine hydrothermal systems (Bischoff and Rosenbauer, 1989;
443 Butterfield et al., 1997; Seyfried et al., 2003; Von Damm et al., 1997).

444

445 ***9.4.1 Phase relations in the H_2O-NaCl system***

446 The phase relations of sub-marine hydrothermal systems are strongly controlled by the
447 presence of salts. Pure water exists as a homogenous supercritical fluid above its critical point
448 (374 °C; 220 bars). In contrast, a critical curve extends beyond the critical point of pure H_2O
449 in any binary H_2O-salt system, and the two-phase region is vastly expanded (Fig 9; e.g.
450 Bischoff and Pitzer, 1989; Driesner and Heinrich, 2007). The critical point of seawater (407
451 °C; 220 bars) lies on the critical curve of the H_2O-NaCl system and joins the boiling curve to
452 the condensation curve in Fig 9a (e.g. Bischoff and Pitzer, 1989; Bischoff and Rosenbauer,
453 1984; Driesner and Heinrich, 2007). Sub-critical phase separation occurring below the critical
454 point of seawater produces a small quantity of vapour, whereas super-critical phase separation
455 occurring above the critical point of seawater produces a small quantity of brine (Fig 9).

456 The slope of the critical curve implies that phase separation will produce progressively
457 more saline brines at higher pressures and temperatures deeper within the oceanic crust (Fig
458 9). The salinity of brines also increases as the L-V isotherms are overstepped, such that at 500
459 °C and 540 bars the first brine exsolved has a salinity of 28 wt. %, but further decompression

460 to 450 bars would yield a brine of 44 wt. % NaCl (points 1 and 2; Fig 9b). It is important to
461 note that the salinities of the vapours and brines produced at different temperature and pressure
462 conditions are controlled exclusively by the shape of the liquid-vapour envelope. For example
463 at 500 °C and 450 bars, parental fluids with salinities of either 3.2 wt. % NaCl (seawater) or 10
464 wt. % NaCl, would both exsolve into conjugate fluids with identical salinities, but at different
465 proportions that can be estimated by the lever rule (point 2; Fig 9b).

466 In addition to the well documented phenomena of liquid-vapour immiscibility,
467 precipitation of hydrothermal-halite is possible under some circumstances (e.g. point 4; Fig 9).
468 This is possible for seawater, which is approximated by the H_2O-NaCl system (Fig 9), because
469 hydrostatic pressures above spreading centres at typical water depths of 2000-2500 m are only
470 ~200-250 bars and seawater heated above ~400 °C would separate into steam and halite (Fig
471 9). Butterfield et al. (1997) presented photomicrographic evidence for halite coating glass
472 surfaces and intergrown with TiO_2, AlO(OH), and sphalerite, that was interpreted as evidence
473 for precipitation of hydrothermal halite during high temperature interaction of seawater with
474 seafloor lavas. The precipitation of hydrothermal halite has also been suggested as a possible
475 cause of Br and Cl fractionation in some hydrothermal vent fluids (Berndt and Seyfried, 1997;
476 Foustoukos and Seyfried, 2007). However, it should be noted that the vapour-salt field is
477 probably restricted to much shallower depths in the multi-component salt systems that are
478 relevant for hydrothermal fluids than in the H_2O-NaCl system that is relevant for seawater
479 (below).

480 ***9.4.2 Complex salt systems and hydrolysis***

481 Hydrothermal vent fluids are better modelled in the ternary H_2O-NaCl-$CaCl_2$ system
482 than in the NaCl-H_2O system (Vanko et al., 1988) because they have Ca/Na and K/Na ratios
483 elevated by 5-10 times compared to seawater (Fig 10). The two phase field is even larger in

these complex salt systems than in the H_2O-NaCl system. The critical curve for H_2O–K/Cl is similar to that of H_2O-NaCl, but the critical curve for H_2O-$CaCl_2$ moves to significantly higher pressure at any given temperature than in the H_2O-NaCl system (Fig 10; Bischoff et al., 1996; Driesner and Heinrich, 2007; Hovey et al., 1990). In addition, at temperatures of 400-450 °C, the vapour-salt field shrinks back from pressures of 180-250 bars in the H_2O-NaCl system (that overlap the seafloor; Fig 10), to 130-170 bars in the H_2O-KCl system and to as little as ~40-65 bars in the H_2O-$CaCl_2$ system (Fig 10; Driesner and Heinrich, 2007; Hovey et al., 1990; Keevil, 1942; Ketsko et al., 1984).

In addition to the role of Cl as an important ligand for metal transport in hydrothermal solutions (e.g. Yardley, 2005), hydrolysis reactions in H_2O-salt systems can have a significant influence on the pH of hydrothermal fluids (e.g. reaction 3; Bischoff et al., 1996; Seyfried et al., 1988; Seyfried and Bischoff, 1981). Hydrolysis reactions in binary salt systems have the general form:

$$xH_2O + M^{x+}Cl^-_x = xHCl + M^{x+}(OH)^-_x \quad (3)$$

The equilibrium lies to the left under Earth's surface conditions, meaning salt solutions have a neutral pH, but the equilibrium can be significantly shifted to the right under some crustal conditions. Bischoff et al. (1996) demonstrated that at temperatures of 350-500 °C hydrolysis is significantly more important in the $CaCl_2$-H_2O system than in the binary NaCl-H_2O system. Fournier and Thompson (1993) reported that hydrolysis does not occur in the liquid-vapour region of the H_2O-NaCl-KCl system, but that HCl is a significant component of the steam in equilibrium with halite in the vapour-salt region of the H_2O-NaCl and H_2O-NaCl-KCl systems. The varying degrees of hydrolysis in the different salt systems are related to the relative solubilities of the metal hydroxide produced by hydrolysis: $Ca(OH)_2$ has a low solubility

meaning it is removed from solution more efficiently than NaOH and as a result reaction 3 is pushed further to the right (Bischoff et al., 1996).

In nature the hydroxide component produced by hydrolysis reacts with silicates to form hydrous silicate minerals in the oceanic crust. For example, hydrolysis of $MgCl_2$ leads to Mg being fixed in hydrous silicate minerals under prograde conditions as seawater is drawn into hydrothermal systems (reaction 2; Seyfried et al., 1988). The reactivity of Mg in the oceanic crust means that it is quickly removed from solution and Mg is not present in the hydrothermal fluids that reach the high temperature reaction zone above the magma chamber. In the absence of $MgCl_2$, hydrolysis of $CaCl_2$ becomes the main acid generating reaction and is important in the hydrothermal upflow zones; hydrolysis of NaCl can be locally important in zones of Na metasomatism (Seyfried et al., 1988). The generation of acidity by hydrolysis reactions is important because it enables mobilisation of heavy metals from seafloor lithologies (Seyfried and Bischoff, 1981). Furthermore, HCl partitions into the vapour produced by phase separation (Fig 10; Bischoff et al., 1996), meaning segregation of vapours and brines enables discrete zones of alkali or acid metasomatism to develop in different parts of the oceanic crust, or waves of acid metasomatism to pass through a hydrothermal system (Kigai and Tagirov, 2010).

9.4.3 Halogen abundance ratios in vent fluids

There has been considerable interest in the relative abundances of halogens in hydrothermal vent fluids. The existing data show vent fluids have F concentrations ranging from ~0.1 to 7 ppm, compared to the seawater value of 1.3 ppm F, and that F varies independently of Cl with vent fluid F/Cl ratios varying by almost two orders of magnitude around the seawater value (Fig 11a; Edmond et al., 1979; Gieskes et al., 2000; Gieskes et al., 2002; James et al., 2014; Mottl et al., 2011; Reeves et al., 2011; Von Damm et al., 1985). The reported variation in F

fits well with experimental studies that demonstrate F is removed from solution as seawater interacts with basalt and is heated from 150 to 250 °C, but re-enters solution with further heating to 300 °C (Seyfried and Ding, 1995). Fluorine is incorporated into Mg-carbonate (cf. Fig 1) and hydrous minerals at low temperature but the direction of hydroxyl-fluoride and carbonate-fluoride exchange reactions reverses at high temperature when the speciation of dissolved F changes from $F^-_{(aq)}$ to $HF_{(aq)}$, which reduces the chemical activity of the F^- anion (Seyfried and Ding, 1995). Consequently the experimental studies imply that while magmatic F might be mobilised in deeper parts of the crust as $HF_{(aq)}$, it is likely that seawater $F^-_{(aq)}$ is removed from solution during heating and is not advected deeply into the crust (Seyfried and Ding, 1995). The co-depletion of some hydrothermal fluids in P as well as F suggests that precipitation of fluorapatite is also important (Fig 6; Gieskes et al., 2002).

A number of studies have investigated Br in hydrothermal fluids and demonstrated that the Br/Cl ratio of the vent fluids is usually within 10 % of the seawater value and that it does not vary systematically as a function of salinity (Fig 11b). Furthermore, conjugate vapours and brines from vent F at 9°16' N on the East Pacific Rise (Von Damm et al., 1997) and Milos Island in the Hellenic Arc (Wu et al., 2012) have similar Br/Cl ratios (Fig 11b). Taken together these data strongly suggest that the Br/Cl ratio is not strongly or systematically altered by liquid-vapour phase separation in the majority of hydrothermal systems investigated (Fig 11b). This conclusion is consistent with experiments on NaCl solutions that show no systematic fractionation of Br and Cl during sub-critical phase separation (Berndt and Seyfried, 1997). Experiments under other conditions have shown fractionation of Br relative to Cl into either vapours or brines during phase separation (see Berndt and Seyfried, 1990; Foustoukos and Seyfried, 2007; Liebscher et al., 2006). However, the results from the different laboratories are not in agreement and the available Br/Cl data summarised for vent fluids in Fig 11 are more

555 easily explained by the conservation of Br/Cl during phase separation with unusual Br/Cl ratios
556 of fluids in specific settings being explained by fluid-rock reactions (below).

557 The unusually high Br/Cl ratios in fluids from a small number of vents (Fig 11b) can
558 be explained by fluid interaction with sedimentary material, because where Br/Cl and I/Cl data
559 are both available these ratios co-vary in a manner comparable to that observed for sedimentary
560 pore waters (Fig 11c; Campbell and Edmond, 1989; Campbell et al., 1994; Gieskes et al., 2002;
561 Kawagucci et al., 2011; Mottl et al., 2011; You et al., 1994). Furthermore, I concentrations are
562 correlated with NH_4 and other sediment-derived components in these fluids (Campbell et al.,
563 1994; You et al., 1994). Note that limited data are available for I or F in vent fluids and halogen
564 data for sedimentary pore fluids with mantle-like $^3He/^4He$ signatures, which are believed to
565 represent hydrothermal fluids from beneath the Escanaba Trough hydrothermal system (Hole
566 1038B-H; Ishibashi et al., 2002; James et al., 1999), are included in Fig 11 as light blue symbols
567 (Gieskes et al., 2000; 2002). These 'hydrothermal pore fluids' have Br/Cl and I/Cl values
568 overlapping the range reported for Escanaba Trough vent fluids (Fig 11c; Campbell and
569 Edmond, 1989; Campbell et al., 1994; You et al., 1994).

570 Unusually low Br/Cl ratios are restricted to a few locations between 9° and 10° N on
571 the East Pacific Rise (Oosting and Von Damm, 1996) and Milos Island in the Hellenic Arc (Fig
572 11b; Wu et al., 2012). It is possible that vent fluids acquired low Br/Cl ratios in these settings
573 by fluid interaction with sedimentary halite or by leaching glassy magmatic rocks that are
574 typically characterised by Br/Cl of less than seawater (see mantle field in Fig 11c; Jambon et
575 al., 1995; Kendrick et al., 2013a; Schilling et al., 1980). Similarly low Br/Cl ratios have been
576 reported for unusual sediment pore waters that have interacted with glassy volcaniclastic rocks
577 in the Aoba Basin of the New Hebrides convergent margin (Martin, 1999). Strongly altered,
578 palagonitised glasses can also be depleted in Cl and Br relative to pristine glasses (Fig 12;

579 Kendrick et al., 2015) confirming that these elements are mobilised during low temperature
580 alteration of glass.

581 Finally, the fact that most vent fluids have Br/Cl ratios within 10 % of seawater (Fig
582 11) implies that in most cases, fluid-rock ratios are sufficiently high that Br and Cl behave
583 conservatively in hydrothermal vent fluids and are not significantly altered by reaction with
584 mafic lithologies (Br concentrations are altered by interaction with sediments; Fig 3;
585 Muramatsu et al., 2007; Price and Calvert, 1977). In contrast, leaching of Cl>Br from glassy
586 rocks is possible and has the potential to lower the Br/Cl ratio of a fluid. Furthermore, at low
587 water-rock ratios, precipitation of OH>Cl>Br in Fe/Mg-hydroxy chlorides, or amphibole, has
588 the potential of increasing a fluid's salinity and Br/Cl ratio (Kendrick et al., 2015b; Seyfried et
589 al., 1986; Svensen et al., 1999, 2001; Vanko, 1986). Therefore, it should not be assumed that
590 Br and Cl behave conservatively under all hydrothermal conditions.

591

592 **9.5 Fluids in the deeper crust**

593 Evidence for the nature of fluids in deeper parts of the oceanic crust comes from mineral
594 alteration (Gillis and Meyer, 2001; Vanko, 1986), fluid inclusions (Fig 13; Kelley et al., 1993;
595 1992; Kendrick et al., 2015b; Nehlig, 1991; Vanko, 1988; Vanko et al., 1992), and studies of
596 magmatic glass that contain assimilated halogens (below; Kendrick et al., 2013a; 2015a). Fluid
597 inclusions have been investigated in minerals such as quartz, anhydrite, sphalerite, epidote,
598 amphibole, and chlorite from a number of dredges and ophiolites. These include samples from
599 within and just below the vent chimney all the way down to upper amphibolite facies
600 metagabbros from layer 3 of the oceanic crust (Castelain et al., 2014; Juteau et al., 2000; Kelley
601 and Delaney, 1987; Kelley and Robinson, 1990; Kelley et al., 1992, 1993; Lécuyer et al., 1999;
602 Nehlig, 1991; Nehlig and Juteau, 1988; Vanko, 1986; 1988; 1992; 2004).

603 Collectively these studies demonstrate the predominance of low salinity Na-Ca-Cl
604 fluids throughout the oceanic crust that are broadly similar to vent fluids. For example, Nehlig
605 (1991) reported that more than 95% of the fluid inclusions examined in samples taken from
606 crustal sections through the Semail and Trinity ophiolites of Oman and California, and in
607 samples from the Gorringe Bank of the East Pacific Rise, had salinities within 1 wt. % of
608 seawater. However, in addition to the dominant fluid inclusions with salinities of 0.1-6 wt. %,
609 which are similar to vent fluids, fluid inclusions with extreme Ca enrichment (Ca/Na = 1),
610 which is stronger than known from vent fluids (Fig 7), have been reported (Vanko et al., 1992)
611 and brine inclusions with salinities of up to 50 wt. % salts appear to be a common minor
612 component at all levels of the oceanic crust (Fig 13; Juteau et al., 2000; Kelley and Delaney,
613 1987; Lécuyer et al., 1999; Vanko, 1988; 2004; Aranovich et al., 2015).

614 Brine inclusions with salinities of ~30 wt. % salts have been reported in the vent
615 chimneys of several systems in the Lau Basin and within a few hundred metres of the seafloor
616 beneath the Pacmanus system, demonstrating that high salinity brines are not restricted to deep
617 parts of the oceanic crust (Lécuyer et al., 1999; Vanko et al., 2004). However, high salinity
618 brine inclusions are most commonly reported from deeper amphibolite settings (Vanko, 1988;
619 Kendrick et al., 2015b) and above newly emplaced gabbroic intrusions (Kelley and Delaney,
620 1987) or plagiogranites that form in the roof zones of crustal magma chambers (Kelley and
621 Robinson, 1990; Nehlig, 1991; Vanko et al., 1992). In many cases the brine inclusions co-exist
622 with more abundant low salinity vapour inclusions that provide evidence for their origin by
623 phase separation (e.g. Juteau et al., 2000; Kelley and Delaney, 1987; Vanko, 1988). The
624 dominance of vapour inclusions is the expected result of seawater undergoing phase separation
625 (e.g. point 2 in Fig 9; Bischoff and Pitzer, 1989). However, the vapour inclusions can have
626 salinities that are even greater than seawater suggesting complex multi-stage histories and/or
627 input of a magmatic component.

In some cases, brine inclusions dominate samples recovered from layer 3 of the crust. These inclusions have been interpreted as brines that have been segregated from their conjugate vapours, but their origin by phase separation cannot be proven (Kelley and Robinson, 1990; Vanko et al., 1992). The fluid inclusion evidence for possible segregation of brines in layer 3 of the oceanic crust is significant because brine segregation and double diffusive convection of fluids in the oceanic crust has previously been invoked to explain the predominance of fluids with lower than seawater salinity emitted from vents on the seafloor (Fig 14; Bischoff and Rosenbauer, 1989). It is suggested the brines would be segregated because of the different wetting properties and buoyancies of vapours and brines in a micro-scale fracture network. Buoyant vapours would be preferentially lost to the overlying hydrothermal system, whereas dense brines could be trapped in the lower crust. If correct, this model implies brines generated by multiple episodes of phase separation gradually accumulate in the deeper crust and they are implied to have long residence times in the crust at very low effective water-rock ratios (Fig 14). The ultimate fate of brines within this model is unknown but brines might eventually be flushed out of the crust by advection of more typical low salinity fluids in the waning stages of hydrothermalism or they might be transported laterally and leak out of the ridge flanks away from the vents (Bischoff and Rosenbauer, 1989). In addition, a portion of these brines could be assimilated by magmas driving the hydrothermal system (Kendrick et al., 2013a; 2015) or involved in flux melting and the genesis of plagiogranites (Aranovich et al., 2010, 2015).

A major uncertainty related to the brine fluid inclusions is whether they originate purely from evolved seawater or include a component derived from late-stage magmatic fluids. Magmatic fluids exsolved from basic rocks are dominated by CO_2 with a low salinity aqueous component (Dixon et al., 1995; Webster et al., 1999). However, more saline fluids might sometimes be exsolved from evolved intrusive rocks such as plagiogranites in magma chamber roof zones (Kelley and Robinson, 1990; Kelley et al., 1992). If magmatic fluids enter the two-

653 phase field, their salinity depends on the shape of the liquid-vapour envelope in the relevant
654 water-salt system (e.g. Figs 9 and 10), meaning that it is not possible to infer the source of the
655 fluid (e.g. seawater or magmatic) from the measured salinity. Vanko et al. (1992) suggested
656 that a minor magmatic component could be present in high salinity CO_2-bearing fluid inclusion
657 assemblages from the Oceanographer Transform, but favoured an origin entirely from evolved
658 seawater for brines trapped without accompanying CO_2 on the Mathematician Ridge (Vanko,
659 1988; 1992; Kendrick et al., 2015b). Reeves et al. (2011) suggested that unusually high F/Cl
660 ratios in Manus Basin vent fluids could result from the input of magmatic volatiles (Fig 11).

661

662 ***9.5.1 Halogens in brines and assimilation by magmas***

663 The systematics of Br/Cl, I/Cl, and F/Cl in brine inclusions can be inferred from two
664 separate lines of evidence. Kendrick et al. (2015b) investigated halogens and noble gases in
665 high salinity brine and vapour fluid inclusions in six quartz/epidote veins from the
666 Mathematician Ridge of the NE Pacific using a bulk extraction technique. The fluid inclusions
667 in all the veins were shown to have a similar range of Br/Cl and I/Cl irrespective of the relative
668 proportions of brine and vapour fluid inclusions (Fig 15). In addition, Br/Cl was not correlated
669 with Ar/Cl, which is strongly altered by phase separation (Kendrick et al., 2015b). Taken
670 together these data suggest that Br/Cl and I/Cl were not fractionated during phase separation
671 of Mathematician Ridge fluids, consistent with the behaviour of Br/Cl in vent fluids (section
672 9.4.3). On average the Mathematician Ridge fluids have Br/Cl ~20% higher than seawater and
673 I/Cl intermediate of seawater and the mantle (Fig 15; Kendrick et al., 2015b). These
674 compositions were attributed to mixing halogens introduced by seawater with halogens
675 mobilised from the crust and preferential exclusion of Br and I relative to Cl from amphibole
676 crystallised at low water rock ratios (Fig 15; Kendrick et al., 2015b). Proton Induced X-ray

677 Emission (PIXE) has been used to analyse some individual brine inclusions from the
678 Mathematician Ridge, Oceanographer Transform and Oman ophiolite (Juteau et al., 2000;
679 Vanko et al., 2001). The majority of the fluid inclusions investigated by PIXE are indicated to
680 have Br/Cl close to or above seawater, but the precision of the analyses is low (Juteau et al.,
681 2000; Vanko et al., 2001).

682 The second constraint on the halogen composition of high salinity brines in the oceanic
683 crust comes from recent studies of magmatic glass (Kendrick et al., 2013a; 2015a). It has long
684 been recognised that some magmatic glasses contain 'excess Cl' introduced by the assimilation
685 of seawater-derived components (Michael and Cornell, 1998; Michael and Schilling, 1989).
686 Most workers have favoured the assimilation of hydrothermally altered crust to account for
687 excess Cl. However, plotting the H_2O/Cl and K/Cl ratios of all known glasses, identified as
688 containing excess seawater-derived Cl (Coombs et al., 2004; Freund et al., 2013; Kent et al.,
689 1999ab; 2002; le Roux et al., 2006; Lytle et al., 2012; Wanless et al., 2010), shows that Cl is
690 introduced into these melts by high salinity brines (e.g. Fig 16; Kendrick et al., 2013a). This
691 is shown by the data in Fig 16 which extend from a range of compositions representative of the
692 mantle to converge on a single component with very low ratios of H_2O/Cl, K/Cl, and F/Cl that
693 are characteristic of a Na-Ca-K-Cl brine with salinity of >50 wt % salts (Fig 16; Kendrick et
694 al., 2013a; 2015a). In contrast, altered crustal material would have much higher H_2O/Cl (Ito
695 et al., 1983). The Br and I data available for glasses, affected by brine assimilation from the
696 NW part of the Lau Basin, the Galapagos, and Samoa, define coherent mixing trends with K,
697 Cl, and H_2O, demonstrating that the assimilated brines are characterised by Br/Cl and I/Cl
698 ratios a few 10's of percent higher than seawater (Figs 15 and 16), that are very similar to the
699 range of compositions determined for Mathematician Ridge fluid inclusions (Kendrick et al.,
700 2015b).

701 The brine assimilation data are significant because: i) some of the glasses affected have
702 high concentrations of H_2O and CO_2, which demonstrate that assimilation must have occurred
703 at depth in crustal magma chambers rather than on the seafloor (Coombs et al., 2004; Kendrick
704 et al., 2013a; le Roux et al., 2006), and ii) the data provide evidence that seawater-derived
705 brines, with Br/Cl and I/Cl distinct from the mantle, not only penetrate the lower crust but come
706 into direct contact with, and are assimilated by crustal magmas (Fig 16). Mass balance
707 calculations suggest the affected magmas from the NW part of the Lau Basin, the Galapagos,
708 and Samoa assimilated up to 0.5 % of their total mass in brine which introduced 0-70 % of
709 their total Cl and 0-30 % of their total H_2O (Kendrick et al., 2013a; 2015). Therefore,
710 assimilation of brines generated in hydrothermal systems can alter the concentrations of
711 halogens and relative abundance ratios (F/Cl, Br/Cl and I/Cl) of newly forming crust (e.g.
712 magma), even before the new crust has been hydrothermally altered. In addition, the ductile
713 zone, surrounding the magma chambers, is not a complete barrier to assimilation of seawater-
714 derived volatiles.

715

716 **9.6 Halogens in altered oceanic crust and lithosphere**

717 A relatively small number of studies have investigated the bulk halogen content of the altered
718 ocean crust with the majority of studies focused on Cl (Barnes and Cisneros, 2012; Bonifacie
719 et al., 2007; Chavrit et al., 2016; Floyd and Fuge, 1982; Ito and Anderson, 1983; Ito et al.,
720 1983; Kendrick et al., 2015b; Magenheim et al., 1995; Sano et al., 2008). The earliest estimates
721 for whole rock Cl concentration were made by electron microprobe measurements of Cl in
722 individual mineral phases, followed by estimation of the modal abundances of the minerals in
723 the rock (Ito et al., 1983). Major problems with this approach are that intra-granular Cl and
724 fluid inclusion hosted Cl, which can account for 100-200 ppm Cl in the bulk sample (Kendrick

et al., 2015b), or Cl present in volumetrically minor phases such as Fe hydroxychlorides are not included in the analysis. In addition, although detection limits of better than 50 ppm Cl can be achieved with sufficiently long counting times (e.g. Michael and Cornell, 1998) most minerals have Cl concentrations of less than the typical 100-300 ppm detection limits for Cl achieved by routine electron microprobe analysis.

Direct measurements of Cl have been achieved by various instrumental neutron activation techniques that provide modest 2σ precision of 15-20 % (Sano et al., 2008) or 200 ppm Cl (Barnes and Cisneros, 2012), and have the significant advantage of requiring minimal sample processing.

Direct measurements of F, Cl, and I have also been achieved by digestion of powders and spectrophotometry (Floyd and Fuge, 1982) and more recently by combining pyrohydrolysis for halogen extraction from powders with ion chromatography for F and Cl analysis (Bonifacie et al., 2007; John et al., 2011; Magenheim et al., 1995; Sharp and Barnes, 2004) and ICP-MS for Br and I analysis (John et al., 2011). These techniques can provide accurate results with internal precision of better than 5%. However, Bonifacie et al. (2007) demonstrated that Cl yields vary between labs with yields as low as 40 % in some of the early studies, implying that significant fractionation of halogens during extraction is possible.

Kendrick et al. (2011, 2013a, 2015) and Chavrit et al. (2016) employed 'the noble gas method' for analysis of Cl, Br, I, and K whereby neutron irradiation is used to generate noble gas proxy isotopes that can be precisely measured by noble gas mass spectrometry (Böhlke and Irwin, 1992; Johnson et al., 2000; Kendrick, 2012). This technique combines the advantages of neutron activation analysis, by avoiding wet chemical extraction of halogens (or K), with high internal precision of ~1-2 %.

748 Finally, the external precision of all methods is limited by the availability of well
749 characterised standards for Br and I (Kendrick, 2012; Kendrick et al., 2013a; Marks et al.,
750 2016). In addition, some differences between laboratories could be introduced by washing
751 procedures, which might completely remove water soluble components from powdered
752 samples. Water soluble halogens are especially important in marine sediments (Turekian and
753 Wedepohl, 1961) and serpentinites (e.g. Sharp and Barnes, 2004).

754

755 ***9.6.1 Mineralogy and Cl content of oceanic crust***

756 The altered oceanic crust comprises relict glass and nominally anhydrous minerals typical of
757 basalts and gabbros (e.g. plagioclase, pyroxene and olivine) and their hydrous alteration
758 products. Parts of the crust that have interacted with cold seawater contain clay minerals
759 (smectites including montmorillonite, and saponite), zeolites, and Fe-hydroxides. Glassy rocks
760 present in hyaloclastites in Layer 2a of the crust can be extensively replaced by palagonite,
761 which is defined as a heterogenous mixture of clays, zeolite, and oxides (Staudigel et al., 2008;
762 Staudigel and Hart, 1983; Stroncik and Schmincke, 2002). At temperatures of 200 to 300°C,
763 prehnite, pumpellyite, and chlorite are important. Actinolite, tremolite, albite, epidote, and
764 sphene become important at >300 °C, and hornblende and phlogopite can be important at >400
765 °C (Alt and Honnorez, 1984; Bideau et al., 1991; Talbi et al., 1999). In addition, a number of
766 minerals, including carbonate and quartz, form over wide temperature ranges. The polymorphs
767 of serpentine (chrysotile, lizardite, and antigorite) form in olivine-rich rocks between 100 and
768 500 °C (Bideau et al., 1991) and talc forms by silica metasomatism under all prograde
769 conditions (Seyfried et al., 1988). Typical water contents and what is known about the halogen
770 contents of some common alteration minerals are summarised in Table 4.

771

772 ***9.6.2 Low temperature seawater alteration***

773 Clay minerals contain a lot of water and significant F, but typically very little Cl (Table 4). For
774 example smectites contain 5-15 wt. % H_2O and the smectite veins analysed by Magenheim et
775 al. (1995) had 150-400 ppm F but only ~20 ppm Cl. Kendrick et al. (2014) reported that
776 palagonite crusts on Samoan glass contain 35 ppm Cl which represented a 97% depletion
777 compared to the pristine glass (Fig 12). Although it is usually assumed that Cl is introduced
778 into the oceanic crust during hydrothermal alteration, the very low Cl content of these clay
779 minerals and palagonite demonstrates that parts of the oceanic crust could be depleted in Cl
780 during low temperature alteration. Alternatively, halogens might be remobilised on a local
781 scale (Floyd and Fuge, 1982), with for example, Cl released during clay alteration taken up by
782 Fe-hydroxy chlorides (Table 4; Seyfried et al., 1986).

783 In comparison to Cl and F, even fewer data are available for Br or I. The palagonite
784 investigated by Kendrick et al. (2015) was less depleted in Br, than Cl, and it was enriched in
785 I relative to pristine glass. Chavrit et al. (2016) also demonstrated I enrichment in some clay-
786 bearing samples of altered basalt. Therefore parts of the crust could be enriched in I relative to
787 unaltered crust, both relative to Cl and in absolute terms (eg. high I and high I/Cl). Iodine could
788 be trapped in altered ocean crust preferentially relative to Cl if it is adsorbed onto clay minerals
789 (Claret et al., 2010; Montavon et al., 2014) or zeolites, which are micro-porous adsorbants.
790 Alternatively, I is a biophilic element and there is growing evidence that microbes are involved
791 in some styles of glass alteration (Alt and Mata, 2000; Fisk et al., 1998; Kruber et al., 2008;
792 Staudigel et al., 2008; Stroncik and Schmincke, 2002) and alteration of some minerals
793 (Ivarsson et al., 2008). Kruber et al. (2008) reported that palagonite formed by the bio-
794 alteration of glass can contain up to 1 wt. % organic C ($\delta^{13}C$ = -22 ‰). If the microbes
795 responsible for this alteration have an $I/C_{organic}$ similar to plankton (0.0002-0.002; Bobrov et
796 al., 2005; Iwamoto and Shiraiwa, 2012; Martin et al., 1993; Price and Calvert, 1977) this would

imply that exceptionally high I concentrations of ~2-20 ppm might be expected in biogenic palagonite.

In summary, low temperature alteration of the crust leading to hydration and formation of clays causes a finite increase in fluid salinity and some remobilisation of heavy halogens from the crust. However, because this alteration takes place at very high water-rock ratios the effects are difficult to discern in alteration fluids (section 5.4). Low temperature alteration of mafic lithologies, either by biological processes or by adsorbtion of I onto reactive minerals, might be significant for the marine I cycle (cf. Leblanc et al., 2006).

9.6.3 High temperature hydrothermal alteration

Amphibole and serpentine are usually the only minerals in which Cl (and more rarely F) can be detected by electron microprobe. Other hydrous minerals such as prehnite, pumpellyite, chlorite and epidote are assumed to contain <100 ppm Cl but remove water from the system implying that they cause a finite increase in the salinity of alteration fluids. In addition to mineral matrices, a number of minerals can be important hosts of fluid inclusions. Fluid inclusions are often estimated to account for up to 1 vol. % of the coarse minerals with abundant inclusions. If these fluid inclusions trapped fluids with average salinities and densities similar to seawater, the fluid inclusions can be estimated to contribute up to 70 ppm Cl and 250 ppb Br but negligible F or I toward the mineral's bulk composition (Table 4). In comparison, Kendrick et al. (2015b) reported bulk halogen concentrations of 100-200 ppm Cl, 300-600 ppb Br and 4-20 ppb I for fluid inclusions bearing vein minerals from the Mathematician Ridge.

819 The concentrations of F and Cl in amphiboles within the oceanic crust are extremely
820 variable ranging from concentrations of 10's of ppm Cl and 100's ppm F in igneous amphibole
821 up to wt. % levels of Cl in late-stage hydrothermal veins (Fig 17; Cortesogno et al., 2004; Gillis
822 and Meyer, 2001; Jacobson, 1975; Nehlig and Juteau, 1988; Vanko, 1986). Actinolite, present
823 under greenschist facies conditions, generally contains <500 ppm Cl (Vanko, 1986), which is
824 consistent with the concentration range of 100-300 ppm expected to result from hydration by
825 fluids with seawater salinity (Cortesogno et al., 2004; Kendrick et al., 2015b). In contrast,
826 amphibolite grade hornblendes contain hundreds to thousands of ppm Cl (Cortesogno et al.,
827 2004; Ito and Anderson, 1983; Nehlig and Juteau, 1988; Prichard and Cann, 1982; Tribuzio et
828 al., 2014; Vanko, 1986; Silantyev et al., 2008). The variability of amphibole Cl concentrations
829 under amphibolite conditions could reflect equilibration with segregated vapours and brines
830 produced by phase separation of seawater that is heterogeneously distributed through this part
831 of the crust (Cortesogno et al., 2004). Amphiboles with 1 to 6 wt. % Cl have been reported
832 from several locations but are always a volumetrically minor component of the rock, which is
833 commonly associated with late-stage veins and/or mylonites (Bideau et al., 1991; Honnorez
834 and Kirst, 1975; Jacobson, 1975; Vanko, 1986). The effect of hydrothermal alteration is to
835 introduce seawater Cl and redistribute igneous Cl and F between a growing number of
836 amphiboles. As a result, amphiboles formed during progressive hydrothermal alteration are
837 distinguished from igneous amphiboles by progressively higher Cl contents and Cl/Na ratios,
838 and lower F/Cl ratios (Fig 17; Coogan et al., 2001; Mevel, 1988).

839 Crystal chemistry exerts an important control on amphibole halogen concentration. For
840 example, the negative correlation between F/Cl and Cl in Fig 17 results in part from F and Cl
841 competing to occupy the same site in amphibole. It has long been assumed that the large Br^-
842 and I^- anions would be preferentially excluded from amphibole relative to Cl^- and F^- (Svensen
843 et al., 1999; 2001), and this has recently been confirmed by the analysis of amphibole and

844 related fluid inclusions in amphibolites and metagabbros from the Mathematician Ridge
845 (Kendrick et al., 2015b).

846 In addition to crystal chemistry, it is now generally agreed that high Cl amphiboles can
847 only form when the chemical activity of Cl is high and the chemical activity of H_2O is low,
848 such as occurs in the presence of saline fluids (Kullerud and Erambert, 1999; Markl and
849 Bucher, 1998; Vanko, 1986). Therefore, Cl-rich amphiboles do not provide a mechanism for
850 reducing fluid salinity; rather, they provide evidence for the presence of high salinity fluids in
851 the crust.

852 If phase separation is the major control on fluid salinity (Kelley and Delaney, 1987;
853 Vanko, 1988), the increase in amphibole Cl content from greenschist to amphibolite facies can
854 be interpreted as evidence for efficient segregation of brines and vapours and support for the
855 idea that brines are preferentially stored in the deeper crust (e.g. Fig 14). However, while it
856 has been recognised that crustal hydration can lead to appreciable increases in fluid salinity,
857 the effect of 'drying up' or 'fluid desiccation' on salinity has not been evaluated within the
858 context of the oceanic crust. For example, Kelley and Delaney (1987) suggest that formation
859 of hydrous minerals could increase seawater salinity by a factor of two but favoured phase
860 separation in the generation of ultra-saline brines. In contrast to this, it is well known that at
861 water/rock ratios of less than 0.1-0.01 'drying up' leads to substantial increases in the
862 concentration of all dissolved components (Reed, 1997). Furthermore, desiccation of
863 metamorphic fluids is implicated in the generation of Cl-rich amphiboles and metamorphic salt
864 in granulites in northern Norway, which provides strong evidence for the generation of ultra-
865 saline fluids (up to 100 % salt) by this process in some settings (Kullerud and Erambert, 1999;
866 Markl and Bucher, 1998). The high Cl content of amphibolite facies amphiboles can therefore
867 also be interpreted as indicating fluid/rock ratios approach zero at the limit of the seafloor
868 hydrothermal system (cf. Fig 14).

869 The relative importance of phase separation and 'drying up' might be tested in future
870 studies of Cl, Br, and I in fluid inclusions and minerals. As Br and I are excluded from
871 amphibole relative to Cl (Kendrick et al., 2015b), drying up should produce fluids with very
872 high Br/Cl and I/Cl ratios (Svensen et al., 2001). Whereas because Br/Cl does not appear to be
873 strongly fractionated by phase separation (Fig 11), phase separation might yield brines with
874 Br/Cl and I/Cl much closer to seawater values (Kendrick et al., 2015b). This line of reasoning
875 suggests that phase separation was the dominant process responsible for the generation of
876 brines in the Mathematician Ridge hydrothermal system (Kendrick et al., 2015b) and brines
877 assimilated by magmas which are all inferred to have Br/Cl ratios of only slightly higher than
878 seawater (Fig 15; Kendrick et al., 2013a; 2015a).

879

880 ***9.6.4 The bulk halogen content of the oceanic crust***

881 Sano et al. (2008) sampled core from Hole 1256D drilled in the Eastern Pacific at intervals of
882 <50 m, over more than 1000 m of core, providing high density Cl concentration data that show
883 a broad increase in Cl as a function of depth in this hole (Fig 18). Four additional studies have
884 investigated Cl and Cl isotopes in seven different cores drilled in the Pacific, Atlantic, and
885 Indian Oceans but sampling within each core is at a much lower density (Barnes and Cisneros,
886 2012; Bonifacie et al., 2007; Chavrit et al., 2016; Magenheim et al., 1995). These studies
887 show similar Cl concentration ranges as observed in Hole 1256D, in which low temperature
888 alteration has a median Cl concentration of 160 ppm and high temperature alteration has a
889 median concentration of 360 ppm Cl, but individual samples contain as little as 11 ppm or as
890 much as 2000 ppm Cl (Fig 18; Barnes and Cisneros, 2012; Bonifacie et al., 2007; Chavrit et
891 al., 2016; Magenheim et al., 1995; Sano et al., 2008). These studies indicate that the real
892 concentration of Cl in the oceanic crust is several times higher than was initially estimated (50
893 ± 25 ppm Cl) on the basis of electron microprobe data (Ito et al., 1983).

894 Unfortunately, because crustal lithologies have extremely variable Cl concentrations
895 (e.g. 200-1200 ppm Cl at 1500 m in Hole 1256D; Fig 18), the low density of data available
896 from the majority of IODP holes means that it is difficult to assess if the broad increase in Cl
897 observed with depth in Hole 1256D (Fig 18; Sano et al., 2008) is a general feature of the oceanic
898 crust (cf. Barnes and Cisneros, 2012). However, the following observations suggest that Cl
899 concentrations are likely to increase with depth: i) Cl and Br are mobilised into the fluid during
900 alteration of glass (Fig 12; Floyd and Fuge, 1982; Kendrick et al., 2015a); ii) low temperature
901 alteration minerals have very low Cl concentrations (section 9.6.2; Table 4); and iii) amphibole
902 Cl concentrations increase from greenschist- to amphibolite-facies providing evidence for
903 fluids becoming increasingly saline at depth in the oceanic crust (section 9.6.3).

904 Finally, the concentration range of Cl in pristine mid-ocean ridge glasses is contrasted
905 with the concentration range in altered oceanic rocks in Fig 19. The pristine glasses include
906 N-MORB and E-MORB and are variably evolved, with MgO mainly between 4 and 9 wt. %
907 but including some dacites from the Galapagos Spreading Centre with 1 wt % MgO. The
908 median Cl concentration of these glasses (120 ± 20 ppm) is suggested here as a proxy for the
909 'initial' concentration of Cl in layer 2 (lavas and dykes) of the oceanic crust. In contrast, the
910 presence of cumulate minerals in layer 3 gabbros implies a much lower initial concentration of
911 Cl (and other incompatible elements) in deeper portions of the crust. The suggested initial Cl
912 concentration of layer 2 (120 ± 20 ppm Cl) is just within uncertainty of the median obtained
913 for the upper portion of Hole 1256D (160^{+140}_{-50} ppm Cl; Figs 18 and 19). Considering the high
914 flux of seawater and very high water/rock ratios in this part of the crust, the lack of pronounced
915 Cl enrichment demonstrates that the dominant effect of low temperature alteration is probably
916 halogen remobilisation and exchange of halogens between seawater and the crust, rather than
917 halogen enrichment. In contrast, the median concentration of Cl in the lower portion of Hole
918 1256D (360^{+120}_{-60} ppm Cl) is probably >3-30 times higher than the initial concentration of Cl in

919 the gabbro cumulates (Fig 18). Therefore, it appears that hydrothermal alteration may mobilise
920 Cl in the upper crust and strongly enrich Cl in the lower crust (Figs 18 and 19). In contrast to
921 Cl, K exhibits the opposite behaviour, being most enriched during low temperature alteration
922 in the upper crust. Therefore, the K/Cl ratio, which is commonly used to measure relative Cl
923 enrichment, changes with increasing crustal depth and alteration much more sharply than the
924 absolute abundance of either element (Fig 18c).

925

926 ***9.6.5 Halogens in serpentinites***

927 The halogen content of seafloor serpentinites has been investigated in several studies (Barnes
928 et al., 2009; Barnes and Sharp, 2006; Bonifacie et al., 2008; Boschi et al., 2013; Debret et al.,
929 2014; John et al., 2011; Kendrick et al., 2013b; Kodolányi et al., 2012; Scambelluri et al., 2004;
930 Sharp and Barnes, 2004). Taken together the data show serpentinites contain from ~100 ppm
931 to 1 wt. % Cl, with a median concentration of 1500^{+300}_{-200} ppm Cl (Fig 20). The maximum
932 concentration of Cl in serpentine is somewhat less than amphibole, but serpentinite rocks,
933 wholly dominated by serpentine, have a higher H_2O and Cl content than any other major
934 subduction zone lithology (Scambelluri et al., 1997; Schmidt and Poli, 1998).

935 The I/Cl ratio of serpentinites is not correlated with Cl concentration (Fig 21a);
936 however, serpentinites have combined Br/Cl and I/Cl that overlap the range of sedimentary
937 marine pore waters and the serpentinites formed at the greatest distances from mid-ocean ridges
938 have the highest I/Cl ratios (Fig 22; Kendrick et al., 2013b). These data can be explained if
939 sedimentary marine pore waters, as well as seawater, are involved in serpentinisation (Kendrick
940 et al., 2013b; 2011b). Sedimentary marine pore waters could be particularly important during
941 serpentinisation at the slab bend and in the forearc (Fig 5; Ranero et al., 2003). The small
942 mismatch between serpentinite Br/Cl-I/Cl and sedimentary marine pore waters could be

943 explained in several ways. The high I and Br content of the serpentinites attests to the high
944 compatibility of all halogens in serpentine. However, it is likely that halogen abundance ratios
945 are fractionated between serpentinites and serpentinising fluids. Alternatively, if serpentinites
946 preserve Br/Cl and I/Cl ratios close to that of the serpentinising fluids, the data indicate that in
947 addition to seawater and sediment-derived halogens, some serpentinites contain an additional
948 small 'mantle' component that could be mobilised from igneous lithologies in the overlying
949 crustal rocks (Figs 22 and 23). Slab fluids with fractionated I/Cl are then required to explain
950 the highest I/Cl of 0.04 in forearc serpentinites because it is greater than observed in
951 sedimentary pore waters (Fig 22a; Kendrick et al., 2013b).

952 In contrast to I/Cl and Br/Cl, the F/Cl ratio is negatively correlated with Cl in
953 serpentinites (Fig 21b) in a similar manner to that observed for amphibole (Fig 17). It is likely
954 that the compatibility of F is at least as high as the heavy halogens in serpentine, but the
955 negative relationship between F/Cl and Cl can be explained if serpentinising fluids introduce
956 variable quantities of seawater and sediment-derived Cl, Br, and I, and relatively little F (Figs
957 22 and 23). There are very few combined F/Cl and I/Cl data available for sedimentary pore
958 waters (Mahn and Gieskes, 2001). However, the low solubility of F in sedimentary pore waters
959 (Frohlich et al., 1983; Rude and Aller, 1994) suggests F/Cl is likely to be maintained fairly
960 close to the seawater value. Therefore, the higher F/Cl of serpentinites and some hydrothermal
961 fluids, relative to seawater, probably results from mobilisation of F from igneous lithologies in
962 the crust (Fig 23).

963 The median Cl concentration of 1500^{+300}_{-200} ppm in serpentinites corresponds to a
964 H_2O/Cl weight ratio of ~80 that is greater than the seawater H_2O/Cl value of 50. Serpentinites
965 with much higher Cl concentrations are probably produced as the water 'drys up' and the
966 salinity of the serpentinising fluid increases (e.g. H_2O/Cl decreases). Kendrick et al. (2011,
967 2013b) suggested a water/rock ratio of <0.1 and that the fluid being spent during

968 serpentinisation (e.g. dried up) might be required to explain the preservation of sediment pore
969 water halogen signatures (Fig 22) and high noble gas concentrations in serpentine. However,
970 metamorphic salts produced by complete drying up (e.g. Markl and Bucher, 1998) have not
971 been identified in crushed serpentinites. The nature of the 'water soluble Cl component' in
972 serpentinites is still unclear (Kodolányi et al, 2012) and experimental studies are required to
973 determine halogen partitioning in serpentinites.

974

975 **9.7 Synthesis and future directions**

976 As shown above there are a relatively large number of data available for F, Cl, Br, and
977 I in sedimentary pore waters and hydrothermal fluids, but the data base for multiple halogens
978 in minerals within sediments and the crustal basement is much smaller. As a result, while Cl,
979 Br, and I are known to exhibit systematic behaviour in sedimentary pore waters and the organic
980 phase within unconsolidated sediment (Figs 2 and 3), the relative abundance ratios of F/Cl,
981 Br/Cl, and I/Cl and the halogen concentrations in lithified sediments are less well known.
982 Chlorine and F data, and limited Br and I data, are available for altered basalts and gabbros,
983 and serpentinites. Despite the limitations imposed by data availability, some general
984 statements about the most important lithologies and guestimates of likely concentration ranges
985 in key crustal lithologies are possible. This is undertaken below for each of the halogens in a
986 'representative crustal section' entering a subduction zone. This is undertaken for the crust
987 immediately prior to subduction, because the final state of the oceanic crust is relevant for
988 assessing possible fluxes of halogens into the deep mantle and through magmatic arcs, which
989 is a critical parameter given the role of halogens in complexing metals and facilitating trace
990 element transport in slab-derived fluids (Migdisov and Williams-Jones, 2014; Yardley, 2005).

991 The representative crustal section investigated comprises 400 m of marine sediment,
992 1500 m of layer 2 lavas and dykes, 4500 m of layer 3 gabbros, and 500 m of serpentinites (Fig
993 24). These thicknesses are based on average crust (Chen, 1992; Snow and Edmonds, 2007)
994 and a band of serpentinite, which could represent either intense local zones of serpentinisation
995 primarily formed at slow spreading centres, or 5% serpentinisation of the uppermost 10 km of
996 the lithospheric mantle formed at the slab bend (Fig 5). The degree of lithospheric
997 serpentinisation is still poorly known, and given that additional serpentinisation occurs in the
998 forearc (Bostock et al., 2002), this figure is considered a very conservative lower limit for the
999 amount of serpentinite subducted into the mantle.

1000 The existing data suggest that Cl concentrations increase with depth in the altered
1001 oceanic crust (Fig 18). However, for simplicity we assume that the upper 1000 m of the oceanic
1002 crust, which has been subjected to relatively low temperature alteration, has a median
1003 concentration of 160^{+140}_{-50} ppm Cl, and that the lower 5000 m has a median concentration of
1004 360^{+120}_{-60} ppm Cl (cf. Figs 18 and 24). It is possible that away from the subduction zones a
1005 large portion of the crust, at depths of 4-6 km, could be unaltered. However, it is assumed that
1006 at the point of subduction, fluids have penetrated the entire crustal section, which is consistent
1007 with seismic evidence for serpentinisation of the mantle lithosphere at the slab bend (Fig 5;
1008 Ranero et al., 2003) and heat flow measurements (Grevemeyer et al., 2005). In this scenario,
1009 it is likely that at increasing depths, zones of relatively unaltered crust are transected by
1010 increasingly Cl-rich zones of alteration, reflecting channelized fluid flow within deep fracture
1011 systems. This would lead to extremely variable concentrations of Cl in the deeper crust, similar
1012 to that observed in existing drill hole data and dredge samples; for example, Fig 18 shows
1013 concentrations ranging from 200 to 1200 ppm Cl at ~1200 m in Hole 1256D (Sano et al., 2008).
1014 In comparison to the oceanic crust, sediments are assumed to have a poorly defined Cl
1015 concentration of 700 ± 500 ppm (cf. Table 2; Muramatsu and Wedepohl, 1998) and

serpentinites are assigned the median value of 1500^{+300}_{-200} ppm Cl (Figs 20 and 24). These figures suggest that the subducting lithosphere could have a bulk Cl concentration on the order of 400 ppm (Fig 24). This figure is close to the median value suggested for altered ocean crust (Fig 24), and implies that due to its size, the altered ocean crust could be the largest single Cl reservoir in subducting slabs (Fig 25). However, it should be stressed that there is considerable uncertainty concerning the degree of deep-crust and lithosphere alteration, and that the relative sizes of the altered ocean crust and serpentinite reservoirs in Fig 24 could be substantially different.

In contrast to Cl, there are fewer data available for F. However, because F is mobilised over relatively short distances during alteration and is not significantly introduced by seawater, we assume the F concentration in layer 2 of altered ocean crust is similar to that of MORB. The average F concentration of MORB is estimated as 260 ± 160 ppm F, based on a F/Nd = 20 ± 12 (Workman et al., 2006) and Nd of ~13 ppm, which is 10 times the primitive mantle value (Hofmann, 2003). Serpentinites have typical F concentrations of 10-100 ppm (Debret et al., 2014; John et al., 2011), which are enriched compared to depleted mantle values of 11-16 ppm F (Pyle and Mather, 2009). We assume this F has been mobilised from overlying lithologies in layers 1-3 of the crust (Fig 23). Marine sediments are assigned a concentration of 1000 ± 300 ppm F (Fig 1; Li, 1991; Rude and Aller, 1991). These assumptions suggest that the altered oceanic lithosphere contains on the order of 100 ± 50 ppm F (Table 5). Therefore, the altered oceanic lithosphere has a F/Cl weight ratio of ~0.25 compared to ~2 for median MORB, with the difference resulting from up to ~90 % of crustal Cl being introduced by hydrothermal alteration.

The Br and I content of altered oceanic crust is poorly known. It has been suggested that low temperature clay-rich alteration could be enriched in I and have higher I/Cl than MORB, whereas high temperature amphibole alteration has Br/Cl and I/Cl of less than MORB

1041 (sections 9.6.2 and 9.6.3; Chavrit et al., 2016; Kendrick et al., 2015). If the altered oceanic
1042 crust retains Br/Cl and I/Cl within a factor of 2 of MORB, we can estimate it has ppb-levels of
1043 Br and I. In contrast, sediments and serpentinites both have extremely variable Br/Cl and I/Cl
1044 ratios with ppm levels of Br and I (Tables 2 and 5). In contrast to the altered oceanic crust,
1045 serpentinites formed in the mantle lithosphere can incorporate substantial Br and I and may
1046 even preserve the Br/Cl, I/Cl, and F/Cl ratios of the serpentinising fluids (cf. Figs 22 and 23).
1047 The small amount of data available mean that the average Br/Cl and I/Cl of the serpentinites is
1048 not known (Fig 22). However, even under the conservative assumptions made above regarding
1049 the extent of lithospheric serpentinisation (Fig 24), serpentinite rocks rich in chrysotile or
1050 lizardite have the potential to be a major reservoir of Br and I (Table 5; Fig 25). As a result,
1051 serpentinites have the potential to be an important pathway for Br and I into subduction zones,
1052 however, it has been suggested that Br and I are preferentially lost relative to Cl during high
1053 grade metamorphism and antigoritisation of serpentine meaning that Br and I are unlikely to
1054 be strongly subducted into the deep mantle (cf. Fig 25; John et al., 2011; Kendrick et al., 2011b,
1055 2013b, 2014, 2017).

1056 Further work combining the analysis of multiple halogens in hydrothermal fluids is now
1057 desirable. In particular, analysis of I in hydrothermal fluids together with Br and Cl would help
1058 confirm if hydrothermal fluids with elevated Br/Cl ratios have interacted with sediments (cf.
1059 Fig 11). In addition, it is important to improve linkages in understanding between the
1060 behaviour of halogens in hydrothermal fluids and changes in alteration mineralogy. This is
1061 required to test the range of conditions under which Br and Cl can be safely regarded as
1062 behaving conservatively. The possible importance of low temperature alteration for the marine
1063 I cycle is yet to be evaluated and further data are required for all the halogens in bulk rock
1064 samples, individual mineral phases, and fluid inclusions within the oceanic crust and
1065 lithospheric mantle. The extreme heterogeneity of alteration in the oceanic crust and

lithosphere implies a high density of data is required to identify broad trends in changing halogen concentration laterally or as a function of depth (e.g. Fig 18).

Words = 13,663

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Table 1. Halogens in seawater and the primitive mantle

	F ppm	Cl ppm	Br ppb	I ppb
Primitive mantle	25	17-20	50	7-10
Seawater	1.3	19,350	67,300	58
Seawater/PM	0.05	1070	1000-1300	6-7

Refs: Drever (1997); Elderfield and Truesdale(1980); Huang et al. (2005); preferred primitive mantle concentrations are based on unpublished data McDonough and Sun (1995) and Kamenetsky and Eggins (2012); a selection of recent estimates where summarised by Pyle and Mather (2009)

Table 2. Representative concentrations of halogens in marine sediment

	H_2O wt. %	Cl wt. %	F ppm	Br ppm	I ppm
Fluids and sediments					
Seawater	96.5	1.93	1.3	67	0.06
Pore fluids	>95	0.17-2.3	0.5-7	2-260	0.1-220
Unlithified pelagic sediments (including pore fluids)*	30*	1*	1000 ± 300	60 ± 60	30 ± 25
Lithified marine sediments		700 ± 500	1000 ± 300	12 ± 10	4 ± 3
Mineral and organic components					
Seaweed				<200 ppm	1-500
Seaweed (Kelp)				1,000-2,000	10,000
Plankton			1000 ± 500	1,000-4,000	200-300
Calcite			300 ± 200		<2 ppm*
aragonite			1000 ± 500		
Mg-carbonate			800 ± 500		
Fluorapatite			0.6-2.6		
Clay minerals	5-15	<100 ppm	1000 ± 300		(I adsorbed?)
Mn-crusts/nodules		0.6–1.1	390	28-140	100-900

References: (Baturin, 1988; Carpenter, 1969; Fehn et al., 2006; Fehn et al., 2000; Fehn et al., 2003; Gieskes and Mahn, 2007; Glasby, 1973; Glasby et al., 1978; Hein and Koschinsky, 2014; John et al., 2011; Kennedy and Elderfield, 1987a, b; Lu et al., 2008; Mahn and Gieskes, 2001; Muinos et al., 2013; Muramatsu et al., 2007; Muramatsu et al., 2001; Muramatsu and Wedepohl, 1998; Ohde and Kitano, 1980; Pyle and Mather, 2009; Rude and Aller, 1991; Tanaka et al., 2013; Tomaru et al., 2007a; Tomaru et al., 2009; Tomaru et al., 2007b; Tomaru et al., 2007c).

Table 3. Halogen signatures of fluids in the oceanic lithosphere

	Salinity	F/Cl	Br/Cl	I/Cl
Seawater	3.5	0.00007	0.0035	0.000003
Sedimentary pore fluids	1-5	0.00005-0.0002	SW*-0.014	SW*-0.04
Vent fluids	0.1-7	0.000006-0.0005	0.001-0.005	SW*-0.001
Crustal brines	10-60	<0.0001	SW*-0.005	SW*-0.00003

SW = seawater*
References are given in Table 1 and Figs 3, 11 and 14.

Table 4. Halogens and water in selected minerals of the Altered Oceanic Lithosphere

Mineral	H_2O	Cl	F	Br	I
Low to intermediate temperature[1]					
clay minerals	5-15	21-23	150-400		(adsorbed I ?)
palagonite	40-50	10's ppm		<20 ppm	50 ppb-20 ppm
zeolites	9-20				(adsorbed I ?)
Fe-hydroxides	25-40	>0.4-0.8 wt. % (?)		$D_{Br/Cl} < 1$	
High temperature[2]					
amphibole	2	<100 ppm to ~6 wt. %	<100 ppm to ~7 wt %	<0.5-2 ppm	<5-70 ppb
Wide temperature range[3]					
Carbonate			1000 ± 300 ppm (?)		<2 ppm ?
talc	5-9	400-900 (?)			
serpentine	12-14	100 ppm-1 wt. %	10-100 ppm	1-24 ppm	0.05-45 ppm
fluorapatite	0-1	1000-2000 ppm	1-3 wt. %		
Fluid inclusions – contribution to bulk Cl concentration					
1 vol. %	0.35	70-200 ppm		250-600 ppb	<1-20 ppb

References:

1 – (Kendrick et al., 2015a; Magenheim et al., 1995; Seyfried et al., 1986; Stroncik and Schmincke, 2002)

2 - (Bideau et al., 1991; Cortesogno et al., 2004; Gillis and Meyer, 2001; Ito and Anderson, 1983; Jacobson, 1975; Nehlig and Juteau, 1988; Prichard and Cann, 1982; Vanko, 1986; Kendrick et al., 2015b).

3 - (Barnes et al., 2009; Bonifacie et al., 2008; Claret et al., 2010; Debret et al., 2014; John et al., 2011; Kendrick et al., 2013b; Sharp and Barnes, 2004).

Table 5. Summary of halogens in sediments, altered ocean crust, and serpentinites

	Thickness (km)	F ppm	Cl ppm	Br ppm	I ppm
Marine sediments	0.4	1000 ± 300	700 ± 500	60 ± 60	30 ± 25
Mature/lith. seds		1000 ± 300	700 ± 500	12 ± 10	4 ± 3
AOC – layer 2	1-1.5	260 ± 160	160^{+140}_{-50}	$0.3^{+0.3}_{-0.2}$	$0.02^{+0.02}_{-0.01}$
AOC – layer 3	4.5-5	50 ± 40	360^{+120}_{-60}	0.7 ± 0.4	0.01 ± 0.01
Serpentinites	0.5	50 ± 40	1500^{+300}_{-200}	5 ± 1	1.5 ± 1.5
Bulk lithosphere	6.9	100 ± 50	380^{+140}_{-90}	3 ± 2	1.6 ± 1.5

Data from Tables 2 and 4 and Figs 1-23. AOC = Altered Ocean Crust.

Fig 1. The F content (ppm) of different types of carbonate. Mg carbonates and aragonite have higher F contents than calcite (Carpenter, 1969; Ohde and Kitano, 1980; Ramos et al., 2005; Rude and Aller, 1991; Tanaka et al., 2013).

Fig 2. Iodine in dry sediments (solid phase) and sedimentary pore waters as a function of depth. a) The top 80 cm of sediments on the Namibian Shelf that contain 2-8 wt % organic carbon are exceptionally enriched in I (Price and Calvert, 1977), but show a typical surface enrichment of I resulting from iodate adsorption (Kennedy and Elderfield, 1987a, b; Price and Calvert, 1977). b) Complex deep sediment profiles on the Nankai Trough show that deeper pore fluids have generally higher I concentrations than shallower pore fluids; this trend is seen most clearly in the top 100 m of the second profile (Muramatsu et al., 2007).

Fig 3. Chlorine, Br and I in sediments and sedimentary pore waters. a) Pore water Br/Cl versus I/Cl on a log-log scale (with linear scale inset). Pore waters define an envelope (shaded grey) extending from seawater (star) and bounded by Br/I slopes of 0.6 and 1.3 [Br* denotes seawater-corrected Br where* $Br^* = Br_{total} - Br_{seawater}$; $Br_{seawater} = 0.0035 \times Cl$ *(Kendrick et al., 2011a)]. In contrast to pore waters, the solid phase in Nankai Trough sediments has a higher Br*/I of 3 ± 1 shown by the yellow envelope. b) I/Cl versus salinity expressed as wt. % NaCl equivalent. Pore fluid chlorinity is close to seawater in most cases, but is significantly altered by the formation and destruction of gas hydrate in some locations. Note that the pore waters have been sampled from IODP drill holes on both passive and convergent continental margins (see Fehn et al., 2000, 2003, 2006; Lu et al.,2008; Mahn and Gieskes, 2001; Muramatsu et al,2001, 2007; Tomaru et al., 2009; 2007bc).*

Fig 4. Schematic diagram showing two end-member styles of oceanic crust. Penrose style homogenous oceanic crust with a well defined layered seismic structure is generated at fast spreading centres (Conference Participants, 1972; Dick et al., 2006). Crustal styles vary at slow spreading centres and may include poorly developed gabbros and dykes or a missing volcanic carapace; peridotites exposed on the seafloor are hydrated to serpentinites and the seismic Moho could represent the hydration front. The diagrams are modified after Dick et al. (2006) with permeability data from Anderson et al. (1985, 2012); Fisher (1998); and Fisher and Becker, (2000). Note that fracture permeability continues to variable and poorly defined depths (see text).

Fig 5. Schematic diagram highlighting the slab bend as an important site for deep (>20 km) fractures and hydrothermal alteration of the lithospheric mantle (see text). Note that fractures at the slab bend provide a possible pathway for sedimentary pore waters to infiltrate the lithosphere.

Fig 6. Comparison of selected elements in seawater and Hanging Garden vent fluids from 21° N on the East Pacific Rise (Von Damm et al., 1985; Li and Schoonmaker, 2003). The diagram shows that relative to the 1:1 line (dashed), most trace elements are strongly enriched in the vent fluids, but that S, F, and P are slightly depleted and Mg is quantitatively removed from the vent fluids. Note that the Hanging Garden Vent fluids have near seawater salinity and that this diagram uses a log scale meaning that small variations in concentration (e.g. a factor of 2) cannot be easily evaluated (see Fig 7).

Fig 7. Ca/Na versus K/Na weight ratios of vent fluids for which Cl and Br data are available (below). Vent fluids are variably enriched in K and Ca, relative to Na in seawater; the seawater ratios are shown by the star (Butterfield et al., 1990; Ishibashi et al., 1994; James et al., 1995; James et al., 2014; Mottl et al., 2011; Pester et al., 2012; Reeves et al., 2011; Seyfried et al., 2011; Seyfried et al., 2003; Von Damm, 2000; Von Damm et al., 1998; Von Damm et al., 1997; Von Damm et al., 2003).

Fig 8. Temperature and salinity data for selected vent fluids. Note that the data show maximum vent temperature and that most of the salinities are for end-member fluids with zero Mg. A conjugate brine and vapour pair emitted from vent F at 9° N on the East Pacific Rise is indicated (below; Von Damm et al., 1997). The data are from numerous sources (Butterfield et al., 1990; Edmond et al., 1979; Ishibashi et al., 1994; James et al., 1995; 2014; Kawagucci et al., 2011; Mottl et al., 2011; Pester et al., 2012; Reeves et al., 2011; Seyfried et al., 2003, 2011; Von Damm et al., 1997, 1998, 2000, 2003, 2005; Wu et al., 2012).

Fig 9. Phase diagrams for the binary H_2O-NaCl system. a) pressure versus temperature and b) pressure versus wt. % NaCl. Note that the approximate depth of different crustal units under hydrostatic pressure is shown and that the wt. % NaCl scale switches from log to linear at 10 wt. %. Part a shows the critical curve, L-V-S boundary that separates the vapour-salt field and the critical point of seawater estimated from 3.2 wt.% NaCl solution. Part b shows the critical curve, liquid-salt field, and isotherms that define the two phase field at selected temperatures. The effects of depressurisation are shown for 4 points (see text). Data and equations used to construct the figures are from Bischoff and Pitzer (1989) and Driesner and Heinrich (2007).

Fig 10. Phase diagrams for various binary salt systems. a) pressure versus temperature plot showing the critical curves for H_2O-NaCl and H_2O-$CaCl_2$, and the L-V-S curves for the H_2O-NaCl, K/Cl, and $CaCl_2$ systems. Note that the vapour-salt field shrinks back from a maximum size in the H_2O-NaCl system to a minimum size in the H_2O-$CaCl_2$ system. b) pressure versus molar equivalent $CaCl_2$, HCl, and $Ca(OH)_2$. The binary H_2O-$CaCl_2$ system differs to the H_2O-NaCl system in that hydrolysis occurs under high temperature - low pressure conditions (see

text). Data and equations used to construct the figures are from Bischoff and Pitzer (1989); Bischoff et al.(1996); Driesner and Heinrich (2007); Hovey et al. (1990) and Ketsko et al. (1984).

Fig 11. The halogen systematics of hydrothermal vent fluids: a) F/Cl versus Br/Cl; b) Br/Cl versus salinity; and c) I/Cl versus Br/Cl (Butterfield et al., 1990; Campbell and Edmond, 1989; Campbell et al., 1994; Edmond et al., 1979; Gieskes et al., 2000; 2002; Ishibashi et al., 2002; James et al., 1999, 2014; Kawagucci et al., 2011; Mottl et al., 2011; Oosting and Von Damm, 1996; Reeves et al., 2011; Schmidt et al., 2007, 2011; Seyfried et al., 2003; Von Damm, 1985, 1997, 1998, 2000, 2003, 2005; Wu et al., 2012; You et al., 1994).

Fig 12. Halogens in pristine glasses and their weakly altered or palagonitised counterparts from Macquarie Island and Samoa (Kendrick et al., 2012, 2015a).

Fig 13. Photomicrographs of vapour and brine fluid inclusions in a quartz vein hosted by amphibolite metagabbro from layer 3 of the crust. This sample (7-45), dredged from the Mathematician Ridge of the Pacific Ocean, has been described in detail by Vanko (1988) and Kendrick et al. (2015b). The vapour bubbles have a high degree of fill in the vapour inclusions. In contrast, brine inclusions have much smaller vapour bubbles and visible halite daughter minerals which have a bright green hue and cubic form.

Fig 14. Schematic diagram illustrating the double diffusive convection concept of Bischoff and Rosenbauer (1989). This model predicts brines are segregated from vapours and preferentially retained in deeper portions of the crust. The presence of brines may help explain some styles of alteration and Cl-rich amphiboles. The ultimate fate of the brines may be to be diluted by lower salinity fluids and flushed out of the crust, to migrate laterally and leak from ridge flanks or be assimilated by magmas (Fig 16).

Fig 15. Halogens in fluid inclusions and amphibole separated from Mathematician Ridge amphibolites and metagabbros. Fluid inclusions where analysed by crushing vein minerals (quartz and epidote) and the amphibole wall-rock in vacuum (Kendrick et al., 2015b). Note that the range of fluid inclusion compositions is very similar to the composition of brines assimilated by submarine magmas dredged from the Lau Basin, Galapagos Spreading Centre and Samoa (Fig 16; Kendrick et al., 2013a; 2015a).

Fig 16. Halogens in magmatic glasses affected by brine assimilation. a) K/Cl versus H_2O/Cl; b) F/Cl versus H_2O/Cl; c) Br/Cl versus K/Cl; and d) Br/Cl versus I/Cl (Kendrick et al., 2013a;

2015a; le Roux et al., 2006; Lytle et al., 2012; Wanless et al., 2011). The mantle field is defined by Kendrick et al., (2012, 2013a; 2014, 2015a). Brines have K/Cl and F/Cl of <0.1 (e.g. Figs. 8) and H_2O/Cl that is proportional to salinity (parts a and b). The altered ocean crust (AOC) is assumed to have low K/Cl and high H_2O/Cl based on existing data and the relatively low compatibility of Cl in hydrous minerals compared to H_2O (Ito et al., 1983; Sano et al., 2008).

Fig 17. F/Cl versus Cl concentration for amphiboles in the oceanic crust. The data of Coogan and Cullen (2009) and Cortesogno et al. (2004) were obtained by ion microprobe, whereas the data of Gillis and Meyer (2001) and Vanko (1986) are based on electron microprobe analyses.

Fig 18. The concentrations of a) Cl and b) K and c) the K/Cl ratio of whole rock samples from IODP Hole 1256D in the East Pacific is shown as a function of depth below the seafloor. The data are from Sano et al. (2008) and Barnes and Cisneros (2012) (green dots in part a). The alteration mineralogy shown on the figure is simplified. The median Cl and K concentrations of low and high temperature alteration zones, with 2σ uncertainties, are shown for comparison.

Fig 19. The Cl concentrations of pristine MORB glasses and altered ocean crust. The data define log-normal distributions that are typical of trace elements. The AOC is indicated to have twice the Cl content of pristine crust on average. Glass data include N-MORB, E-MORB, and evolved glasses from the Galapagos spreading centre that have assimilated seawater Cl (Danyushevsky et al., 2000; Kamenetsky and Eggins, 2012; Kendrick et al., 2012a, 2013a; Le Roux et al., 2002; Michael and Cornell, 1998; Saal et al., 2003; Sims et al., 2002; 2003). Altered Ocean Crust data are from Barnes and Cisneros (2012), Bonifacie et al.(2007), Floyd and Fuge (1982), Magenheim et al. (1995), and Sano et al. (2008).

Fig 20. Histogram and probability density function of serpentinite Cl concentration data. As with all trace elements, Cl tends toward a log-normal distribution, meaning the median is better defined than the mean. Data from Barnes et al (2006, 2009), Bonifacie et al. (2008), Debret et al. (2014), John et al. (2011), Kendrick et al. (2013b), Kodalanyi et al (2012), Scambelluri et al. (2004) and Sharp and Barnes (2004).

Fig 21. Halogen abundance ratios as a function of Cl concentration (ppm) in lizardite and chrysotile 'pre-subduction' serpentinites. a) I/Cl and b) F/Cl (antigorite serpentinites are not included in these plots). The data of Kendrick et al. (2013b) are differentiated the same way as in Figure 22. Additional data are from John et al. (2011) and Debret et al. (2014).

Fig 22. Br/Cl versus I/Cl for serpentinites: a) linear scale and b) log-log scale. The trend of sedimentary marine pore waters (Fig. 3), gas hydrate, MORB, and the compositions on amphibole and mica are shown for reference. Serpentinite data from Kendrick et al. (2011b, 2013b);MORB field from Kendrick et al. (2013a); mica/amphibole data from Kendrick (2012) and Kendrick et al. (2015b), see Fig 15.

Fig 23. Serpentinite F/Cl versus I/Cl data. Serpentinite data from John et al. (2011). Pore fluid data from Gieskes and Mahn (2007). Escanaba Trough high $^{3}He/^{4}He$ pore fluid data (representative of hydrothermal fluids) from Gieskes et al. (2002).

Fig 24. Schematic diagram of a representative, oceanic lithospheric cross section with estimated Cl concentrations at the point of subduction. Note that the average extent of alteration in the deep crust and lithospheric mantle are poorly defined and these figures assume significant alteration at the slab bend prior to subduction (see text for discussion).

Fig 25. Pie charts showing the relative importance of sediments, altered ocean crust and serpentinites as reservoirs for F, Cl, Br and I in the oceanic lithosphere, under the assumptions used to construct Fig 24 (Table 5; section 9.7).