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# Systematics of halogen elements and their radioisotopes in thermal springs of the Cascade Range, Central Oregon, Western USA

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## Abstract

This study quantifies the cycling of halogen elements through the Cascadia subduction zone based on the chemistry of thermal springs in the Central Oregon Cascade Range and of a mineral spring in the forearc (Willamette Valley). Considerations based on mass balances, element ratios, and <sup>36</sup>Cl/Cl and <sup>129</sup>I/I ratios suggest that halogens discharged through the thermal springs in the Cascade Range are probably derived from magma degassing. Our results indicate that <35% of the subducted Cl and <20% of the subducted Br and I could be transported through arc volcanism and the thermal springs, a considerably lower percentage than estimated for other volcanic arcs along the Pacific Rim. A likely explanation for this difference is that a large fraction of the halogens is released from the slab at shallow depths into the serpentinized sub-forearc mantle because of the relatively high temperatures in the subducting Juan de Fuca plate. The small fraction of halogens subducted to depth probably also indicates a low rate of water transport, which is consistent with the observation that the Cascade Range sub-arc mantle is relatively dry and has a low degree of volcanic vigor, compared with other arcs.

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## 1. Introduction

Large-scale release of H<sub>2</sub>O-rich fluids from subducting oceanic crust and sediments into the overlying

mantle wedge generates the partial melting that ultimately results in arc volcanism (e.g., [1–9]). Enrichment of trace elements such as boron and lithium commonly found in arc lavas is ascribed to transport of a hydrous component (either H<sub>2</sub>O-rich fluid or silicate melt) from the descending slab into the mantle wedge. Across-arc traverses indicate that the concentrations of these fluid-mobile elements decrease from the forearc to the back-arc, suggesting progressive

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release of fluids from the slab [10–14]. The release of fluids from the slab is not uniform among subduction zones and is controlled by the subduction angle and the thermal regime in the subduction zone. Whereas in relatively cold subduction zones fluid-mobile elements may be entrained to depths of at least 40 km, in relatively young and warm subduction zones (e.g., Cascadia), a large fraction of the fluid-mobile elements may be removed by forearc devolatilization [11].

There is still considerable uncertainty about the relationship between H<sub>2</sub>O and various incompatible elements during enrichment of the mantle wedge by subduction processes. In particular, little is known about the behavior of halogen elements (F, Cl, Br, and I) during subduction and the associated arc volcanism. In the past decade partitioning of halogens between aqueous fluids and magma has been investigated experimentally (e.g., [15,16]), and improved analytical techniques enabled determinations of low-level concentrations in natural samples (e.g., [17,18]). However, despite these advances and studies that have quantified some aspects of halogen systematics across subduction zones [19–23], issues such as mode of transport and partitioning between brine, vapor and melt remain unresolved.

Because halogens are rarely incorporated into minerals and have high aqueous fluid-silicate melt partition coefficients, they (especially Cl) may be the most reliable tracers for H<sub>2</sub>O cycling through the subduction zone and volcanic arc and are used as tracers for shallow magma degassing [24]. Cl discharge through thermal springs in volcanic arcs is also used as a proxy for intrusive activity and advective heat discharge [25,26].

The Cascade Range in northwestern USA provides a unique opportunity to quantify halogen cycling through the subduction zone and volcanic arc because of available data on halogen concentrations in pore fluids in the accretionary prism obtained by the Ocean Drilling Program, subducted Cl flux in sediments and altered oceanic crust [27,28], Cl flux from thermal springs along the volcanic arc [29], and extensive data regarding the structure of the Cascadia subduction zone [30,31]. The segment of the Cascade Range in Central Oregon is the most volcanically active along the 1200-km arc [32] formed by the subduction of the Juan de Fuca Plate under the North American Plate (Fig. 1). Discharge of chlorine (as HCl) and other halogen compounds from fumarolic vents on volcano summits in the region is negligible [33] and therefore, essentially all the Cl (and other halogens) transported

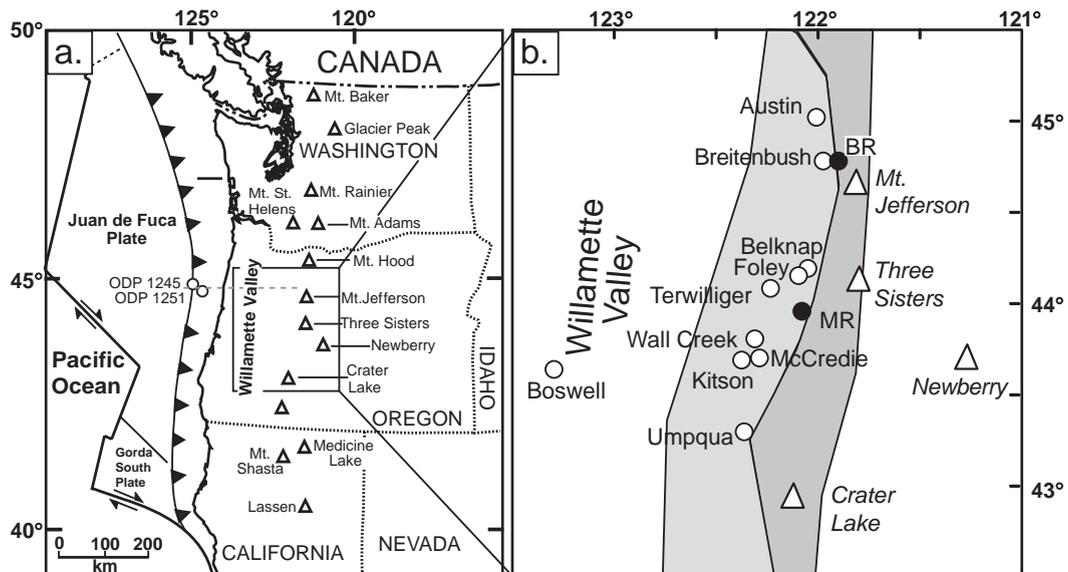


Fig. 1. (a) Location map of the study area. (a) Regional map showing the major tectonic features, the Cascade Range (grey shaded) and its Quaternary volcanoes ( $\Delta$ ), location of ODP sites ( $\circ$ ) discussed in the paper, and the location of the cross-section in Fig. 6 (dashed grey line). (b) The High Cascades (dark shaded), Western Cascades (light shaded), volcanoes ( $\Delta$ ), springs (circles), and river sampling locations ( $\bullet$ ; BR—Breitenbush River, MR—McKenzie River).

by magma is retained in erupted lava, stored in the crust, or discharged through springs [34]. Based on the Cl flux from thermal springs along this 260-km long segment of the Cascade Range (Fig. 1b), it was estimated that the advective heat transport is 148 MW, in good agreement with the estimated magma intrusion rate of  $2.3\text{--}8.6 \times 10^6 \text{ km}^3/(\text{km-arc} \cdot \text{m.y.})$  [34]. However, the actual origin of Cl in the thermal springs remains controversial. Mariner et al. [35] proposed that much of the discharged Cl is derived from sediments underlying the volcanic units, whereas van Soest et al. [36] suggested that most Cl is transported towards the surface by magmatic intrusions, based on a positive correlation between Cl concentration and He isotopes in the thermal springs.

In this study, we examine the concentrations of halogen elements and the isotopic ratios of  $^{36}\text{Cl}/\text{Cl}$  and  $^{129}\text{I}/\text{I}$  in thermal springs along the volcanic arc and a non-thermal mineral spring in the forearc (Willamette Valley) in conjunction with halogen fluxes and element ratios in the subducting slab. The goal of this study is to determine the source of the halogens, which in turn provides quantitative information on halogen cycling and other major processes within the subduction zone and volcanic arc.

## 2. Halogen systematics in natural systems

Halogen elements are all heavily concentrated in the crust [37], but are partitioned differently in crustal reservoirs. Whereas fluorine is not very soluble in water, chlorine is mainly stored in seawater [38]. Iodine is strongly associated with organic material (“biophilic”) [39] and, because of its large ionic radius, is rarely incorporated into mineral phases. Approximately 70% of the crustal iodine is found in marine sediments and less than 1% resides in the oceans, where the concentration is 56 ppb [40]. Bromine characteristics lie between those of chlorine and iodine. Its major crustal reservoir is seawater, but it is also associated with organic material, although to a lesser degree than iodine, and is enriched relative to seawater in pore fluids entrapped in organic-rich marine sediments (e.g., [41]). In volcano-hydrothermal systems, Cl and Br released from magma are considered “conservative” tracers and are expected to be enriched in groundwater, because of their high aqueous solubilities.

The concentrations of halogens in magmatic rocks increase from I (4 to 70 ppb) [40,42], to Br (50–1100 ppb) [24,38,43], to Cl and F (100–2000 ppm) [15,38]. Higher concentrations of halogen elements in magmatic rocks are usually associated with more silicic compositions [24]. Experimental data relevant for crustal pressures and temperatures indicate that halogens are highly incompatible in magmas, and partition into  $\text{H}_2\text{O}$ -rich phases. Fluorine is an exception by being highly soluble in silicate melts [15]. The distribution coefficients of halogen elements between  $\text{H}_2\text{O}$ -rich fluids and melts are strongly dependent on temperature, pressure, melt composition, and dissolved  $\text{H}_2\text{O}$  and/or halogen content of the melt (e.g., [44–47]). The coefficients increase strongly (e.g., stronger partitioning into the aqueous phase) from fluorine to iodine (e.g., [16,24,46]).

Two of the halogens have cosmogenic isotopes useful for dating and tracer studies of volcanic and geothermal fluids. The cosmogenic isotope of iodine,  $^{129}\text{I}$  (half-life 15.7 m.y.), is produced by the spallation of atmospheric Xe and by spontaneous fission of  $^{238}\text{U}$  in crustal rocks [48]. Iodine has just one stable isotope,  $^{127}\text{I}$ , and the isotope ratio of this system is given as  $^{129}\text{I}/\text{I}$ . Recent marine sediments without anthropogenic iodine have a  $^{129}\text{I}/\text{I}$  of  $1500 \times 10^{-15}$  [49,50]. The addition of anthropogenic  $^{129}\text{I}$  has increased the isotopic ratios in surface reservoirs by two to six orders of magnitude [51], and it remains at elevated levels because of the continuing release from nuclear reprocessing plants. This isotopic system has been used in investigations of sediment recycling in subduction zones [19–22], because remobilized iodine from marine sediments has a specific isotopic composition representing the age of iodine in the subducted sediments.

Chlorine has two stable isotopes,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ , and one radioisotope,  $^{36}\text{Cl}$  (half-life 0.3 m.y.). While stable isotope studies have been used for the tracing of fluid flow in subduction zones and gas hydrate deposits (e.g., [52]), the  $^{36}\text{Cl}$  system has been applied frequently in hydrologic studies, alone or in conjunction with the  $^{129}\text{I}$  system (e.g., [53]). As with  $^{129}\text{I}$ , there are three sources of  $^{36}\text{Cl}$ : cosmogenic, fissiogenic, and anthropogenic.  $^{36}\text{Cl}$  shows a pronounced bomb peak and has largely returned to pre-bomb ratios since about 1980 [54]. It can be used to indicate an anthropogenic or young (e.g., <100 ky) Cl com-

ponent in the springs or to estimate contributions of fissiogenic  $^{129}\text{I}$  in a given situation.

### 3. Geological setting

The Cascade Range volcanic arc extends from southern British Columbia to northern California, paralleling the Pacific coastline (Fig. 1a). The subducted Juan de Fuca plate is among the warmest on earth because of the young age of the plate (5–10 Ma) [55], and the thick (3–3.5 km) blanket of insulating sediments [56].

In central Oregon, the Cascade Range is 250–300 km east of the convergent margin and approximately 90 km above the top of the descending Juan de Fuca plate [30,31]. This segment of the arc consists of two physiographic and geologic provinces: the volcanic rocks of the High Cascades are <10 m.y. old and form a continuous belt with prominent stratovolcanoes extending from Mount Hood in the north to Crater Lake in the south [57,58]. Magma extrusion and intrusion rates in this segment of the arc are 3–6 km<sup>3</sup>/(km-arc · m.y.) [59] and 9–33 km<sup>3</sup>/(km-arc · m.y.) [26], respectively. Basaltic andesite flows predominate in the High Cascades, but basalt and some rhyolite are also present [58]. The second province is the Western Cascades, which range in age between 10 and 42 m.y. and consist predominately of altered basalt, andesite, and dacite lava flows [51,58].

Between the Cascade Range and the Oregon Coast range lies the Willamette Valley, a deep forearc basin filled by a thick sequence of mid-Eocene to early Oligocene sediments, most of which were deposited in a marine environment [60]. These sediments overlie the early to mid-Eocene oceanic crustal rocks of the Siletz terrane, which forms the basement of the Oregon continental shelf. Currently this forearc is being compressed arcward (N80°E) by coupling to the subducting Juan de Fuca Plate [61]. Seaward of the Siletz terrane is a well-developed accretionary prism that has formed since convergence and subduction of the Juan de Fuca plate was initiated during the late Eocene [62]. At the edge of the continental shelf, the thickness of accumulated sediment scraped from the descending plate is ~7 km, but the subducted sedimentary pile thickens to 20 km beneath the coast [30].

## 4. Chemistry of springs

### 4.1. Cascade range

The thermal springs we studied are in the Western Cascades, 10 to 40 km west of the arc crest (Fig. 1b). Spring temperature varies from 40 to 89 °C, independent of distance from the arc. Total advective heat transport by the hot spring system in this segment of the Cascade Range is 148 MW [29,34]. A significant fraction of the regional heat budget and magmatic volatiles are also discharged through weakly thermal springs along this segment of the arc [63,64].

Major element chemistry, stable isotope and gas compositions of the thermal spring waters have been published elsewhere [29,34,35]. Total dissolved solids vary from 970 mg/l (Austin) to 7300 mg/l (Umpqua), and the major element chemistry covers a wide range of compositions, with sodium as the major cation, followed by calcium and chloride as the major anion. The oxygen and deuterium isotopic composition of waters suggests that they were recharged at high elevations along the arc [26].

Nitrogen is the major gas (90–99%) in the springs (except for Umpqua with 99% CO<sub>2</sub>), and argon is the most significant minor gas, except for Austin and Belknap, which contain 3% methane, and all springs have N<sub>2</sub>/Ar values above air saturated water [35]. The  $^3\text{He}/^4\text{He}$  ratios in gases from thermal springs range from 1.2 to 6.7 R<sub>A</sub> (R/R<sub>A</sub>—ratio in sample over the atmospheric ratio) [35,36]. Larger ratios of 7–9 R<sub>A</sub> are found in weakly thermal springs with Cl anomalies located <10 km from the crest of the arc [36,64]. These larger values are within the range found in MORB glass [65]. In these weakly thermal springs, as well as in some of the thermal springs studied here, there is a positive correlation between Cl and  $^3\text{He}$  concentrations. This suggests that Cl in these weakly thermal springs, and at least 54% of the Cl discharged through the thermal springs, is of magmatic origin [36]. The  $^3\text{He}/^4\text{He}$  values decrease with increasing distance from the axis of the arc, indicating some radiogenic contribution from uranium and thorium decay [36,64].

### 4.2. Willamette valley

We also sampled Boswell Spring located on the western margin of the southern Willamette Valley. It

discharges Ca–Na–Cl waters with 29,800 mg/l total dissolved solids [66] from mid-Eocene sandstones at 13°C. Gas composition is dominated by nitrogen, but the fraction of methane (7%) is higher than any of the springs in the Cascade Range. The isotopic composition of oxygen ( $\delta^{18}\text{O} -2.1\text{‰}$ ) and deuterium ( $\delta\text{D} -8.4\text{‰}$ ) in Boswell water suggests that the source of water is local and not from high elevations in the Cascade Range.

### 5. Sampling and analytical methods

Sampling of hot springs, rivers and one well (Bigelow well) from the Central Oregon Cascade Range was carried out between 1994 and 2003. Samples were collected in 1- to 20-l plastic bottles. F, Cl, and Br concentrations were determined with a Dionex ion chromatograph at the USGS in Menlo Park, CA. I concentrations were determined with a Perkin Elmer ELAN 6000 inductively coupled plasma mass spectrometry (ICP-MS) at the USGS in Menlo Park by established methods [18] with analytical errors better than 3%.

Nine samples were selected for  $^{129}\text{I}/\text{I}$  determinations and three for  $^{36}\text{Cl}/\text{Cl}$  determinations. For these samples, I was extracted and precipitated as AgI and chlorine as AgCl, in both cases following established methods (e.g., [53]). The samples were analyzed by accelerator mass spectrometry at PrimeLab, Purdue University following established routines [67]. The

analytical error ( $1\sigma$ ) for each analyzed sample is included in Table 1.

### 6. Results

Concentrations and isotope ratios for the samples are listed in Table 1 and shown in Figs. 2 and 3. Chloride concentrations in the thermal springs of the Cascade Range vary between approximately 1000 and 3500 mg/l (Table 1). Fluoride concentrations display a poor correlation with chloride (Fig. 2a), either because it is highly reactive in the shallow hydrothermal system, and/or is less volatile in the magma [15]. Bromide and Chloride concentrations in samples from the Cascade Range correlate well (Fig. 2b), resulting in relatively uniform Br/Cl ratios which are slightly lower than in seawater, but within the range of MORB values (Fig. 3). Springs from the northern part of the arc segment have slightly higher ratios than those in the southern part. I concentrations also correlate well with those of Cl (Fig. 2c), but I/Cl is considerably higher than in seawater and overlaps the MORB values (Fig. 3).

The characteristics of Boswell Spring in the Willamette Valley are quite different. The concentrations of Cl, Br, and I in are an order of magnitude higher than those in the Cascade Range (Fig. 2b,c) and, despite the high salinity, F is below detection limit. Cl, Br, and I concentrations in Boswell are similar, slightly lower, and more than two orders of magnitude

Table 1  
Concentration of halogen elements and their radiogenic isotopes in hot springs, wells and rivers of the Oregon Cascade Range

Sample	Cl (mg/l)	F (mg/l)	Br (mg/l)	I ( $\mu\text{g/l}$ )	$^{129}\text{I}/\text{I} \times 10^{-15}$	$^{36}\text{Cl}/\text{Cl} \times 10^{-15}$
Austin	393	1.30	1.10	20		
Belknap	1330	1.20	3.60	103	$2700 \pm 1300$	$8.7 \pm 1.3$
Bigelow well	970	3.20	2.60	200	$1501 \pm 532$	$12.3 \pm 9.9$
Boswell	19,080	bdl	48.00	7004	$370 \pm 120$	
Breitenbush	1168	3.80	3.00	80	$2260 \pm 590$	$7.0 \pm 1.0$
Foley	1402	0.40	3.54	220		
Kitson	3470	2.50	7.00	390	$2100 \pm 700$	
McCredie	2245	2.50	5.00	239	$1600 \pm 700$	
Terwilliger	822	0.80	1.82	180		
Umpqua	3495	1.50	7.50	436	$2300 \pm 1100$	
Wall Creek	1210	8.60	2.70	72		
Mackenzie R.	0.59	0.02	bdl	3	$196,000 \pm 16,000$	
Breitenbush R.	0.39	0.01	bdl	4	$256,000 \pm 15,000$	

bdl—Below detection limit.

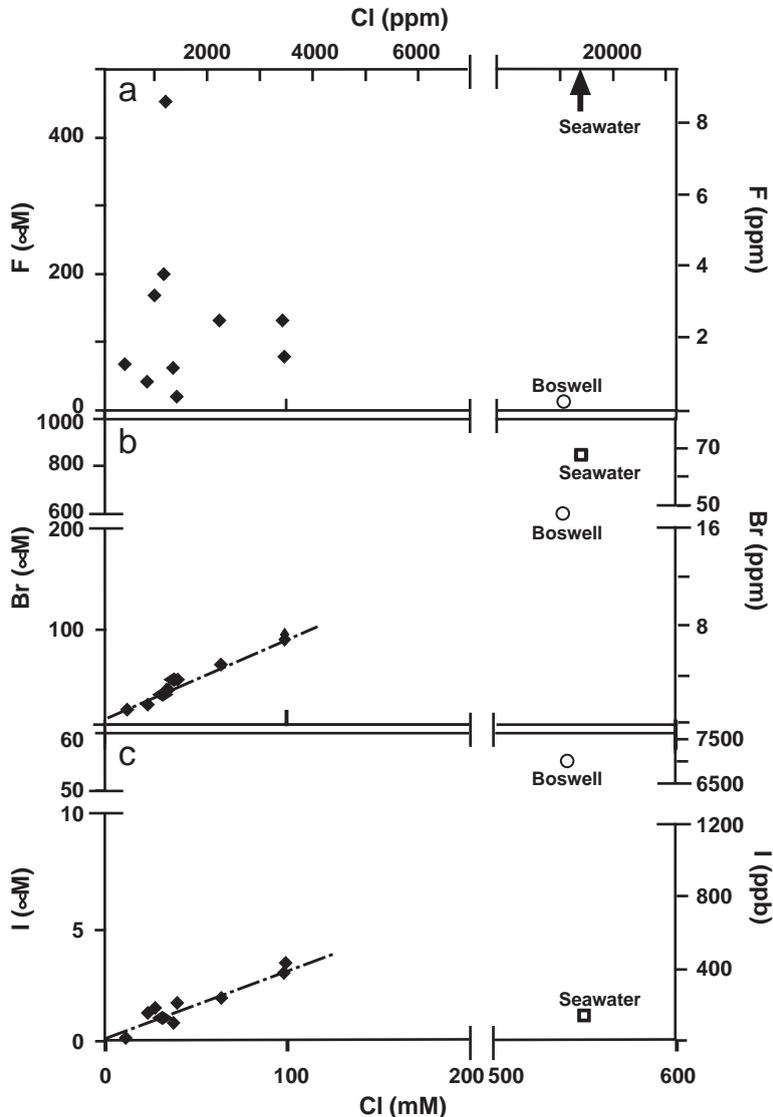


Fig. 2. Plots showing concentrations of halogen elements in thermal springs of the Cascade Range (◆), Willamette Valley (○) and seawater (□). (a) fluoride, (b) bromide and (c) iodide, versus chloride.

higher than seawater, respectively. The I/Cl ratio in Boswell is intermediate between the springs of the Cascade Range and pore fluids in the marine sediments of the Cascadia subduction zone (Fig. 3).

Despite the “biophilic” behavior of I (and Br to a lesser extent), their concentrations in the springs do not correlate well with methane concentration and  $N_2/Ar$ , which are indicators of organic-rich sedimentary units (Fig. 4). Rather, I and Br concentrations better correlate with Cl concentrations (Fig. 2b,c), suggest-

ing that the halogens are derived from the same source, probably volcanic, although some contributions from organic-rich sediments cannot be ruled out.

The concentration of I in samples from the Cascade Range is between 20 (Austin) and 436 ppb (Umpqua) and  $^{129}I/I$  ratios vary between  $1501 \pm 532 \times 10^{-15}$  and  $2700 \pm 1300 \times 10^{-15}$  (Table 1 and Fig. 5), slightly above the pre-anthropogenic level of  $1500 \times 10^{-15}$  [50]. Among the samples from the Cascade Range, there is no obvious correlation between the isotopic

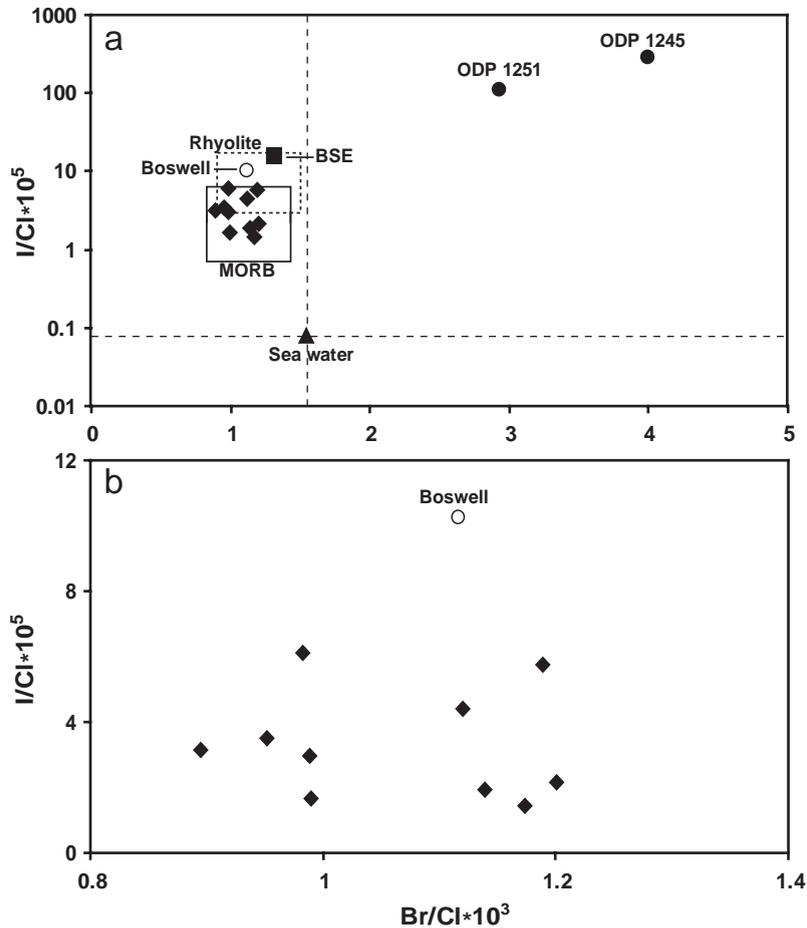


Fig. 3. Fig. 3 I/Cl ratios versus Br/Cl ratios (both molar) in samples from the Cascade Range (◆) and Willamette Valley (○). (a) Log/log plot of all samples, together with seawater (▲), Bulk Silicate Earth (■) [38], ranges for MORB (solid box) and Rhyolite (broken box), respectively [40,42,43] and interstitial water from ODP cores (●) [70]. (b) Close-up of the samples from the Cascade Range and Willamette Valley, using a linear scale.

concentration and I concentration. The sample from Boswell has a much higher I concentration (7004 ppb), and a much lower isotopic ratio ( $370 \pm 120 \times 10^{-15}$ ). The measured ratio provides an age using a standard decay equation:

$$t = \ln(R_m/R_i)/(-\lambda_{129}) \quad (1)$$

where  $R_m$  is the measured ratio,  $R_i$  the initial ratio ( $1500 \times 10^{-15}$ ) and  $\lambda_{129}$  the decay constant of  $^{129}\text{I}$  ( $4.41 \times 10^{-8} \text{ yr}^{-1}$ ). The  $^{129}\text{I}/\text{I}$  ratio for Boswell results in an age of  $32 +9/-7$  m.y. (Fig. 5). This calculated age should reflect the time since the iodine-bearing marine sediments were subducted. It is a minimum age because contribution of fissiogenic  $^{129}\text{I}$  and/or

anthropogenic sources reduces the calculated age. This calculated age is greater than the age of the subducted sediment beneath the Willamette Valley (10–12 Ma) and the age of the crust entering the trench (6–8 Ma) [55], but in range with the age of the underlying mid-Eocene marine sediments (Fig. 5).

The  $^{129}\text{I}/\text{I}$  ratios of the thermal springs in the Cascade Range should reflect the age of the slab beneath the volcanic arc (12–14 Ma) plus some additional time for transport from the slab to the ground surface. In Fig. 5, the shaded area represents the expected iodine concentrations and isotopic ratios, if all the iodine in the springs was derived from the slab. The greater  $^{129}\text{I}/\text{I}$  ratios seen in all the Cascades

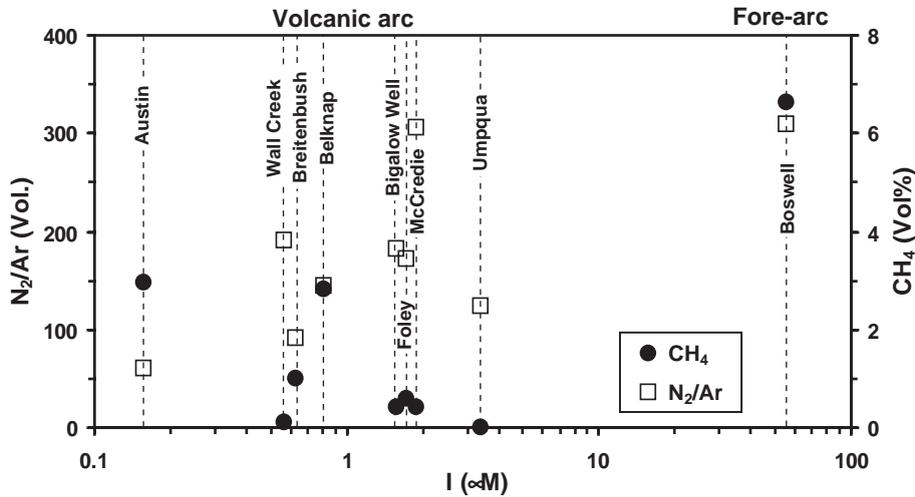


Fig. 4. Excess nitrogen ( $N_2/Ar$ ) and methane in free gas [35] versus iodide concentration in the springs.

samples could be explained either by fissiogenic contributions or anthropogenic or pre-anthropogenic sources (Fig. 5).

The  $^{36}Cl/Cl$  values are all at, or just above the detection limit of the AMS system ( $1 \times 10^{-15}$ ), which is much lower than the current ratio in precip-

itation from the area ( $250 \times 10^{-15}$ ) or pre-anthropogenic meteoric water ( $40\text{--}1600 \times 10^{-15}$ ) [54]. Thus, the low ratios in the thermal springs imply that nearly all of the discharged Cl was disconnected from the atmosphere for at least 1 Ma. The maximum possible contribution from anthropogenic or pre-anthropogenic

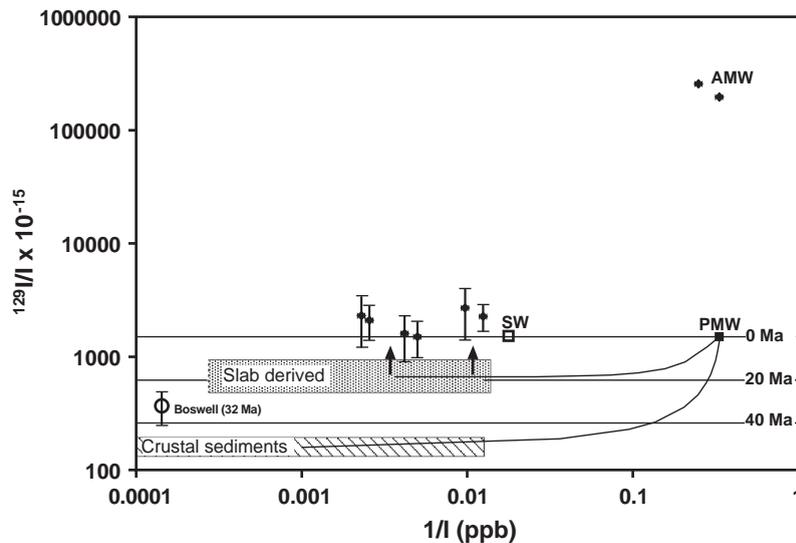


Fig. 5. Iodine isotope ratios versus the reciprocal of iodine concentration. AMW—anthropogenic meteoric water corresponding to values from the Breitenbush and McKenzie Rivers, PMW—pre-anthropogenic meteoric water [50], SW—seawater [48]. Shaded rectangle represents the expected characteristics of iodine derived from the slab beneath the volcanic arc (see text for details), diagonally hatched rectangle represents the expected characteristics of iodine derived from the  $\sim 50$  m.y. crustal sediment [60], and age contours are derived with a standard decay equation. The curves represent mixing between the slab-derived crustal sediments components with PMW, and the vertical arrows represent fissiogenic contributions.

meteoric Cl sources is  $\leq 30\%$  (Bigelow Well), assuming that these sources mix with a deep source that has a  $^{36}\text{Cl}/\text{Cl}$  of  $1 \times 10^{-15}$ . The  $^{36}\text{Cl}/\text{Cl}$  values may also be consistent with some addition of fissiogenic  $^{36}\text{Cl}$  derived from uranium and thorium decay along the transport path.

## 7. Discussion

Mass balance-considerations, halogen element ratios, and constraints from  $^{129}\text{I}/\text{I}$  and  $^{36}\text{Cl}/\text{Cl}$  provide some quantitative insights on the source of halogen elements discharged through thermal springs, and their cycling through subduction and arc volcanism. The quantitative analysis provides inference on the sub-arc mantle and volcanic processes along the Cascade Range.

### 7.1. Origin of halogens in the thermal springs

A simple mass-balance approach suggests that the underlying mid-Eocene sedimentary rocks are unlikely to be the major source for the halogens in the thermal springs. Using conservative values of a sedimentary unit with a thickness of 2 km [60] over an area of  $1.3 \times 10^4 \text{ km}^2$  ( $260 \text{ km} \times 50 \text{ km}$ ) with a porosity of 5%, that was initially saturated with seawater and has released Cl at a constant rate similar to that needed to support the current Cl discharge, it would take only 5 m.y. to discharge all the Cl. This is only a fraction of the time since active volcanism in the Cascades commenced (44 Ma). Further, the lack of correlation between I concentrations and  $\text{N}_2/\text{Ar}$  or methane concentration in the springs (Fig. 4) and the good correlation with Cl is not consistent with a deep marine sedimentary source rich in organic material.

The halogen element ratios in the thermal springs are also not consistent with a marine sedimentary source. Such a source is expected to have a Br/Cl ratio similar to or above the seawater ratio (as represented by the offshore samples in Fig. 3a), because of the biophilic affinity of bromine. In addition, if the iodine in the thermal springs was derived from the crustal marine sediments beneath the volcanics, the I/Cl ratio would probably be similar or higher than the ratio in Boswell spring. The similarity of Br/Cl and I/

Cl ratios to those measured in MORB glasses [40,42,43] may suggest that the ratio in MORB is preserved in altered oceanic crust, and that fluids migrating from the slab towards the volcanic arc maintain this ratio with insignificant modifications.

Although the  $^{129}\text{I}/\text{I}$  ratios do not provide a unique solution for the age of the iodine discharged from the thermal springs, they may be consistent with a slab-derived component mixed with minor pre-anthropogenic meteoric water and a small fissiogenic contribution (Fig. 5), consistent with the low tritium [66], and  $^{36}\text{Cl}$  concentrations. Alternatively, the  $^{129}\text{I}/\text{I}$  ratios of the thermal springs may reflect mixing between the underlying  $\sim 50$  m.y. marine sediments [60] and pre-anthropogenic meteoric water and a significant fissiogenic component (Fig. 5). However, a fissiogenic contribution is generally within the uncertainties of the age calculations, and was shown to be negligible in other subduction settings [21,22].

Leaching of volcanic rocks is probably not a major source of discharged Cl. With an extrusion rate of  $6 \text{ km}^3/\text{km-m.y.}$  [59] and Cl concentrations lower than 1000 ppm in the rocks (concentration in undegassed magmas), even complete leaching of the rock would produce a Cl flux lower than the Cl flux observed from the thermal springs.

The most probable source of Cl in the thermal springs is degassing of magma intrusions that initially have concentrations of  $\sim 1000$  ppm, consistent with the average concentration in melt inclusions trapped in picrites from Mount Shasta [68]. Assuming that magma intrusion rates and Cl discharge through springs are at some long-term steady state, and that upon ascent to the crust and cooling all the Cl is released from the magma, then intrusion rates of 9 to  $33 \text{ km}^3/\text{km/Ma}$  [26] correspond to Cl fluxes of  $7 \times 10^6$  to  $26 \times 10^6 \text{ kg/yr.}$  These fluxes are larger than the total discharge through springs ( $5 \times 10^6 \text{ kg/yr.}$ ) allowing for Cl to be retained in the magma or enriched in rhyolitic melt [69].

A volcanic origin of Cl is also consistent with the correlation between magma extrusion rate and heat flow and Cl discharge in the different segments along the entire Cascade Range [29]. The segment in Central Oregon has the highest heat flow and highest Cl flux. The high degree of correlation between  $^3\text{He}$  concentration in the free gas and Cl concentration also supports the notion that both were transported

towards the springs by magma [36]. In addition, the Br/Cl and I/Cl ratios of the Cascade Range thermal springs are within the range of MORB and rhyolite glass samples (Fig. 3a), but not in range with seawater and forearc basin values (Fig. 3a).

## 7.2. Halogen transport through the subduction zone

Previous studies showed that much more chlorine enters subduction zones than is recycled by arc magmatism [27,28], and that reflux (mainly along the decollement) may expel approximately two-thirds of the subducted water and Cl from the slab at depths <45 km [27]. We calculate Cl mass balance across the subduction zone by comparing the flux of subducted Cl with the flux of Cl through thermal springs. We expect that most of the Cl discharge from the volcanic arc is through these springs because there are no fumaroles along this segment of the arc. Elsewhere in the Cascade Range, where fumaroles are present (e.g., Mt. Hood) HCl flux is negligible [33]. If the total subducted Cl flux (sediment and altered oceanic crust) along the 260 km segment of the arc is  $2 \times 10^8$  kg/yr [see [27] for calculation details], and the total discharge of Cl through thermal springs along the segment of the arc is  $5 \times 10^6$  kg/yr [29], then only ~3% of the subducted Cl discharges via thermal springs of the Cascade Range (Fig. 6).

Assuming a maximum calculated error of a factor of two in both, the subducted Cl flux and the Cl discharge through springs, the imbalance between subducted and discharged Cl is between 1 and 11%. Further, if we assume that all subducted sediment is scraped off at shallower depths and compare only the flux of Cl subducted in the altered oceanic crust, which is 19% of the total subducted flux [27], and again assume a factor of two error in the calculated Cl discharge, then the imbalance is between 9 and 35%. The imbalance might be even greater (smaller percentage) if some of the Cl in the thermal springs is derived from the underlying crustal sediments, or leaching of rocks.

Although little is known about the distribution of Br and I in the subducted sediment and oceanic crust, some bounds can be placed on their subduction flux. By assuming that the subducted Br/Cl and I/Cl is similar to the ratios in interstitial waters in core from offshore sediment on Hydrate Ridge [70] and the thermal springs (Fig. 6), we calculate that only about 1.5% of the subducted Br and 0.5% of the subducted I are discharged through thermal springs. If Br/Cl and I/Cl in the subducted slab are similar to the ratios in MORB and in the thermal springs, and that only halogens in the oceanic crust are subducted (no sediment subduction) then 20% of the subducted Br and I are discharged through the thermal springs.

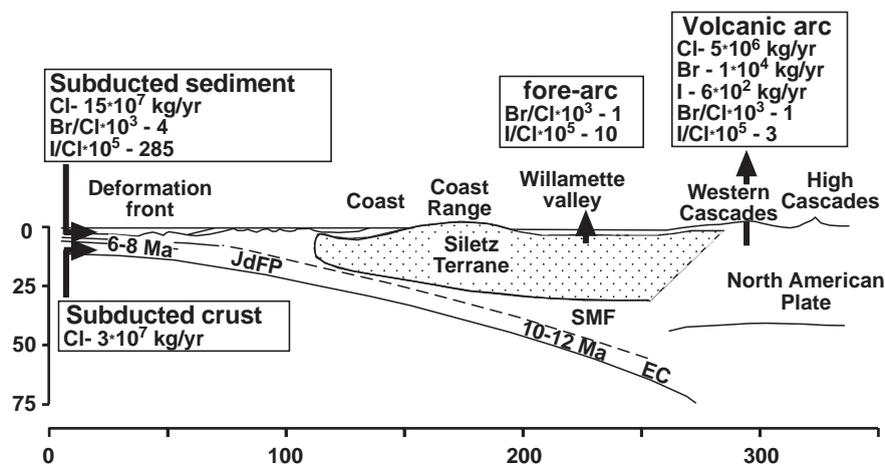


Fig. 6. Cross-section from the accretionary prism in the west to the Cascade Range in the east (location in Fig. 1a) modified from [52]. Subducted Cl fluxes are from [27] modified for arc length, and element ratios in pore fluids from the accretionary prism are from [70]. Cl flux in the volcanic arc are from [29]. JdFP—Juan de Fuca Plate, SMF—serpentinized forearc mantle, and EC—eclogitic crust [31]. Slab ages are from [55].

The halogen fluxes in the Cascade Range are smaller than typical for volcanic arcs. For example, the total Cl discharge from thermal springs along the arc segment is an order of magnitude lower than the Cl flux from fumaroles at individual volcanoes such as Masaya [71], Poas [72], Popocatepetl [73], and Fuego [74] in Central America and Satsuma Iwojima [75] and Miyakejima [76] in Japan. Iodine discharge along the arc segment (0.6 ton yr) is an order of magnitude less than the flux from individual arc volcanoes in Japan [20], Central America [21], and New Zealand [77]. Further, the iodine discharge from other volcanic arcs on Earth accounts for 1–38% of the subducted iodine [21], which in most plausible scenarios is greater than the percentage in the Cascade Range.

### 7.3. Transport from slab

The transport mechanism of H<sub>2</sub>O-rich fluids and dissolved constituents under deep slab conditions (2–4 GPa and >1000 °C) is poorly understood [7], and experimental data for halogen partitioning into an aqueous phase under these conditions are limited [78]. Nevertheless, available data on the structure of the slab, halogen partitioning into serpentinites and data from this study provide some inference for halogen subduction cycling.

In the Cascadia subduction zone, the thermal transformation of the basaltic and gabbroic sections to eclogite occurs at ~50 km depth, about 100–150 km west of the volcanic arc, where a rapid increase in slab dip occurs [31]. Models predict that significant amounts of H<sub>2</sub>O should be released at this depth, leading to serpentinization of the sub-arc mantle [79], and recent studies suggest that serpentinized mantle may be a large sink for halogens [80,81]. Based on these observations and the extremely small halogen flux through the volcanic arc, we suggest that most of the subducted halogens are released from the slab into the forearc mantle where the transition to eclogite occurs.

The above proposition is supported by the high concentrations of halogen elements and the relatively high Br/Cl and I/Cl in Boswell Spring, which is located above the serpentinized body. It is also consistent with calculated <sup>129</sup>I/I age for Boswell Spring (average of 32 Ma), which is much greater

than the age of the subducted sediment beneath the Willamette Valley (10–12 Ma) and the age of the crust entering the trench (6–8 Ma) [55]. It was suggested that it should take 10–20 m.y. to hydrate the entire forearc mantle by aqueous fluids released from the metamorphosed slab [31]. In this case, the <sup>129</sup>I/I age for Boswell Spring might represent leakage of iodine from the reservoir that began to be serpentinized during initial stages of subduction. The large discrepancy between predicted and calculated iodine ages was also found in other forearc settings [19,22], and may indicate that serpentinized mantle may be a large iodine reservoir, and may account for some of the imbalance in crustal iodine cycling [40].

### 7.4. Implication for volcanism

Compared with other volcanic arcs along the Pacific Rim, the degree of volcanic vigor in the Cascade Range appears to be relatively low [82,83]. This is expressed by the paucity of Holocene volcanoes, large volumes of basaltic andesite compared with more silicic compositions in other arcs, and the frequency of known eruptions. Thermal models [79,84] have suggested that the amount of melting in the mantle wedge is dependent on the water content, and field observations provide evidence that in young and warm subduction zones a large fraction of the fluid-mobile elements may be released in the sub-forearc region [10–12]. Our mass-balance calculations suggest that only a small fraction of subducted halogens are transported through the mantle wedge. The low transport rate of halogens probably is accompanied by a similarly low rate of water transport within the basalts and gabbros of the subducting oceanic crust of the Juan de Fuca Plate. As a consequence of this proposition, large-scale dehydration of the subducting oceanic lithosphere is likely to take place before the slab descends beneath the Cascade volcanic arc, and to limit melting beneath the volcanic arc [82].

## 8. Summary and conclusions

In this study, we used the concentrations of halogen elements and the isotopic ratios of <sup>36</sup>Cl/Cl and <sup>129</sup>I/I discharged from thermal springs along the vol-

canic arc (Cascade Range) and a mineral spring in the forearc (Willamette Valley) to show that:

1. Halogens discharged through the springs in the Central Oregon Cascade Range are mainly derived from magma degassing rather than from the underlying crustal sediments.
2. An unusually small fraction of the subducted halogens is actually transported to the surface through the volcanic arc. This fraction is smaller than in other volcanic arcs along the Pacific Rim. We relate this observation to the temperatures in the subducting Juan de Fuca plate, which are considerably higher than in other subduction zones.
3. The low rate of halogen transport to depth suggests that only a relatively small fraction of the subducted water reaches the sub-arc mantle. This may explain the observation that compared with other arcs, the sub-arc mantle is relatively dry and the degree of volcanic vigor in the Cascade Range is quite low.

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