Volatile fluxes at rifting and subduction margins: Review of results from the NSF MARGINS and GeoPRISMS programs

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The NSF MARGINS and GeoPRISMS programs have generated and applied new knowledge through community-driven interdisciplinary research on focus sites. In both programs, the role of volatiles in many aspects of the Earth system was recognized, and science plans developed through community meetings and workshops highlighted volatiles and their exchange between the Earth's interior and exterior. As a result, not only were numerous key discoveries made, but also known processes were quantified and allowed for consideration within the broader Earth science framework. Results related to volatile fluxes at subduction zones and rifted continental margins are briefly reviewed here. Research advances catalyzed through these two programs include better quantification of volatiles stored in the oceanic and continental lithosphere, the processes of hydration of subducted lithosphere and their effect on volatile transport into the mantle, quantification of carbon fluxes from continental rifts, quantification of volatile fluxes into and out of subduction zones, and the role of the forearc for volatile storage. Here we provide a short summary of some of the accomplishments regarding volatiles, with a focus on MARGINS and GeoPRISMS sites.

Introduction

The NSF MARGINS and its successor GeoPRISMS programs are type examples of a community-based approach to shoreline-crossing science. From the beginning, both of these programs highlighted the importance of volatiles with regards to magmatic processes, the geochemical evolution of the Earth's interior, and influencing the rheology that affects rates and processes on Earth. The MARGINS program drew broad attention to the notion that subduction zones are efficient recycling machines of volatiles from the subducted slab to the surface via volcanism and past the zones of arc magma generation to the Earth's interior. The site-focused and interdisciplinary nature of these programs allowed for the acceleration of discoveries and interpretations by providing geochemists with the geophysical frameworks critical for deciphering processes. The Central America, Izu-Bonin-Mariana, New Zealand, and Nankai Subduction Factory sites enabled individual Principal Investigators or small groups of investigators working on volatiles to leverage their data by taking advantage of discoveries made by groups from around the world that were attracted to the same sites because of the questions posed and the excitement of doing research in such a dynamic environment. We note that although many projects on these focus sites were not directly funded by MARGINS or GeoPRISMS, they likely also benefitted from these programs through community building workshops, meetings and accessible data. This synergy and leveraging has reached an even higher level during the GeoPRISMS program, in particular with the work on volatiles in the East African Rift and the New Zealand and Aleutian-Alaskan Subduction Zones.

Volatile storage in the lithosphere

Mantle volatile fluxes are strongly dependant on magma production rates and original mantle volatile concentrations (e.g., Fischer, 2008). A recent synthesis of these concentrations is provided by Gibson et al. (2020) and shown in Figure 1. Broadly, the volatile content of convecting mantle is relatively well-constrained from mantle melts and experimental studies (Jambon and Zimmerman, 1990; Marty, 1995; Salters and Stracke, 2004; Hauri et al., 2006; Palme and O'Neill, 2007; Gibson et al., 2020), whereas volatile contents in the continental lithospheric mantle are comparatively less constrained, especially in regions of long-lived metasomatism and volatile sequestration (Foley and Fischer, 2017; Malusà et al., 2018). For example, carbon contents in cratonic mantle could theoretically be enriched up to 100 times their original values (Foley and Fischer, 2017), due to infiltration of plume and carbon-rich silicate melts generated during mantle convection and subduction (Kelemen and Manning, 2015; Foley and Fischer, 2017; Malusà et al., 2018). Studies in the East African Rift System (EARS) reveal that carbonatite and potassium-enriched melts with high CO_2 contents occur in and around the Tanzania craton, which exhibits geophysical and petrological evidence for previous metasomatism (Rudnick et al., 1993; Koornneef et al., 2009; Mana et al., 2015; Selway, 2015). Volatiles stored within this lithosphere can be mobilized during heating and rifting (Bailey, 1980; Lindenfeld et al., 2012; Lee et al., 2016, 2017; Foley and Fischer, 2017; Hunt et al., 2017; Malusà et al., 2018).

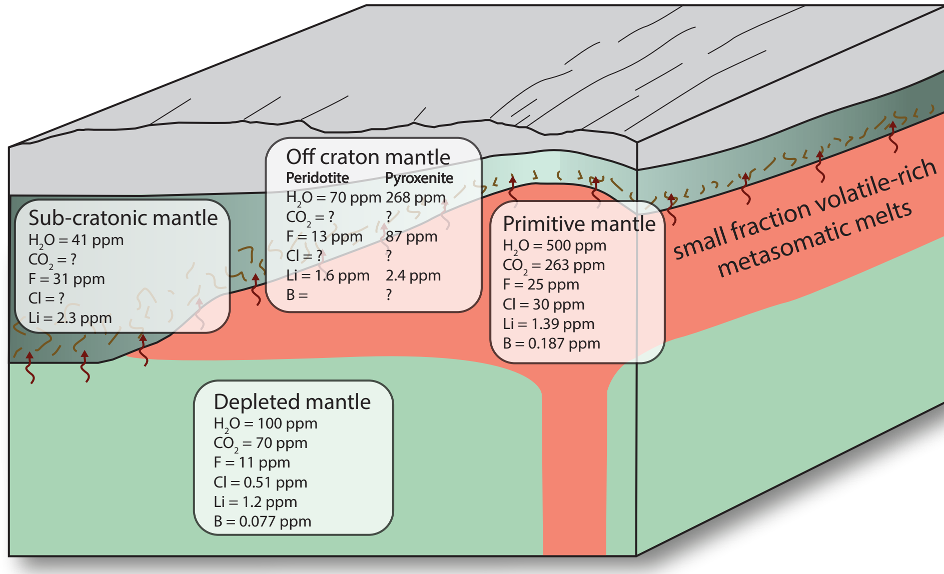

Figure 1. Block diagram slightly modified from Gibson et al. (2020) showing mantle volatile concentrations in various on- and off-craton localities. References are provided in Figure 9 of Gibson et al. (2020).

The volatile content of the oceanic crust and lithosphere evolves in response to magmatism and hydrothermal circulation near the mid-ocean ridge, off-axis circulation of seawater, and by faulting and hydration at the outer rises of subduction zones. The upper oceanic mantle is generally thought to be relatively depleted in volatiles due to melt extraction at the mid-ocean ridge, with important implications for viscosity (e.g., Hirth and Kohlstedt, 1996). Hydrothermal circulation near the ridge axis leads to the formation of hydrous minerals in the upper crust (e.g., Alt, 1995) at all spreading rates. Deeper circulation in the lower crust at fast-spreading ridges has been suggested (e.g., Hasenclever et al., 2014) but remains controversial. At slow-spreading ridges, faulting and exposure of the lower crust and upper mantle enables more pervasive hydration of the crust and upper mantle than at fast-spreading ridges. The extent of off-axis circulation is proposed to be controlled by the sediment cover, spreading rate and thermal structure of the oceanic crust (e.g., Alt, 1995; Gillis et al., 2015). Increasing seismic velocity of the upper crust with age is likely caused by the precipitation of hydrous minerals in pore-space; the most rapid reduction is observed in the first ~10-16 million years (e.g., Nedimovic et al., 2008), but could continue for much longer (e.g., ~60 million years, Kardell et al., 2019; Estep et al., 2019). On- and off-axis hydration also vary along-strike (e.g., across transform faults, Roland et al., 2012).

Just prior to subduction, the incoming oceanic plate is flexed as it approaches the trench axis and begins its descent. The associated bending stresses are often large enough to generate a network of densely spaced normal faults at the outer rise (e.g., Naliboff et al., 2013). Peacock (2001) was one of the first to hypothesize that these faults may act as fluid conduits for seawater to infiltrate and hydrate the oceanic mantle, sparking wide interest in this topic during the initiation of the MARGINS program. Active-source seismic and electromagnetic imaging studies at the Central America focus site have since confirmed that bending faults do indeed penetrate into the lithosphere (Ranero et al., 2003), drive fluids into the crust (Naif et al., 2015), and likely hydrate the uppermost mantle (Ivandic et al., 2008, Van Avendonk et al., 2011). This final stage of hydration has the potential to significantly increase the amount of volatiles transported by subducting oceanic plates (Rüpke et al., 2004; Hacker, 2008). Different scales of imaging this hydration process in the incoming plate are shown in Figure 2.

Studies at MARGINS and GeoPRISMS sites also revealed significant along-strike variations in hydration that often correlated with processes occurring downdip within the subduction zone (e.g., intraplate seismicity rates and arc chemistry) where the slab volatiles are eventually released via dehydration reactions (e.g., Van Avendonk et al., 2011; Shillington et al., 2015; Canales et al., 2017; Fujie et al, 2018). Because active-source seismic methods are often limited in their depth-sensitivity and typically image only the uppermost mantle, the availability of new offshore broadband seismic data along subduction margins provides critical constraints on the deeper parts of subducting oceanic plate, as in the case of the Marianas where extensive hydration is observed ~25 km into the mantle (Cai et al., 2018, Fig. 2C). This has global implications on the magnitude of water and carbon that are exchanged and recycled between the surface and deep mantle.

Forearcs may also be important stores of volatiles delivered into the subduction zone by subducting sediments and oceanic lithosphere. Many studies point to higher volatile fluxes and storage in the shallow forearc than previously thought (e.g., Kastner et al., 2014; and references therein). Hydrocarbons are also generated and transported with fluids expelled from subducted sediments and are often stored as seafloor gas hydrates beneath forearcs (e.g., Barnes et al, 2010). In addition to being a potential energy resource, constraining the formation and distribution of hydrates has broad applications for forearc hydrogeology and associated regional hazards to global climate predictions (e.g, Torres et al., 2004; Collett et al., 2010; Johnson et al., 2019). The forearc mantle wedge is often thought to be a major store of volatiles dehydrated from the subducting plate trenchward of the arc (e.g., Hyndman and Peacock, 2003), although recent studies have questioned the extent of hydration in all but the warmest subduction zones (Abers et al., 2017). Such revisions are critical since they change the overall slab volatile budget transported beneath the arc, back-arc and beyond.

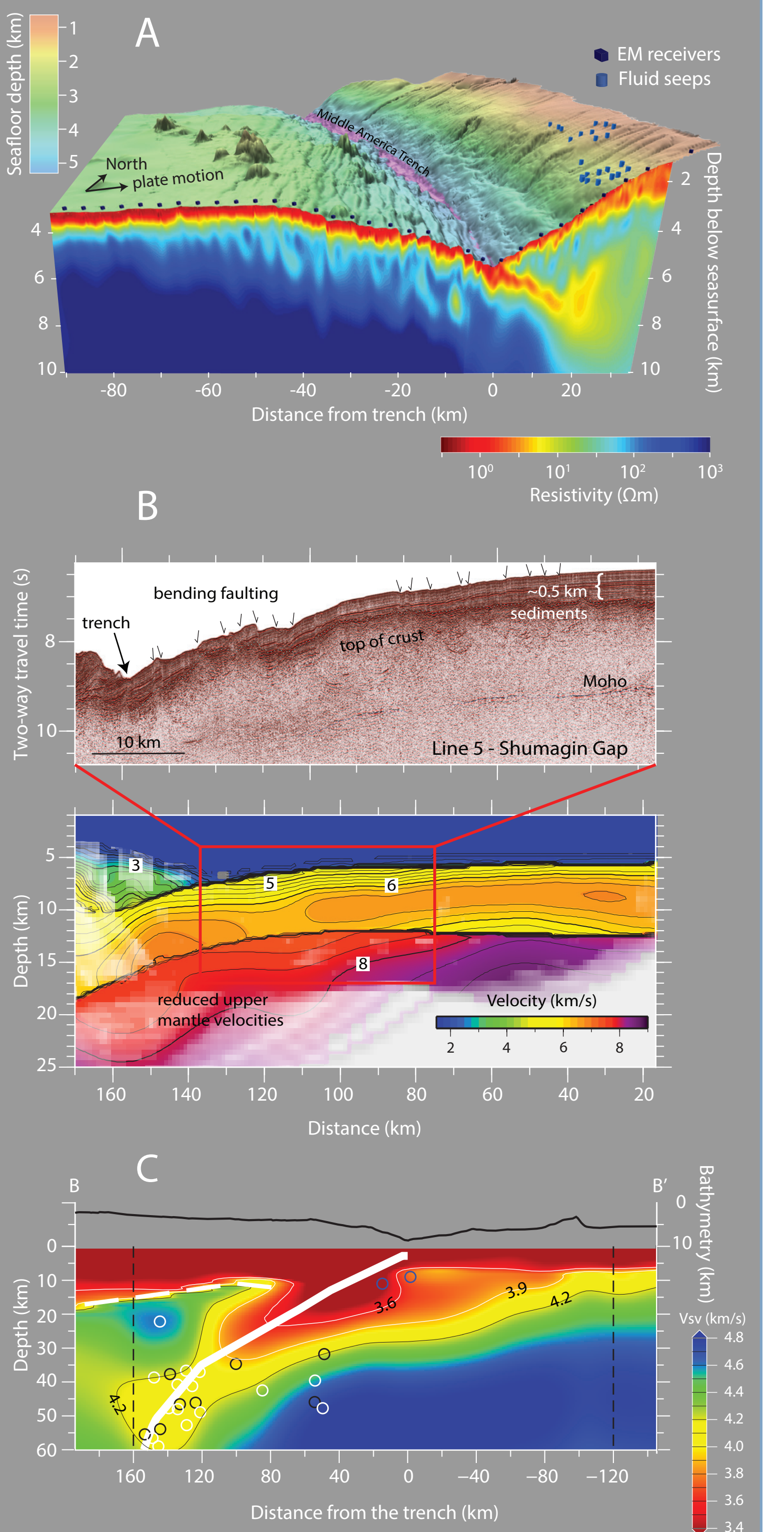

Figure 2. Bending of the incoming plate has been recognized to result in faults that drive fluids into the crust and even the mantle below. Panels shows geophysical imaging of this process at different scales. Panel A shows imaging of conductive zones inferred to arise from fluids along faults in the upper crust for the Central American subduction zone (Naif et al., 2016). Panel B shows seismic reflection imaging of bending faults (upper panel) and reduced P-wave velocities in the upper mantle interpreted to arise from hydration outboard of the Alaska subduction zone (Shillington et al., 2015). Panel C shows reduced shear wave velocities continuing >20 km into the mantle for the Mariana subduction zone, interpreted as evidence for deep hydration (Cai et al., 2018).

Another potentially important store of volatiles are magma-poor rifted margins, where seawater can penetrate to the upper mantle once the crust is thinned enough to be entirely brittle (e.g., Pérez-Gussinye and Reston, 2001). At these settings, reduced upper mantle velocities interpreted to result from serpentinization are widely observed (e.g., Dean et al., 2000; Funck et al., 2003), and the inferred degree of mantle hydration correlates with faulting (Bayrakci et al., 2016).

Subduction zone volatile fluxes

Given the complexities of volatile storage that were constrained through recent studies, particularly at MARGINS and GeoPRISMS sites, new and more realistic volatile inventories and recycling budgets are still emerging to date. It has been long recognized that subduction zones are efficient recycling machines of volatiles from the Earth's surface to its interior. Allard (1983) was one of the first to propose this, based on the stable isotope composition of volatiles measured in volcanic gas emissions, a significant proportion of these elements (H_2O, C, S, N) may come from the subducted slab. Work by Alt et al. (1993) and Alt and Teagle (1999) showed how much sulfur and carbon can be stored in the subducted crust (i.e., sediments and altered igneous oceanic crust). The global compilation of subducted sediment compositions by Plank and Langmuir (1998) provided firm trace element evidence that subducted slab components are recycled in to arc magmas (Plank and Langmuir, 1993), allowing researchers to place constraints on the amount and composition of materials delivered to zones of arc magma generation and beyond. This framework provided the basis for an early global and arc-by-arc estimate of volatiles delivered to zones of arc magma generation (Hilton et al., 2002), utilizing experimental work that assessed volatile retention and release during subduction (Schmidt and Poli, 1998). These early investigations have been improved upon with new volatile data from oceanic drilling (Li et al., 2007), the assessment of additional volatile components (Barnes et al., 2019), the quantification of depth-dependant release of water from the slab (van Keken et al., 2011), the realization that mass transfer from the slab directly leads to the oxidation of the mantle wedge (Kelly and Cottrell, 2009) and new insights on how volatiles are transported from the slab to the surface (Kelemen and Manning, 2015). MARGINS- and GeoPRISMS-supported work led to key insights and global quantifications of volatile cycling and transport into the deep mantle, summarized in Wallace (2005), utilizing work from melt inclusions and later by Dasgupta (2013) showing how volatile cycles evolved through Earth's geologic history. More recent summaries provide new and critical insights on the storage, release and transport of carbon from the subducted slab (Kelemen and Manning, 2015; Plank and Manning, 2019).

In particular for carbon, it was recognized early on that a large portion of carbon emitted by arc volcanoes was sourced from the subducted slab (Marty and Jambon, 1987; Marty et al., 1989; Sano and Marty, 1995). However, it was work by Sano and Williams (1996) that first utilized the actual volcanic arc outputs (Marty et al., 1989; Williams et al., 1992), in combination with volatile provenance, to discriminate between the volumetric contributions of the mantle wedge and subducted slab. They also compared these values to mid-ocean ridge and plume emissions. Around the same time Giggenbach (1992) and Taran (1992) argued that much of the water coming out of volcanoes is magmatic, not meteoric water, and sourced from the subducting slab, coining the term "andesitic water". This caused an uproar in the geochemistry community, who mostly believed the gospel of Harmon Craig's meteoric water-dominated steam discharges, based only on low temperature and mostly continental gases that were indeed mainly surface water (Craig, 1963). For nitrogen, it was Matsuo et al. (1978), Kiyosu (1986) and then Kita et al. (1993) who first showed, again with gases from Japan, that N_2 is sourced primarily from the subducting slab, contrasting with the notion that all nitrogen in volcanic gases is essentially air-derived. The next logical step was to combine what we knew about subduction inputs, volcanic gas outputs and the sources of these gases to test whether the amount supplied by subduction explained the volumetric outputs of a single arc volcano (Fischer et al., 1998). Around this time, researchers expressed the need for more rigorous and systematic approaches to address hypotheses surrounding subduction zones and geochemical cycles, which were tackled through community-based research as part of the NSF MARGINS program.

Research in the Central American Arc led to major advances in our understanding of transport of slab-derived carbon beyond zones of arc magma generation (de Leeuw et al., 2007; Shaw et al., 2003; Snyder et al., 2001), the first quantification of emissions of CO_2 in the forearc (Furi et al., 2010), recycling of nitrogen from the slab back to the surface (Elkins et al., 2006; Fischer et al., 2002; Snyder et al., 2003; Zimmer et al., 2001) and chlorine isotopes as slab tracers for serpentine-derived fluids (Barnes et al., 2009). Some of these early studies were complemented and expanded through later interdisciplinary studies that highlighted the importance of biological processes for CO_2 uptake in the forearc (Barry and al., 2019) and new insights into the role of the incoming plate for the nitrogen budget (Lee et al., 2017). Mass balance approaches relied heavily on off-shore studies constraining subduction inputs through ocean drilling (Li and Bebout, 2005) and stood in contrast to work utilizing volatile elements measured in metamorphic rocks and phase relations that provided a transport process-based approach to understanding subduction zones (Busigny et al., 2003). These studies were on-going whilst other groups utilized trace elements (Patino et al., 2000; Walker et al., 2003) and melt inclusions (Sadofsky et al., 2007) to constrain sources and recycling efficiencies that built on early work that unambiguously identified a young subduction component in arc magmas (Morris et al., 1990).

Like in Central America, the Izu-Bonin-Mariana focus site offered the opportunity to study volatile cycles. Here, gas studies (Mitchell et al., 2010) were performed in tandem with petrological studies focusing on melt inclusions and radiogenic isotopes (Kelley et al., 2002; Kent and Elliott, 2002; Shaw et al., 2008), which built on early work on fluid transport processes constrained from radiogenic isotopes and trace elements in the region and elsewhere (Gill et al., 1993; Gill and Williams, 1990; Lin et al., 1990), and benefitted greatly from off-shore drilling data of subducted slab compositions (Li et al., 2007; Sadofsky and Bebout, 2004).The Izu-Bonin-Mariana focus site led to new insights into the redox budget of the mantle wedge and showed that oxidizing slab fluids significantly elevate the oxygen fugacity of the mantle wedge (Brounce et al., 2019). This work furthermore showed that much of those oxidizing phases are transported into the deeper mantle where they may contribute to the oxidation of Ocean Island Basalts.

The framework of investigating volatile recycling through subduction zones, that was to a large extent set during the MARGINS program, was taken to a new level of collaboration by targeted expeditions to the Aleutians Volcanic Arc in 2015, where joint USGS-NSF-DCO-funded scientists sampled rocks and volcanic fluids on volcanoes along the entire chain. New air-borne sample collection and ship-based isotope analyses were utilized (Fischer and Lopez, 2016). As these results emerge, volatile emissions and sources of Alaska-Aleutian volcanoes are being constrained (Lopez et al., 2017) and better quantitative constraints on the sources of carbon in volcanic arcs are becoming apparent (Lopez et al., 2019). Within the framework of the role of water for generating Aleutian magmas (Zimmer et al., 2010), it is now recognized that high oxygen fugacities can drive Fe-depletion and calc-alkaline differentiation trends (Cottrell et al., 2020). The New Zealand focus site, which includes the Hikurangi Trench and the Taupo Volcanic Zone, is providing details on volatile cycling through the forearc. With the application of a combination of isotopic tracers (Cl, Li, B), this site is providing unprecedented constraints on the role of the fluid permeability of the upper plate (Barnes et al., 2019). Likewise, in the Cascadia subduction zone, the role of subduction fluids in affecting the major and trace element compositions and oxygen fugacities of erupted arc magmas has been elucidated in detail by Rowe et al. (2009), with global implications for the significance of subducted fluids for arc magma genesis. The most recent compilation of global volcanic volatile fluxes that encompasses much of the work started during MARGINS and continued through GeoPRISMS and the Deep Carbon Observatory is from Fischer et al. (2019) and summarized in Table 1.

As volatiles are subducted, they have a profound influence on processes throughout the subduction zone, from slip behavior on the megathrust to arc magmatism. For example, data from several MARGINS and GeoPRISMS focus sites suggest that fluid pressure conditions may influence slip behavior along the megathrust at a range of depths (e.g., Bangs et al., 2015; Naif et al., 2016; Han et al., 2017, Li et al., 2018, Barnes et al., 2019; Audet et al., 2009), again highlighting the value of targeted cross-disciplinary studies. Recent geophysical imaging and numerical modeling studies, together with constraints from petrology, are also beginning to elucidate the pathways of volatiles from the slab to the arc (e.g., Wilson et al., 2014; McGary et al., 2014; see Fig. 3), which strongly depends on the permeability and viscosity of the mantle wedge.

	CO_2 (Tg/y)	SO_2 (Tg/y)	CO_2 (10^9 mol/yr)	SO_2 (10^9 mol/yr)	H_2O (10^9 mol/yr)	HCl (10^9 mol/yr)
ARCS						
South America	6.44	7.81	146	122	1680	7
Central Am. + Mex	4.14	2.05	94	32	3759	14
Alaska + Aleutians	1.66	0.72	38	11	1407	17
Kamchatka+Kuriles	4.28	2.18	97	34	5117	25
Japan	2.79	1.53	63	24	18243	72
IBM	1.07	1.07	24	17		
PNG	5.40	3.01	123	47	1958	13
Indonesia	7.55	2.56	172	40	2739	19
Philippines	1.10	0.27	25	4	400	3
Lesser Antilles	1.43	0.47	33	7		
New Zealand	0.87	0.15	20	2		
N and S Vanuatu	7.77	4.5	177	70		
Scotia	0.79	0.15	18	2		
Italy	3.76	0.81	86	13	619	3
Total ARC	49.06	27.28	1115	426	35923	173
Continental RIFT						
Congo	1.00	1.29	22.66	20.16	60.56	0.22
Tanzania	0.29		6.64			
Yemen	0.16	0.04	3.64	0.59		
Ethiopia		0.02				
Antarctica		0.02				
Total RIFT	1.45	1.37	32.93	20.74	60.56	0.22
PLUMES						
Iceland						
Galapagos	0.14	0.01	3.27			
Hawaii	1.16	1.83	26.33	28.62	17.09	0.23
Reunion	0.04	0.09	0.80	1.33		
Total PLUME	4.24	4.67	96.27	71.45	17.09	0.23

Table 1. Global fluxes of major volatiles from subaerial volcanoes from Fischer et al. (2019).

Continental rifts and mid-ocean ridges volatile fluxes

Mid-ocean ridges

The global mid-ocean ridge system represents the largest plate boundary on Earth, with an estimated total length of ~57,000 km (Gale et al., 2013; Burley and Katz, 2015; Wong et al., 2019). Globally, it is the dominant region of magma production and associated heat loss. Recent estimates of magma production rates are based on measured crustal thicknesses and observed spreading rates (e.g., Le Voyer et al., 2019), or numerical model simulations of mantle melting during sea-floor spreading (e.g., Keller et al., 2017), with estimates varying from 16.5 $km^3\ yr^{-1}$ to 22 $km^3\ yr^{-1}$.

Direct measurements of volatile outgassing at mid-ocean ridges are largely prohibited, and thus global estimates of volatile discharges consider magma production rates within the context of estimated mantle volatile contents and dissolved magmatic gases (e.g., Marty and Tolstikhin, 1998; Fischer, 2008; Keller et al., 2017; Le Voyer et al., 2019). Volatile fluxes commonly examined at mid-ocean ridges include H_2O, SO_2, H_2S, CO_2, CH_2, N_2, Cl, and F (Fischer, 2008). Estimated volatile fluxes from arc volcanoes typically exceed those of mid-ocean ridges; for example, recent estimates of sulphur fluxes from mid-ocean ridges are seven times less than those from arc volcanoes (Kagoshima et al., 2015). Deep carbon released from the global mid-ocean ridge system (MOR) is arguably the most critical volatile component, as it has important implications for understanding climate in deep time. The solubility of CO_2 in basaltic magma is low compared to other volatiles (e.g., Dixon and Stolper, 1995; Jendrzejewski et al., 1997; Shishkina et al., 2010), and thus nearly all magmas erupted at mid-ocean ridges have degassed the majority of their original carbon. Deep carbon flux estimates are thus based on known $CO_2/^3He$ combined with MOR ^3He fluxes or trace elements ratios (e.g., CO_2/Ba) combined with numerical modelling of sea-floor spreading (e.g., Marty and Tolstikhin, 1998; Resing et al., 2004; Shaw et al., 2010; Burley and Katz, 2015; Keller et al., 2017). Estimates for deep carbon fluxes from mid-ocean ridges developed in the last decade typically vary between 10 and 40 Mt yr^{-1}, with an average value of ~21 Mt C yr^{-1} (see compilation by Wong et al., 2019, Plank and Manning 2019). All other volatile fluxes from MOR are usually linked to MORB magma production rates through ratios with trace elements (Le Voyer et al., 2019) or other volatiles, usually ^3He (Marty and Tolstikhin, 1998). Therefore, accurate magma productions rates remain a key parameter for quantification of volatiles fluxes at MOR as well as continental rifts, discussed in the next section.

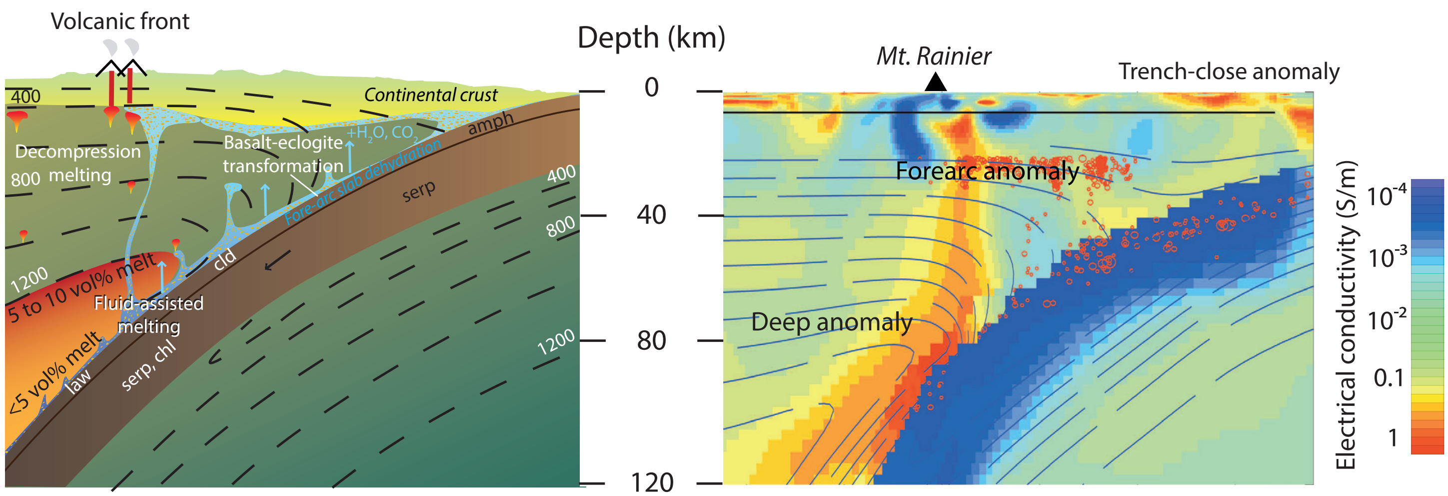

Figure 3. Comparison of a schematic representation of a subduction zone on the left with a geophysical image of electrical conductivity from Cascadia on the right (McGary et al., 2014), from Pommier and Evans (2017). When combined with petrology, the geometry of the high conductivity anomaly constrains slab fluid sources and the flow path of mantle melts and fluids to the arc and forearc.

Continental rifts

Continental rifts represent the other common divergent plate boundary on Earth, which, in some cases, can evolve to the point of complete lithospheric rupture and initiation of sea-floor spreading (Dunbar and Sawyer, 1989; Whitmarsh et al., 2001; Ebinger, 2005; Corti, 2009). The cumulative length of continental rifts globally is a maximum of ~15,000 km (Brune et al., 2017; Wong et al., 2019). Estimating magma production rates from this global rift system is problematic, given that a significant volume of magma is intruded within the lower crust (Coffin and Eldholm et al., 1994; Thybo et al., 2000, 2009; Keir et al., 2009; White et al., 2008), particularly during early rift stages (Ebinger et al., 2017; Roecker et al., 2017; Weinstein et al., 2017). Furthermore, crustal magma additions likely vary over many orders of magnitude between different continental rift systems, and are shown to vary between basins along individual rift systems, including in the Gulf of California, East Africa Rift System and Eastern North American Margin (e.g., Lizarralde et al, 2007; Shillington et al., 2009; Franke, 2013; O'Donnell et al., 2015; Ebinger et al., 2017; Accardo et al., 2017, 2020; Keranen et al., 2004; Shuck et al., 2019; Lau et al., 2019; Marzen et al., 2020).

Despite these variations, recent geophysical studies in the some parts of the apparently magma-poor Western Branch of the EARS support the presence of minor magmatic additions in the lower crust (e.g., Lake Tanganyika; Hodgson et al., 2017), and a number of magmatic provinces are situated within transfer zones between major rift segments (e.g., the Virunga, South Kivu and Rungwe Provinces; Furman, 2007; Corti et al., 2004; Wauthier et al., 2013). A recent compilation of erupted products of the Kenya Rift of the EARS reveal eruption rates of 7.2 km^3 kyr^{-1} since 5 Ma (Guth, 2015). Modelled cumulate proportions of erupted products in Ethiopia suggest that intrusive volumes in the Eastern Branch are 3-5 times greater than erupted volumes (Hutchison et al., 2018), suggesting magma fluxes between 28.8-43.2 km^3 kyr^{-1} when applied to the Kenyan example. These data crudely support magma flux rates ranging 48-72 km^3 km^{-1} Myr^{-1} across the ~600 km-long Kenya Rift and 0.1-0.14 km^3 yr^{-1} for the Eastern Branch, when extrapolated ~2000 km from Erta Ale (Ethiopia) to the northern end of the Manyara basin (Tanzania).

Although magma fluxes in the EARS are lower than mid-ocean ridges, volatile fluxes (particularly mantle CO_2) are comparatively high. Active rift volcanoes, such as Nyiragongo, exhibit estimated SO_2 and CO_2 fluxes of 1.2 and 3.4 Mt yr^{-1}, respectively (Sawyer et al., 2008), and Oldoinyo Lengai volcano emits an estimated 2.42 Mt yr^{-1} of CO_2 (Brantley and Koepenick, 1995), although this high number has recently been revised to 0.3 Mt/yr to reflect more recent estimates (Fischer et al., 2019). Geophysical studies in the Eastern Branch of the East African Rift also provide evidence for significant magma volumes trapped in the crust and upper mantle away from these volcanic centers (Mechie et al., 1994; Keranen et al., 2004; Kendall et al., 2005; Roecker et al., 2017; Plasman et al., 2017). These magma bodies, which likely tap an enriched subcontinental lithospheric mantle source in Kenya and Tanzania (Halldórsson et al., 2014; Mana et al., 2015; Lee et al., 2017), provide a potential source for massive CO_2 emissions (Foley and Fischer, 2017; Malusà et al., 2018). Recent diffuse degassing and geophysical observation studies in the EARS suggest this exsolved CO_2 is transported along the pervasive extensional fault systems (Lindenfeld et al., 2012; Hutchison et al., 2015; Lee et al., 2016; Hunt et al., 2017; Roecker et al., 2017; Weinstein et al., 2017), resulting in an estimated mantle CO_2 release of ~20 Mt yr^{-1} (Hunt et al., 2017) or even up to ~ 70 Mt/yr (Lee et al., 2016). Similar geophysical and geochemical observations from the Eger and Rio Grande Rifts support significant CO_2 discharges along rift faults (Geissler et al., 2005; Smith, 2016; Tamburello et al., 2018; Kämpf et al., 2019). Global estimates of deep carbon fluxes from continental rifts are 2.5 ± 2.0 kt C km^{-1} yr^{-1}, compared to an estimated 0.37 ± 0.23 kt C km^{-1} yr^{-1} for mid-ocean ridges (summarized and compiled in Wong et al., 2019). CO_2 from extrusive and intrusive magmatism associated with continental rupture may contribute to environmental changes and biotic crises, such as the Triassic extension following the Central Atlantic Magmatic Province (e.g., Marzoli et al., 2018 and references therein; Capriolo et al., 2020).

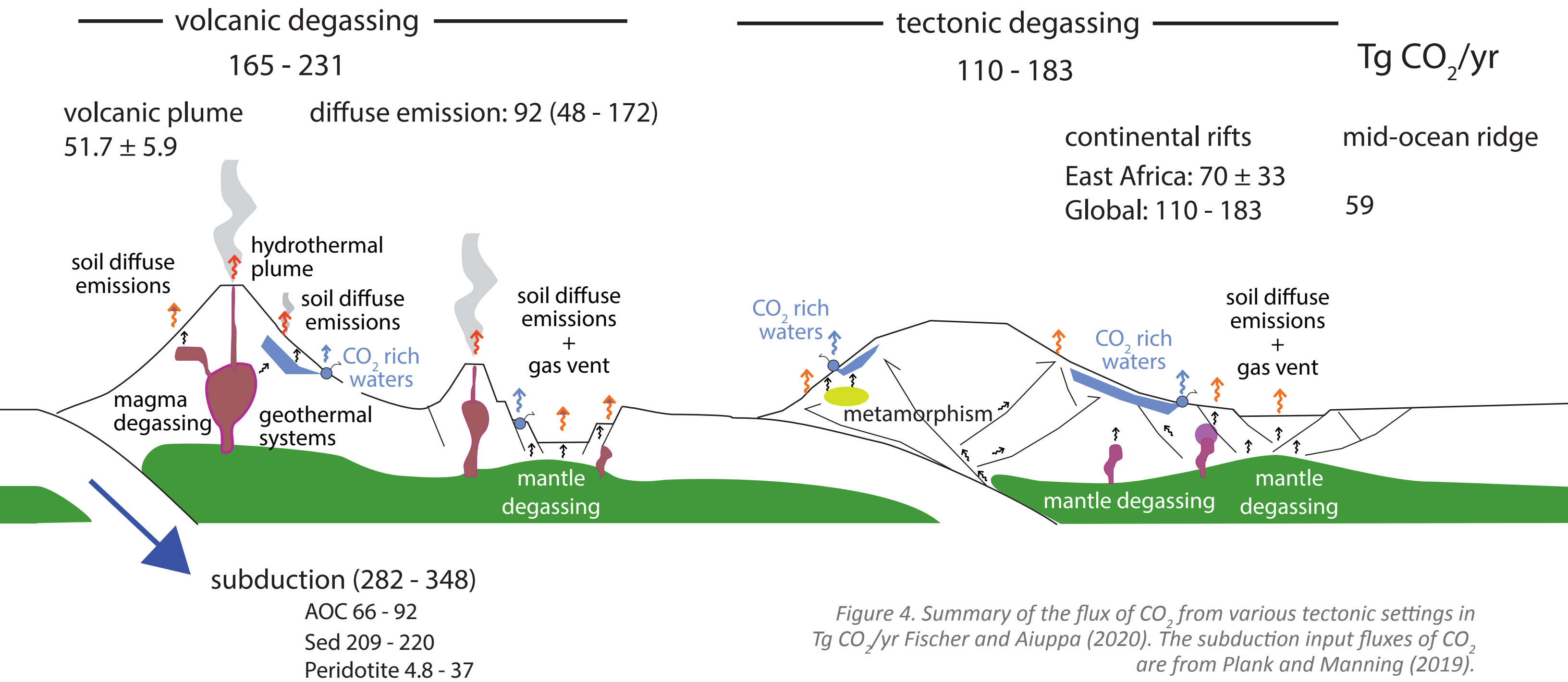

Figure 4. Summary of the flux of CO_2 from various tectonic settings in Tg CO_2/yr Fischer and Aiuppa (2020). The subduction input fluxes of CO_2 are from Plank and Manning (2019).

Despite significant advances in the last few decades constraining volatile fluxes from volcanic arcs and mid-ocean ridges, global volatile fluxes from continental rifts remain comparatively uncertain. Given the propensity for widespread diffuse degassing along extensional fault systems at rift settings, constraining volatile fluxes from continental rifts remains an ongoing challenge (e.g., Werner et al., 2019), with recent examinations into rift-wide diffuse CO_2 degassing highlighting continental rifts as critical sites of mantle volatile discharge. Much of the recent work in the volatiles fluxes community has focussed on CO_2, where we now have significantly better constraints on emission from the various tectonic settings summarized in Figure 4.

Future directions

MARGINS- and GeoPRISMS-related research over the last twenty years has yielded fundamental new constraints on the storage and transport of volatiles and their significance for the suite of processes operating at plate tectonic boundaries. Many key questions have emerged whilst others remain. Late-stage hydration of oceanic plates at the trench-outer rise is now a widely recognized phenomenon, yet the volume and distribution of volatiles is still poorly constrained (Grevemeyer et al., 2018), particularly the extent of lower crustal and upper mantle hydration, and the relative contributions of hydrous minerals and cracks in explaining reduced seismic velocities in the subducting plate (Korenaga, 2017). Coupled numerical models and new observations are needed to delineate whether this hydration is focused along narrow fault zones or more broadly distributed, which in the former case would reduce the hydration estimates by up to an order of magnitude (Miller and Lizarralde, 2016). Volatile distribution will also impact the release of volatiles at depth (Wada et al., 2012). Recent results suggesting hydration of the subducting mantle up to ~25 km below the Moho in the Marianas raise questions about the balance of volatile input and output (Cai et al., 2018). Finally, controls on variability between and within subduction zones remain a major uncertainty; for example, recent studies come to conflicting conclusions on the role of pre-existing features in the oceanic lithosphere (Shillington et al., 2015; Fujie et al., 2018). Following the onset of subduction, there are myriad questions concerning the flow of volatiles and their interactions with the surrounding lithosphere at every stage, from slab release to surface escape and from trench to arc and back-arc. The MARGINS and GeoPRISMS programs have demonstrated that tackling these critical questions requires focused, shoreline crossing, cross-disciplinary studies.

Although much progress has been made toward constraining the global CO_2 flux from volcanoes (Aiuppa et al., 2019; Fischer et al., 2019; Werner et al., 2019), built on decades of research, much uncertainty remains on tectonic and diffuse CO_2 emissions, which are likely equally significant, as well as the role of the overlying crust as a CO_2 contributor and the extrapolation of CO_2 fluxes throughout geologic history (Fischer and Aiuppa, 2020). Furthermore, our knowledge of other major volatile species currently lags behind. While the volcanic emissions of sulfur are now well constrained thanks to satellite data (Carn et al., 2017) and continuous global ground-based networks (Galle et al., 2010), subduction zone input data remains sparse and the effect of sulfur as an oxidizing agent of the mantle wedge is potentially significant (de Moor et al., 2013). The volatile budgets of the reduced species (H_2, CO, H_2S, CH_4), critical for understanding the rise of oxygen on the planet (Holland, 2002), also remain poorly constrained. The rates of volatile release during early Earth are being revised through novel applications of noble and radiogenic gases (Marty et al., 2019), while the relative recycling efficiencies of H_2O, C, and N continue to be investigated (Hirschmann, 2018). These remaining questions and research avenues necessitate further data acquisition utilizing sophisticated field, laboratory, experimental, and modeling approaches. ■

References

Abers, G.A., P.E. van Keken, B.R. Hacker (2017). The cold and relatively dry nature of mantle forearcs in subduction zones. Nat Geosci, 10

Accardo, N.J., et al. (2017). Surface wave imaging of the weakly extended Malawi Rift from ambient-noise and teleseismic Rayleigh waves from onshore and lake-bottom seismometers. Geophys J Int , 209, 3, 1892-1905

Aiuppa, A., T.P. Fischer, T. Plank, P. Bani (2019). CO_2 flux emissions from the Earth's most actively degassing volcanoes, 2005–2015. Scientific Reports, 9, 5442, doi.org/10.1038/s41598-019-41901-y

Allard, P., 1983. The origin of hydrogen, carbon, sulphur, nitrogen and rare gases in volcanic exhalations; evidence from isotope geochemistry. In: H. Tazieff and J. Sabroux (Editors), Forecasting volcanic events. Elsevier, New York, 337-386

Alt, J.C., W.C.I. Shanks, M.C. Jackson (1993). Cycling of sulfur in subduction zones; the geochemistry of sulfur in the Mariana island arc and back-arc trough. Earth Planet Sci Lett, 119, 477-494

Alt, J.C. (1995). Subseafloor processes in mid-ocean ridge hydrothermal systems, seafloor hydrothermal systems: Physical, chemical, biological, and geological interactions, Geophysical Monograph 91. American Geophysical Union, 85-114

Alt, J.C., D.A.H. Teagle (1999). The uptake of CO_2 during alteration of the oceanic crust. Geochim Cosmochim Acta, 63, 1527-1535

Audet, P., M.G. Bostock, N.I. Christensen, S.M. Peacock (2009). Seismic evidence for overpressured subducted oceanic crust and megathrust fault sealing. Nature, 457, 7225, 76–78

Bailey, D.K. (1980). Volcanism, earth degassing and replenished lithosphere mantle. Philosophical Transactions of the Royal Society of London. Series A, Math and Phys Sciences, 297, 1431, 309-322

Bangs, N.L., K.D. McIntosh, E.A. Silver, J.W. Kluesner, C.R. Ranero (2015). Fluid accumulation along the Costa Rica subduction thrust and development of the seismogenic zone. J Geophys Res: Solid Earth, 120, 67–86, doi.org/10.1002/2014JB011265

Barnes, J.D., J. Cullen, S. Barker, S. Agostini, S. Penniston-Dorland, J.C. Lassiter, A. Kluegel, L. Wallace (2019). The role of the upper plate in controlling fluid-mobile element (Cl, Li, B) cycling through subduction zones: Hikurangi forearc, New Zealand. Geosphere, 15, 642-658

Barnes, J.D., Z.D. Sharp, T.P. Fischer, D.R. Hilton, M.J. Carr (2009). Chlorine isotope variations along the Central American volcanic front and back arc. Geochem Geophys,10, Q11S17, doi:10.1029/2009GC002587

Barnes, P.M., G. Lamarche, J. Bialas, S. Henrys, I. Pecher, G.L. Netzeband, J. Greinert, J.J. Mountjoy, K. Pedley, G. Crutchley (2010). Tectonic and geological framework for gas hydrates and cold seeps on the Hikurangi subduction margin, New Zealand. Mar Geol, 272, 1-4, 26-48

Barry, P.H. et al. (2019). Forearc carbon sink reduces long-term volatile recycling into the mantle. Nature, 568, 487-492

Bayrakci, G., T.A. et al. (2016). Fault-controlled hydration of the upper mantle during continental rifting. Nat Geosci, 9, 384-388

Brantley, S.L., K.W. Koepenick (1995). Measured carbon dioxide emissions from Oldoinyo Lengai and the skewed distribution of passive volcanic fluxes. Geology, 23, 10, 933-936

Brounce, M.J., E. Cottrell, K.A. Kelly (2019). The redox budget of the Mariana subduction zone. Earth Planet Sci Lett, 528

Brune, S., S.E. Williams, R.D. Müller (2017). Potential links between continental rifting, CO_2 degassing and climate change through time. Nat Geosci, 10, 12, 941-946

Burley, J. M., R.F. Katz (2015). Variations in mid-ocean ridge CO_2 emissions driven by glacial cycles. Earth Planet Sci Lett, 426, 246-258

Busigny, V., P. Cartigny, P. Philippot, M. Ader, M. Javoy (2003). Massive recycling of nitrogen and other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP oceanic metasediments of the Schistes Lustres nappe (western Alps, Europe). Earth Planet Sci Let, 6809, 1-16

Cai, C., D.A. Wiens, W. Shen, M. Eimer (2018). Mariana subduction zone water input estimated from broadband ocean-bottom seismic data. Nature, 563, 389, doi:310.1038/s41586-41018-40655-41584

Canales, J.P., S.M. Carbotte, M.R. Nedimović, H. Carton (2017). Dry Juan de Fuca slab revealed by quantification of water entering Cascadia subduction zone. Nat Geosci, 10, 11, 864–870

Capriolo, M., et al. (2020). Deep CO_2 in the end-Triassic Central Atlantic Magmatic Province. Nat Commun

Carn, S.A., V.E. Fioletov, C.A. McLinden, C. Li, N.A. Krotkov (2017). A decade of global volcanic SO_2 emissions measured from space. Scientific Reports, 7, 44095, doi: 10.1038/srep44095

Coffin, M.F., O. Eldholm (1994). Large igneous provinces: Crustal structure, dimensions, and external consequences. Reviews of Geophysics, 32, 1-36

Collett, T.S., A. Johnson, C.C. Knapp, R. Boswell, eds. (2010). Natural Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards, AAPG Memoir 89, 89, AAPG

Corti, G., M. Bonini, D. Sokoutis, F. Innocenti, P. Manetti, S. Cloetingh, G. Mulugeta (2004). Continental rift architecture and patterns of magma migration: A dynamic analysis based on centrifuge models. Tectonics, 23, 2

Cottrell, E., L. Waters, M.L. Coombs, K.A. Kelly, J. Andrys (2020). Calc-alkaline magmatic trends at crustal pressure and high fO_2. Goldschmidt abstract

Craig, H. (1963). The isotopic geochemistry of water and carbon in geothermal areas, Nuclear Geology on Geothermal Areas. CNR, Pisa, 17-53

Dasgupta, R. (2013). Ingassing, storage, and outgassing of terrestrial carbon through geologic time. Rev Mineral Geochem, 75, 183-220

de Leeuw, G.A.M., D.R. Hilton, T.P. Fischer, J.A. Walker (2007). The He-CO_2 isotope and relative abundance characteristics of geothermal fluids in El Salvador and Honduras: New constraints on volatile mass balance of the Central American Volcanic Arc. Earth Planet Sci Lett, 158, 132-146

de Moor, J.M., T.P. Fischer, Z.D. Sharp, P.L. King, M. Wilke, R.E. Botcharnikov, E. Cottrell, M. Zelenski, B. Marty, D. Ayalew (2013). Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems. Geochem Geophys, doi: 10.1002/ggge.20255

Dean, S.M., T.A. Minshull, R.B. Whitmarsh, K.E. Louden (2000). Deep structure of the ocean-continent transition in the southern Iberia Abyssal Plain from seismic refraction profiles: The IAM-9 transect at 40o20'N. J Geophys Res, 105, 5859-5885

Dixon, J. E., E.M. Stolper (1995). An experimental study of water and carbon dioxide solubilities in mid-ocean ridge basaltic liquids. Part II: applications to degassing. J Petrol, 36, 6, 1633-1646

Dunbar, J.A., D.S. Sawyer (1989). How preexisting weaknesses control the style of continental breakup. J Geophys Res: Solid Earth, 94, B6, 7278-7292

Ebinger, C.J. (2005). Continental break-up: The East African perspective. Astronomy & Geophysics, 46, 2, 16–21

Ebinger, C.J., D. Keir, I.D. Bastow, K. Whaler, J.O. Hammond, J. O., A. Ayele, M.S. Miller, C. Tiberi, S. Hautot (2017). Crustal structure of active deformation zones in Africa: Implications for global crustal processes. Tectonics, 36, 12, 3298-3332

Elkins, L., T.P. Fischer, D.R. Hilton, Z.D. Sharp, S. McKnight, J.A. Walker (2006). Tracing nitrogen in volcanic and geothermal volatiles from the Nicaraguan volcanic front. Geochim Cosmochim Acta, 70, 5215-5235

Estep, J., R. Reece, D.A. Kardell, G.L. Christeson, R.L. Carlson. (2019). Seismic Layer 2A: The evolution and thickness from 0-70 Ma crust in the slow-intermediate spreading South Atlantic. J Geophys Res: Solid Earth, 124

Fischer, T.P. (2008). Fluxes of volatiles (H_2O, CO_2, N_2, Cl, F) from arc volcanoes. Geochem J, 42, 1, 21-38

Fischer, T.P., A. Aiuppa (2020). AGU Centennial Grand Challenge: Volcanoes and Deep Carbon Global CO_2 emissions from subaerial volcanism: Recent progress and future challenges. G-cubed, 21,3 e2019GC008690

Fischer, T.P., et al. (2019). The emissions of CO_2 and other volatiles from the world's subaerial volcanoes. Scientific Reports, 9, 18716

Fischer, T.P., W.F. Giggenbach, Y. Sano, S.N. Williams (1998). Fluxes and sources of volatiles discharged from Kudryavy, a subduction zone

volcano, Kurile Islands. Earth Planet Sci Lett, 160, 81-96
Fischer, T.P., D.R. Hilton, M.M. Zimmer, A.M. Shaw, Z.D. Sharp, J.A. Walker (2002). Subduction and recycling of nitrogen along the Central American margin. Science, 297, 1154-1157
Fischer, T.P., T.M. Lopez (2016). First airborne samples of a volcanic plume for $\delta^{13}C$ of CO_2 determinations. Geophys Res Lett, 43
Foley, S.F., T.P. Fischer (2017). An essential role for continental rifts and lithosphere in the deep carbon cycle. Nat Geosci, 10, 12, 897-902
Franke, D. (2013). Rifting, lithosphere breakup and volcanism: Comparison of magma-poor and volcanic rifted margins. Marine and Petroleum geology, 43, 63-87
Fujie, G., S. Kodaira, Y. Kaiho, Y. Yamamoto, T. Takahashi, S. Miura, T. Yamada (2018). Controlling factor of incoming plate hydration at the north-western Pacific margin. Nat Communi, 9, 3844
Funck, T., J.R. Hopper, H.C. Larsen, K.E. Louden, B.E. Tucholke, W.S. Holbrook (2003). Crustal structure of the ocean-continent transition at Flemish Cap: Seismic refraction results. J Geophys Res, 108
Furi, E., D.R. Hilton, M.D. Tryon, K.M. Brown, G.M. McMurtry, W. Bruckmann, C.G. Wheat (2010). Carbon release from submarine seeps at the Costa Rica fore arc: Implications for the volatile cycle at the Central America convergent margin. Geochem Geophys, 11, 4
Galle, B., M. Johansson, C. Rivera, Y. Zhang , M. Kihlman, C. Kern, T. Lehmann, U. Platt, S. Arellano, S. Hidalgo (2010). Network for Observation of Volcanic and Atmospheric Change (NOVAC) - A global network for volcanic gas monitoring: Network layout and instrument description. J Geophys Res, 115, D05304, doi:10.1029/2009JD011823
Gale, A., C.A. Dalton, C.H. Langmuir, Y. Su, J.G. Schilling (2013). The mean composition of ocean ridge basalts. Geochem Geophys, 14, 3, 489–518
Geissler, W.H., et al. (2005). Seismic structure and location of a CO_2 source in the upper mantle of the western Eger (Ohře) Rift, central Europe. Tectonics, 24, 5
Giggenbach, W.F. (1992). Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. Earth Planet Sci Lett, 113, 495-510
Gibson, S.A., E.E. Rooks, J.A. Day, C.M. Petrone, P.T. Leat (2020). The role of sub-continental mantle as both "sink" and "source" in deep Earth volatile cycles. Geochim Cosmochim Acta, 275, 140-162
Gill, J.B., J.D. Morris, R.W. Johnson (1993). Timescale for producing the geochemical signature of island arc magmas: U-Th-Po and Be-B systematics in recent Papua New Guinea lavas. Geochim Cosmochim Acta, 57, 4269-4283
Gill, J.B., R.W. Williams (1990). Th isotope and U-series studies of subduction-related volcanic rocks. Geochim Cosmochim Acta, 54, 1427-1442
Gillis, K.M., L.A. Coogan, C. Brant (2015). The role of sedimentation history and lithology on fluid flow and reactions in off-axis hydrothermal systems: A perspective from the Troodos ophiolite. Chem Geol, 414, 84-94
Grevemeyer, I., C.R. Ranero, M. Ivandic (2018). Structure of oceanic crust and serpentinization at subduction trenches. Geosphere, 14, 2, 395–418, doi.org/10.1130/GES01537.1
Guth, A.L. (2015). Volcanic volumes associated with the Kenya Rift: recognition and correction of preservation biases. Geol Soc, London, Special Pub, 420,1, 31-42
Hacker, B.R. (2008). H_2O subduction beyond arcs. Geochem Geophys, 9, Q03001, doi.org/10.1029/2007GC001707
Halldórsson, S.A., D.R. Hilton, P. Scarsi, T. Abebe, J. Hopp (2014). A common mantle plume source beneath the entire East African Rift System revealed by coupled helium-neon systematics. Geophys Res Lett, 41, 7, 2304-2311
Han, S., N.L. Bangs, S.M. Carbotte, D.M. Saffer, J.C. Gibson (2017). Links between sediment consolidation and Cascadia megathrust slip behaviour. Nat Geosci, 10, 954–959
Hasenclever, J., S. Theissen-Krah, L.H. Rupke, J.P. Morgan, K. Iyer, S. Petersen, C.W. Devey (2014). Hybrid shallow on-axis and deep off-axis hydrothermal circulation at fast-spreading ridges. Nature, 508, 508-512, doi:510.1038/nature13174
Hauri, E.H., G.A. Gaetani, T.H. Green (2006). Partitioning of water during melting of the Earth's upper mantle at H_2O-undersaturated conditions. Earth Planet Sci Lett, 248, 715–734
Hilton, D.R., T.P. Fischer, B. Marty (2002). Noble gases in subduction zones and volatile recycling. In: D. Porcelli, C. Ballentine, R. Wieler (eds.), MSA special volume: Noble gases in geochemistry and cosmochemistry, 47, 319-362
Hirschmann, M. (2018). Comparative deep Earth volatile cycles: The case for C recycling from exosphere/mantle fractionation of major (H_2O, C, N) volatiles and from H_2O/Ce, CO_2/Ba, and CO_2/Nb exosphere ratios. Earth Planet Sci Lett, 502, 262-273
Hirth, G., D.L. Kohlstedt (1996). Water in the oceanic upper mantle: implications for rheology, melt extraction and the evolution of the lithosphere. Earth Planet Sci Lett, 144, 1-2, 93-108
Hodgson, I., F. Illsley-Kemp, R.J. Gallacher, D. Keir, C.J. Ebinger, K. Mtelela (2017). Crustal structure at a young continental rift: A receiver function study from the Tanganyika Rift. Tectonics, 36, 12, 2806-2822
Holland, H.D. (2002). Volcanic gases, black smokers and the Great Oxydation Event. Geochim Cosmochim Acta, 66, 3811-3826
Hunt, J.A., A. Zafu, T.A. Mather, D.M. Pyle, P.H. Barry (2017). Spatially variable CO2 degassing in the Main Ethiopian Rift: Implications for magma storage, volatile transport, and rift-related emissions. Geochem Geophys, 18, 10, 3714-3737
Hutchison, W., T.A. Mather, D.M. Pyle, J. Biggs, G. Yirgu (2015). Structural controls on fluid pathways in an active rift system: A case study of the Aluto volcanic complex. Geosphere. 11,3, 542–562, doi: 10.1130/GES01119.1
Hutchison, W., et al. (2018). The evolution of magma during continental rifting: New constraints from the isotopic and trace element signatures of silicic magmas from Ethiopian volcanoes. Earth Planet Sci Lett, 489, 203-218
Hyndman, R.D., S.M. Peacock (2003). Serpentinization of the forearc mantle. Earth Planet Sci Lett, 212, 3-4, 417-432
Ivandic, M., I. Grevemeyer, A. Berhorst, E.R. Flueh, K. McIntosh (2008). Impact of bending related faulting on the seismic properties of the incoming oceanic plate offshore of Nicaragua. J Geophys Res, 113, B05410. doi.org/10.1029/2007JB005291
Jambon, A., J.L. Zimmermann (1990) Water in oceanic basalts; evidence for dehydration of recycled crust. Earth Planet Sci Lett 101, 323–331
Jendrzejewski, N., T.W. Trull, F. Pineau, M. Javoy (1997). Carbon solubility in Mid-Ocean Ridge basaltic melt at low pressures (250–1950 bar). Chem Geol, 138, 1-2, 81-92
Johnson, H.P., S. Merle, M. Salmi, R. Embley, E. Sampaga, M. Lee (2019). Anomalous concentration of methane emissions at the continental shelf edge of the Northern Cascadia Margin. J Geophys Res: Solid Earth, 124, 3, 2829-2843
Kagoshima, T., Y. Sano, N. Takahata, T. Maruoka, T.P. Fischer, K. Hattori (2015). Sulphur geodynamic cycle. Scientific reports, 5, 1, 1-6
Kämpf, H., A.S. Broge, P. Marzban, M. Allahbakhshi, T. Nickschick (2019). Nonvolcanic carbon dioxide emission at continental rifts: The Bublak Mofette Area, Western Eger Rift, Czech Republic. Geofluids, 2019
Kardell, D.A., G.L. Christeson, J.D. Estep, R.S. Reece, R.L. Carlson (2019). Long-lasting evolution of layer 2A in the Western South Atlantic: Evidence for low-temperature hydrothermal circulation in old oceanic crust. J Geophys Res, 124, 2252-2273, doi:2210.1029/2018JB016925
Kastner, M., E.A. Solomon, R.N. Harris, M.E. Torres (2014). Fluid origins, thermal regimes, and fluid and solute fluxes in the forearc of subduction zones. In Developments in Mar Geol, 7, 671-733
Kelemen, P.B., C.R. Manning (2015). Reevaluating carbon fluxes in subduction zones, what goes down, mostly comes up. Proc Nat Acad Sci, 112, E3997-E4006
Keller, T., R.F. Katz, M.M. Hirschmann (2017). Volatiles beneath mid-ocean ridges: Deep melting, channelised transport, focusing, and metasomatism. Earth Planet Sci Lett, 464, 55-68
Kelley, K.A., S. Newman, T. Plank, T.L. Grove, S. Parman (2002). Subducted fluid and sediment compositions preserved in Mariana Arc melt inclusions. EOS Trans AGU, 83, 47, Fall Meeting Suppl. Abstract V21C-10
Kelly, K.A., E. Cottrell (2009). Water and the oxidation state of subduction zone magmas. Science, 325, 605-607
Kendall, J.M., G.W. Stuart, C.J. Ebinger, I.D. Bastow, D. Keir (2005). Magma-assisted rifting in Ethiopia. Nature, 433, 7022, 146-148
Kent, A.J.R., T.R. Elliott (2002). Melt inclusions from Marianas arc lavas: Implications for the composition and formation of island arc magmas. Chem Geol, 183, 263-286

Keranen, K., S.L. Klemperer, R. Gloaguen, E.W. Group (2004). Three-dimensional seismic imaging of a protoridge axis in the Main Ethiopian rift. Geology, 32,11, 949-952

Keir, D., I.D. Bastow, K.A. Whaler, E. Daly, D.G. Cornwell, S. Hautot (2009). Lower crustal earthquakes near the Ethiopian rift induced by magmatic processes. Geochem Geophys, 10, 6

Kita, I., K. Nitta, K. Nagao, S. Taguchi, A. Koga (1993). Difference in N_2/Ar ratio of magmatic gases from northeast and southwest Japan: New evidence for different states of plate subduction. Geology, 21, 391-394

Kiyosu, Y., (1986). Variations in N_2/Ar and He/Ar ratios of gases from some volcanic areas in northeastern Japan. Geochem J, 19, 275-281

Koornneef, J. M. et al. (2009). Nature and timing of multiple metasomatic events in the sub-cratonic lithosphere beneath Labait, Tanzania. Lithos, 112, 896–912

Korenaga, J. (2017). On the extent of mantle hydration caused by plate bending. Earth Planet Sci Lett, 457, 1–9, doi.org/10.1016/j.epsl.2016.10.011

Lau, K.W.H., M.R. Nedimovic, K.E. Louden (2019) Along-Strike Variations in Structure of the Continent-Ocean Transition at the Northeastern Nova Scotia Margin From Wide-Angle Seismic Observations. J Geophys Res, 124, doi.org/10.1029/2018JB016894

Lee, H., T.P. Fischer, J.M. de Moor, Z.D. Sharp, N. Takahata, Y. Sano (2017). Nitrogen recycling at the Costa Rican subduction zone: The role of incoming plate structure. Scientific Reports, 13933

Lee, H., et al. (2017). Incipient rifting accompanied by the release of subcontinental lithospheric mantle volatiles in the Magadi and Natron basin, East Africa. J Volcanol Geotherm Res, 346, 118-133

Lee, H., J.D. Muirhead, T.P. Fischer, C.J. Ebinger, S.A. Kattenhorn, Z.D. Sharp, G. Kianji (2016). Massive and prolonged deep carbon emissions associated with continental rifting. Nat Geosci, 9, 2, 145-149

Le Voyer, M., et al. (2019). Carbon Fluxes and Primary Magma CO_2 Contents Along the Global Mid-Ocean Ridge System. Geochem Geophys, 20, 3, 1387-1424

Li, J., D.J. Shillington, D.M. Saffer, A. Bécel, M.R. Nedimovic, H. Kuehn, S.C. Webb, G.A. Abers, K.M. Keranen (2018). Connections between subducted sediment, pore-fluid pressure, and earthquake behavior along the Alaska megathrust. Geology, doi:10.1130/G39557.39551

Li, L., G.E. Bebout (2005). Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: insights regarding paleoproductivity and carbon and nitrogen subduction fluxes. J Geophys Res, 110: 10.1029/2004JB003276

Li, L., G.E. Bebout, B.D. Idleman (2007). Nitrogen concentration and _15N of altered oceanic crust obtained on ODP Legs 129 and 185: Insights into alteration-related nitrogen enrichment and the nitrogen subduction budget. Geochim Cosmochim Acta, 71, 2344-2360

Lin, P.N., R.J. Stern, J. Morris, S.H. Bloomer (1990). Nd-isotopic and Sr-isotopic compositions of lavas from the Northern Mariana and Southern Volcano Arcs - Implications for the origin of island arc melts. Contr Min Pet, 105, 381-392

Lindenfeld, M., G. Rümpker, K. Link, D. Koehn, A. Batte (2012). Fluid-triggered earthquake swarms in the Rwenzori region, East African Rift—Evidence for rift initiation. Tectonophysics, 566, 95-104

Lizarralde, D., et al. (2007). Variation in styles of rifting in the Gulf of California. Nature, 448, 466-469

Lopez, T., F. Tassi, A. Aiuppa, B. Galle, A.L. Rizzo, J. Fiebig, F. Capecchiacci, G. Giudice, S. Caliro, G. Tamburello (2017). Geochemical constraints on volatile sources and subsurface conditions at Mount Martin, Mount Mageik, and Trident Volcanoes, Katmai Volcanic Cluster, Alaska. J Volcanol Geotherm Res, 347, 64-81

Lopez, T.M., et al. (2019). Along-arc variations in volatile cycling across the Aleutian Arc (Abstract). AGU Fall Meeting, abstract V53C-05

Malusà, M.G., M.L. Frezzotti, S. Ferrando, E. Brandmayr, F. Romanelli, G.F. Panza (2018). Active carbon sequestration in the Alpine mantle wedge and implications for long-term climate trends. Scientific reports, 8, 1, 1-8

Mana, S., T. Furman, B.D. Turrin, M.D. Feigenson, C.C. Swisher III (2015). Magmatic activity across the East African north Tanzanian divergence zone. J of the Geol Soc, 172, 3, 368-389

Marty, B. (1995). Nitrogen content of the mantle inferred from N_2/Ar correlations in oceanic basalts. Nature, 377, 326–329

Marty, B., D.V. Bekaert, M.W. Broadley (2019). Geochemical evidence for high volatile fluxes from the mantle at the end of the Archaean. Nature, 575, 4865, 485–488

Marty, B., A. Jambon (1987). C/^{3}He in volatile fluxes from the solid earth: Implications for carbon geodynamics. Earth Planet Sci Lett, 83, 16-26

Marty, B., A. Jambon, Y. Sano (1989). Helium isotopes and CO_2 in volcanic gases of Japan. Chem Geol, 76, 25-40

Marty, B., I.N. Tolstikhin (1998). CO_2 fluxes from mid-ocean ridges, arcs and plumes. Chem Geol, 145, 3-4, 233-248

Marzen, R.E., D.J. Shillington, D. Lizarralde, J.H. Knapp, D.M. Heffner, J.K. Davis, S.H. Harder (2020). Limited and localized magmatism at the heart of the Central Atlantic Magmatic Province, Nature Communi, 11, 3397, 10.1038/s41467-020-17193-6

Marzoli, A., S. Callegaro, J. Dal Corso, J.H.F.L. Davies, M. Chiaradia, N. Youbi, H. Bertrand, L. Reisberg, R. Merle, F. Jourdan (2018). The Central Atlantic Magmatic Province (CAMP): A Review, in: Tanner, L.H. (Ed.), The Late Triassic World, Topics in Geobiology. Springer International Publishing, 91-125

Matsuo, S., M. Suzuki, Y. Mizutani (Editors) (1978). Nitrogen to Argon ratio in volcanic gases. Japan Scientific Societies Press, Tokyo, 17-26

McGary, R.S., R.L. Evans, P.E. Wannamaker, J. Elsenbeck, S. Rondenay (2014). Pathway from subducting slab to surface for melt and fluids beneath Mount Rainier. Nature, 511, 7509, 338–340

Mechie, J., et al. (1994). Crustal structure beneath the Kenya Rift from axial profile data. Tectonophysics, 236, 1-4, 179-200

Miller, N.C., D. Lizarralde (2016). Finite-frequency wave propagation through outer rise fault zones and seismic measurements of upper mantle hydration. Geophys Res Lett, 43, 7982-7990

Mitchell, E.C., T.P. Fischer, D.R. Hilton, E. Hauri, A.M. Shaw, J.M. de Moor, Z.D. Sharp, K. Kazahaya (2010). Nitrogen sources and recycling at subduction zones: Insights from the Izu-Bonin-Marianas arc. Geochem Geophys, 11, Q02X11, doi:10.1029/2009GC002783

Morris, J.D., W.P. Leeman, F. Tera (1990). The subducted component in island arc lavas: Constrains from Be isotopes and Be-B systematics. Nature, 344, 31-36

Naif, S., K. Key, S. Constable, R.L. Evans (2015). Water-rich bending faults at the Middle America Trench. Geochem Geophys, 16, 8, 2582–2597

Naif, S., K. Key, S. Constable, R.L. Evans (2016). Porosity and fluid budget of a water-rich megathrust revealed with electromagnetic data at the Middle America Trench. Geochem Geophys, 17, 11, 4495–4516

Naliboff, J.B., M.I. Billen, T. Gerya, J. Saunders (2013). Dynamics of outer-rise faulting in oceanic-continental subduction systems. Geochem Geophys, 14, 7, 2310–2327, doi.org/10.1002/ggge.20155

O'Donnell, J.P., K. Selway, A.A. Nyblade, R.A. Brazier, N.E. Tahir, R.J. Durrheim (2015). Thick lithosphere, deep crustal earthquakes and no melt: a triple challenge to understanding extension in the western branch of the East African Rift. Geophys J Int, 204, 985–998

Palme, H., O'Neill H. St. C. (2007). Cosmochemical estimates of mantle composition. In Treatise on Geochemistry (ed. K.K. Turekian). Pergamon, Oxford, 1–38

Patino, L.C., M.J. Carr, M.D. Feigenson (2000). Local and regional variations in Central American arc lavas controlled by variations in subducted sediment input. Contrib Min Pet, 138, 265-283

Peacock, S.M. (2001). Are the lower planes of double seismic zones caused by serpentine dehydration in subducting oceanic mantle? Geology, 29, 4, 299–302

Perez-Gussinye, M., T.J. Reston (2001). Rheological evolution during extension at nonvolcanic rifted margins: Onset of serpentinzation and development of detachments leading to continental breakup. J Geophys Res, 106, 3962-3975

Plank, T., C.H. Langmuir (1993). Tracing trace elements from sediment input to volcanic output at subduction zones. Nature, 362, 739-742

Plank, T., C.H. Langmuir (1998). The chemical composition of subducting sediment and its consequences for the crust and mantle. Chem Geol, 145, 325-394

Plank, T., C.E. Manning (2019). Subducting Carbon. Nature, 574, 343–352

Plasman, M., et al. (2017). Lithospheric low-velocity zones associated with a magmatic segment of the Tanzanian Rift, East Africa. Geophys J Int, 210, 1, 465-481

Pommier, A., R.L. Evans (2017). Constraints on fluids in subduction zones from electromagnetic data. Geosphere, GES01473.1

Ranero, C.R., J. Phipps Morgan, K. McIntosh, C. Reichert (2003). Bending-related faulting and mantle serpentinization at the Middle America trench. Nature, 425, 6956, 367–373. doi.org/10.1038/nature01961

Resing, J.A., J.E. Lupton, R.A. Feely, M.D. Lilley (2004). CO_2 and ^3He in hydrothermal plumes: implications for mid-ocean ridge CO_2 flux. Earth Planet Sci Lett, 226, 449–464.

Roecker, S., et al. (2017). Subsurface images of the Eastern Rift, Africa, from the joint inversion of body waves, surface waves and gravity: investigating the role of fluids in early-stage continental rifting. Geophys J Int, 210,2, 931-950

Roland, E., D. Lizarralde, J.J. McGuire, J.A. Collins (2012). Seismic velocity constraints on the material properties that control earthquake behavior at the Quebrada-Discovery-Gofar transform faults, East Pacific Rise. J Geophys Re,117, B11102

Rowe, M.C., A.J.R. Kent, R.L. Nielsen (2009). Subduction influence on Oxygen fugacity and trace and volatile elements in basalts across the Cascade Volcanic Arc. J Petrol, 50, 61-91

Rudnick, R.L., W.F. Mcdonough, B.W. Chappell (1993). Carbonatite metasomatism in the northern Tanzanian mantle: petrographic and geochemical characteristics. 114, 463–475

Rüpke, L.H., J. Phipps Morgan, M. Hort, J.A.D. Connolly (2004). Serpentine and the subduction zone water cycle. Earth Planet Sci Lett, 223, 1-2, 17–34, doi.org/10.1016/j.epsl.2004.04.018

Sadofsky, S.J., G.E. Bebout (2004). Nitrogen geochemistry of subducting sediments: New results from the Izu-Bonin-Mariana margin and insights regarding global nitrogen subduction,. Geochem Geophys, 5, Q03I15, doi:10.1029/2003GC000543

Sadofsky, S.J., M. Portnyagin, K. Hoernle, K. P. van den Boogard (2007). Subduction cycling of volatiles and trace elements through the Central American volcanic arc: Evidence from melt inclusions. Contrib Mineral Petrol, 155, 433-456

Salters V.J.M., A. Stracke (2004). Composition of the depleted mantle. Geochem Geophys, 5, 200410.1029/2003GC000597

Sano, Y., B. Marty (1995). Origin of carbon in fumarolic gas from island arcs. Chem Geol, 119, 265-274

Sano, Y. S.N. Williams (1996). Fluxes of mantle and subducted carbon along convergent plate boundaries. Geophys Res Lett, 23, 20, 2749-2752

Sawyer, G.M., S.A. Carn, V.I. Tsanev, C. Oppenheimer, M. Burton (2008). Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo. Geochem Geophys, 9, 2

Schmidt, M.W., S. Poli (1998). Experimentally based water budgets for dehydrating slabs and consequences for arc magma generation. Earth Planet Sci Lett, 163, 361-379

Selway, K. (2015). Negligible effect of hydrogen content on plate strength in East Africa. Nat Geosci, 8, 543-546

Shaw, A.M., M.D. Behn, S.E. Humphris, R.A. Sohn, P.M. Gregg (2010). Deep pooling of low degree melts and volatile fluxes at the 85 E segment of the Gakkel Ridge: evidence from olivine-hosted melt inclusions and glasses. Earth Planet Sci Lett, 289, 3-4, 311-322

Shaw, A.M., E. Hauri, T.P. Fischer, D.R. Hilton, K.H. Kelly (2008). Hydrogen isotopes in Mariana arc melt inclusions: implications for subduction dehydration and the deep-Earth water cycle. Earth Planet Sci Lett, 275, 138-145

Shaw, A.M., D.R. Hilton, T.P. Fischer, J.A. Walker, G. Alvarado (2003). Contrasting He-C relationships in Nicaragua and Costa Rica: Insights into C cycling through subduction zones. Earth Planet Sci Lett, 214, 499-513

Shillington, D.J., A. Bécel, M.R. Nedimović, H. Kuehn, S.C. Webb, G.A. Abers, K.M. Keranen, J. Li, M. Delescluse, G.A. Mattei-Salicrup (2015). Link between plate fabric, hydration and subduction zone seismicity in Alaska. Nat Geosci, 8, 12, 961–964

Shillington, D.J., C.L. Scott, T.A. Minshull, R.A. Edwards, P.J. Brown, N. White (2009). Abrupt transition from magma-starved to magma-rich rifting in the eastern Black Sea. Geology, 37, 1, 7-10

Shishkina, T.A., R.E. Botcharnikov, F. Holtz, R.R. Almeev, M.V. Portnyagin (2010). Solubility of H_2O-and CO_2-bearing fluids in tholeiitic basalts at pressures up to 500 MPa. Chem Geol, 277, 1-2, 115-125

Shuck, B., H. Van Avendonk, A. Becel (2019). The role of mantle melts in the transition from rifting to seafloor spreading offshore eastern North America. Earth Planet Sci Lett, 525, 1

Smith, J. (2016). CO_2 flux along faults of the Central Rio Grande Rift, New Mexico. https://digitalrepository.unm.edu/eps_etds/108

Snyder, G., R. Poreda, A. Hunt, U. Fehn (2001). Regional variations in volatile composition: Isotopic evidence for carbonate recycling in the Central American volcanic arc. G-cubed, 2: 2001GC000163

Snyder, G., R.J. Poreda, U. Fehn, A. Hunt (2003). Sources of nitrogen and methane in Central American geothermal settings: Noble gas and 129I evidence for crustal and magmatic volatile components. G-cubed, 4, 9001, doi:9010.1029/2002GC000363, 002003

Tamburello, G., S. Pondrelli, G. Chiodini, D. Rouwet (2018). Global-scale control of extensional tectonics on CO_2 earth degassing. Nat Communi, 9,1, 1-9

Taran, Y.A. (1992). Chemical and isotopic composition of fumarolic gases from Kamchatka and Kuriles volcanoes. Ret. Geol. Survey Japan, 279, 183-186

Thybo, H., P.K.H. Maguire, C. Birt, E. Perchuć (2000). Seismic reflectivity and magmatic underplating beneath the Kenya Rift. Geophys Res Lett, 27, 17, 2745-2748

Thybo, H., C.A. Nielsen (2009). Magma-compensated crustal thinning in continental rift zones. Nature, 457, 7231, 873-876

Torres, M.E., Teichert, B.M.A., Trehu, A.M., Borowski, W. and Tomaru, H., 2004. Relationship of pore water freshening to accretionary processes in the Cascadia margin: fluid sources and gas hydrate abundance. Geophys Res Lett, 31, 22

Van Avendonk, H.J.A., W.S. Holbrook, D. Lizarralde, P. Denyer (2011). Structure and serpentinization of the subducting Cocos plate offshore Nicaragua and Costa Rica. Geochem Geophys, 12, Q06009

Van Keken, P., B. Hacker, E.M. Syracuse, G.A. Abers (2011). Subduction factory: 4. Depth-dependent flux of H_2O from subducting slabs worldwide. J Geophys Res: Solid Earth, 116, 1B

Wada, I., M.D. Behn, A.M. Shaw (2012). Effects of heterogeneous hydration in the incoming plate, slab rehydration, and mantle wedge hydration on slab-derived H_2O flux in subduction zones. Earth Planet Sci Lett, 353-354, 60–71, doi.org/10.1016/j.epsl.2012.07.025

Walker, J.A., K. Roggensack, L.C. Patino, B.I. Cameron, O. Matias (2003). The water and trace element contents of melt inclusions across an active subduction zone. Contrib Mineral Petrol, 146, 62-77

Wallace, P.J., 2005. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. J Volcanol Geotherm Res, 140, 217-240

Weinstein, A., et al. (2017). Fault-magma interactions during early continental rifting: Seismicity of the M agadi-Natron-Manyara basins, Africa. Geochem Geophys, 18, 10, 3662-3686

Werner, C., et al. (2019). Carbon dioxide emissions from subaerial volcanic regions. In Deep Carbon: Past to Present. Edited by Beth N. Orcutt, Isabelle Daniel, Rajdeep Dasgupta. Cambridge University Press

Whitmarsh, R.B., G. Manatschal, T.A. Minshull (2001). Evolution of magma-poor continental margins from rifting to seafloor spreading. Nature, 413, 6852, 150-154

White, R.S., L.K. Smith, A.W. Roberts, P.A.F. Christie, N. J. Kusznir, the rest of the iSIMM Team (2008). Lower-crustal intrusion on the North Atlantic continental margin. Nature, 452, 460-464

Williams, S.N., S.J. Schaefer, V. Calvache D. Lopez (1992). Global carbon dioxide emission to the atmosphere by volcanoes. Geochim Cosmochim Acta, 56, 1765-1770

Wilson, C. R., M. Spiegelman, P.E. van Keken, B.R. Hacker (2014). Fluid flow in subduction zones: The role of solid rheology and compaction pressure. Earth Planet Sci Lett, 401, 261–274

Wong, K., E. Mason, S. Brune, M. East, M. Edmonds, S. Zahirovic (2019). Deep carbon cycling over the past 200 million years: A review of fluxes in different tectonic settings. Frontiers in Earth Science, 7, 1-22

Wauthier, C., V. Cayol, M. Poland, F. Kervyn, N. d'Oreye, A. Hooper, S. Samsonov, K. Tiampo, B. Smets (2013). Nyamulagira's magma plumbing system inferred from 15 years of InSAR. Geological Society, London, Special Publications, 380, 1, 39-65

Zimmer, M.M., T.P. Fischer, D.R. Hilton, A.M. Shaw, Z.D. Sharp, G. Alvarado (2001). Volatile chemistry and fluxes along the Costa Rican segment of the Central American volcanic arc. EOS Trans. AGU, 82, 47

Zimmer, M.M., T. Plank, E.H. Hauri, G.M. Yogodzinski, P. Stelling, J. Larsen, B. Singer, B. Jicha, C.W. Mandeville, C.J. Nye (2010). The Role of water in generating the calc-alkaline trend: New volatile data for Aleutian magmas and a new tholeiitic index. J Petrol, 51, 12, 2411–2444