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

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 CO₂ 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).
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 \(-10\) to \(-16\) 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 (Rüpeke 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 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).
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, O, 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\textsubscript{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\textsubscript{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\textsubscript{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 volcanic 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 arc magmas 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.
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$_2$O, SO$_2$, CO$_2$, CH$_4$, 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$_2$/He combined with MOR He 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 through ratios with trace elements (Le Voyer et al., 2019) or other volatiles, usually He (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.

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<th>ARCS</th>
<th>CO$_2$ (Tg/yr)</th>
<th>SO$_2$ (Tg/yr)</th>
<th>CO$_2$ (10$^9$ mol/yr)</th>
<th>SO$_2$ (10$^9$ mol/yr)</th>
<th>H$_2$O (10$^9$ mol/yr)</th>
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Table 1. Global fluxes of major volatiles from subaerial volcanoes from Fischer et al. (2019).
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; Whitemarsh 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, 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 since 5 Ma (Guth, 2015). Modelled cumulative 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 when applied to the Kenyan example. These data crudely support magma flux rates ranging 48-72 km$^3$/kyr$^1$ 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 Koeppenick, 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 (Geisler 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).
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$_2$S, 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$_2$O, 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.

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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).
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