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Subduction Zone Geochemistry

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Definition

The exchange of chemical components between the Earth's interior and exterior driven by plate subduction.

Introduction

Subduction zones are not just sites of plate convergence but regions where the interior and exterior of the Earth chemically exchange (Fig. 1). Like a factory, raw material from the Earth's exterior is fed into the subduction zone and transformed in a series of chemical reactions driven by increasing pressure (P) and temperature (T) in the sinking plate. Some of the products are buoyant and so rise, drive melting in the mantle, and return back to the Earth's crust via intrusion and volcanism. Dense waste products continue to sink into the deep mantle, perhaps to the boundary with the core. This subduction factory is ultimately responsible for generating continental crust, re-enriching the mantle, and redistributing water and carbon dioxide in the planet. The processes that occur inside the factory are hidden from view, inferred from comparison of oceanic input and volcanic output chemical fluxes, laboratory experiments that simulate high P–T reactions, thermodynamic calculations, and exhumed high-pressure rocks.

Input Materials

The input to the subduction zone is the incoming plate, which consists of three layers of fundamentally different chemical compositions: the basaltic oceanic crust created at mid-ocean ridges, its mantle residuum substrate that moves with the plate, and marine sediments that deposit on top (Fig. 1). Each of these layers interacts differently with the ocean as the plate travels from mid-ocean ridge to deep sea trench. Most information on the chemical composition of the subducting plate has come from the international scientific ocean

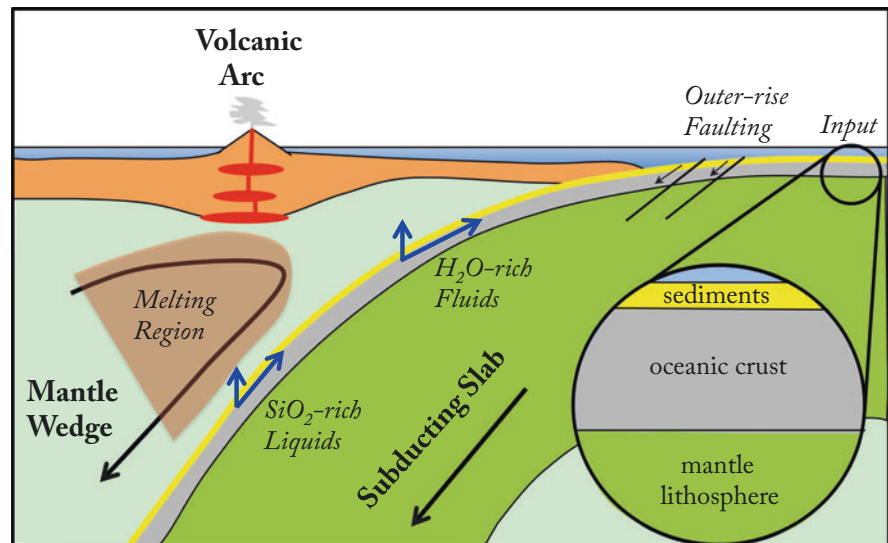
drilling programs through direct sampling and borehole observatories.

The basaltic oceanic crust represents the melt layer segregated from the melting mantle at mid-ocean ridges, and its initial chemical composition reflects the degree of melting and history of the upper mantle source region. Hydrothermal circulation near the active spreading center then decorates the oceanic crust with secondary minerals such as smectite and Fe oxides and introduces chemical components such as H_2O , S, U, Li, B, and alkalis (Kelley et al. 2003). Carbonate veins precipitate at lower temperatures as the plate moves off the ridge axis (Alt and Teagle 1999). Near the trench, plate bending opens new fractures that hydrate the oceanic crust. The sum of these chemical interactions produces an altered basaltic crust with very different parent-daughter isotope ratios, such as high $^{238}\text{U}/^{206}\text{Pb}$ and $^{87}\text{Rb}/^{87}\text{Sr}$, which initiate distinct isotopic evolutionary paths (Kelley et al. 2005; Porter and White 2009).

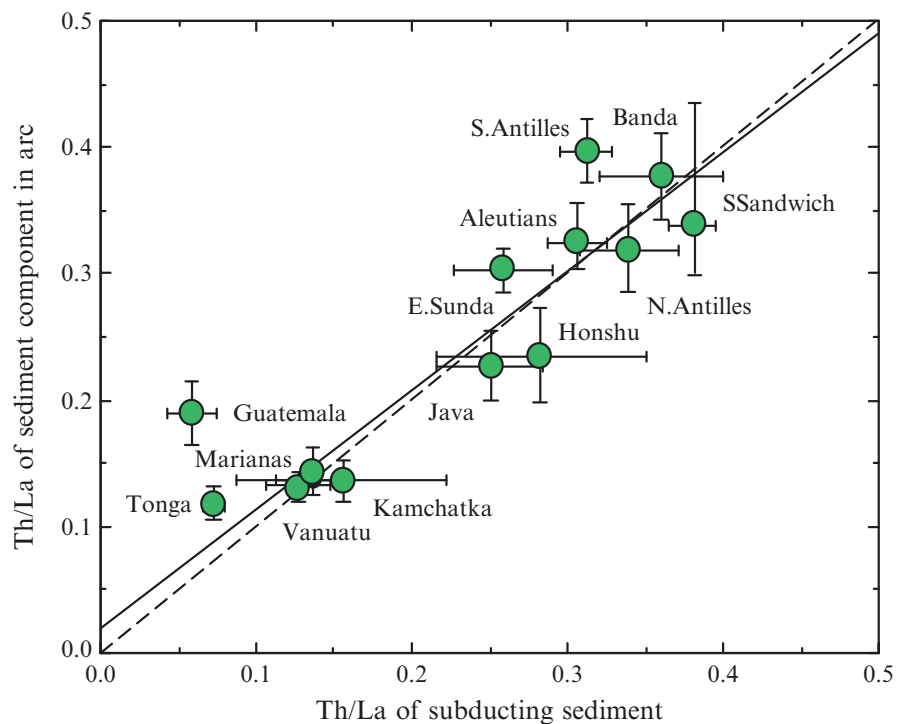
The extent to which the mantle peridotite substrate reacts with the ocean is debated, but critical to the fate of water at the surface of our planet. The primary mineral in peridotite is olivine, which may undergo rapid and extensive hydration, even at ambient temperatures, to the mineral serpentine (a hydrous mineral with an abundance of H_2O , ~12–13 wt%). The peridotite section of the oceanic plate is thus a sponge to water if it can be delivered to depth. The primary evidence for serpentinization of the oceanic plate comes from a reduction in seismic velocity toward the trench, observed at the Central American, Andean, and Aleutian margins (Shillington et al. 2015). As little as 2% serpentinization of the top few km of incoming peridotite holds enough water to subduct the entire ocean every billion years (Hacker 2008). Although H_2O is the dominant chemical component attending serpentinization, other diagnostic features include elevated Cl and $\delta^{11}\text{B}$ (Vils et al. 2009; Debret et al. 2014).

Sediments deposited on the seafloor constitute the greatest chemical heterogeneity injected into the subduction zone, from pure silica chert to nearly pure calcium carbonate chalks and metal-rich red clays (Plank 2014). Marine sediments are physical mixtures of variable amounts of continental detritus, delivered by wind, rivers, and/or volcanic eruption, biogenic accumulations of primarily carbonate, opal and apatite organism hard parts, and hydrothermal particulates as the complements to seafloor alteration. All of these phases may be seeds for adsorption of chemical complexes from seawater itself, a hydrogenetic component. Globally, marine sediments are dominated by continental detritus and so have a composition very similar to that of average shales and the upper continental crust. Biogenic phases are largely diluents to most chemical species in the detritus, except for Sr, Ba, and U in carbonates, rare earth element (REE) in phosphates, and Ba associated with biogenic opal. In regions of the oceans far from wind or river inputs, sediments are dominated by

Subduction Zone Geochemistry, Fig. 1 Cartoon of subduction zone depicting some key sources and processes that affect geochemistry



Subduction Zone Geochemistry, Fig. 2 One-to-one correlation between the Th/La of bulk sediment subducting into different trenches and Th/La measured in the corresponding arc volcanoes. This relationship demonstrates the geochemical connection between sediment input and volcanic output at subduction zones. The sediment component in each arc is calculated by linear regression of Th/La-Sm/La in basaltic samples (Plank 2005)

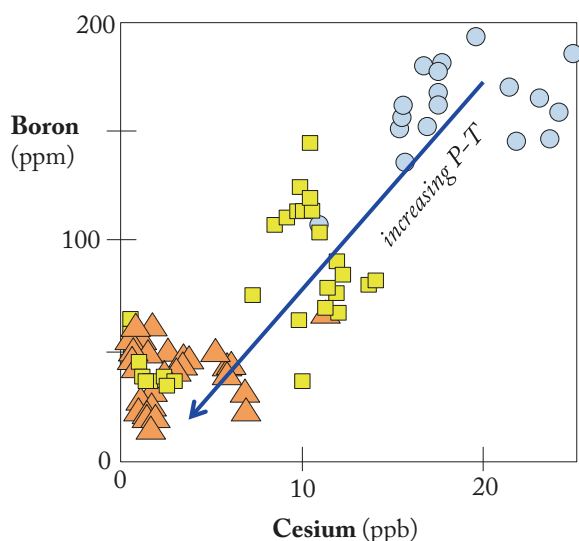


hydrogenetic or hydrothermal components, rich in Fe-Mn oxides, REE, Th, Pb, Co, and other metals. Unlike most planetary reservoirs, marine sediments may have distinctive Nd-Hf isotopic compositions due to the strong enrichment of REE in some phases and the lack of the heavy mineral zircon in sediments far from land (Vervoort et al. 2011). The oceanic realm also may lead to the distinctive fractionation of Ce (which is highly particle reactive when 4+) from the other dominantly trivalent REE. The sedimentary input to different subduction zones is widely variable, depending on the

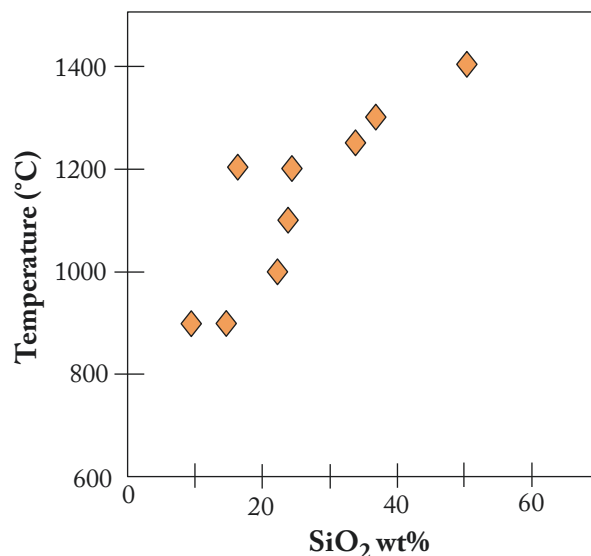
paleogeography and paleoceanography of each site. The unique geochemical characteristics of each sedimentary section is shared by its adjacent volcanic arc (Fig. 2), providing strong evidence for cycling through the subduction zone.

On the Way Down

As oceanic material enters the subduction zone, it begins a path of increasing T and P that drives mineral transformations,



Subduction Zone Geochemistry, Fig. 3 The loss of boron and cesium during subduction, as recorded in micas from metasedimentary rocks of the Catalina Schist during increasing P (pressure) – T (temperature) grade from ~200 °C to 600 °C. Circles are lowest grade lawsonite-albite schists; squares medium grade blueschists; triangles higher-grade amphibolites (From Bebout (2014))



Subduction Zone Geochemistry, Fig. 4 SiO₂ concentration of high P-T fluids generated in the laboratory (equilibrated with basalt at 6 GPa). Fluids evolve continuously from low-SiO₂ aqueous fluids at low T to high-SiO₂ melt-like supercritical fluids at high T (Figure from Kessel et al. (2005))

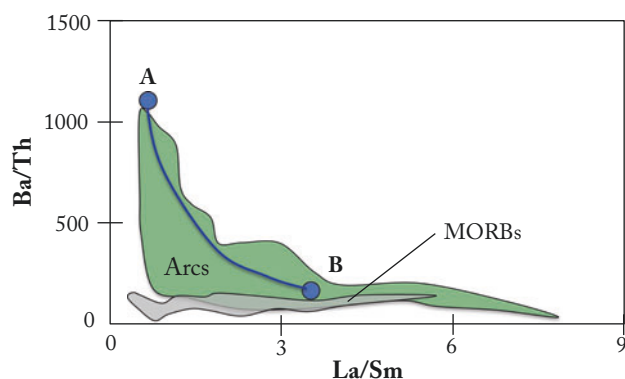
devolatilization reactions, fluid evolution from aqueous to solute rich, and an increase in the solubility of many trace-element-bearing minerals. Mineral reaction and fluid production in turn accompany a spectrum of fault slip behavior in the subduction zone, from slow and silent slip to the world's largest intraplate earthquakes.

The lowest P-T conditions involve compaction and dehydration of the sedimentary section as the clay mineral smectite transforms to illite and the light elements Li and B as well as alkalis Cs and Rb are liberated into a water-rich fluid (Ishikawa et al. 2008; Bebout 2014; Fig. 3). At higher P-T, the dominant minerals in the basaltic crust become lawsonite, garnet, and clinopyroxene (Klimm et al. 2008), while quartz and mica also form in sediments. A plethora of accessory mineral phases and their T-dependent solubility control the behavior of key tracers, such as REE, Th, and U in monazite and allanite, Nb and Ta in rutile, and Zr, Hf, U, and HREE in zircon (Hermann and Rubatto 2009; Skora and Blundy 2010). Serpentine minerals have a maximum stability of 600–700 °C (Schmidt and Poli 1998), but may persist to >200 km depth in the peridotite section because the slab interior heats up more slowly (Hacker 2008). Deformation within the subduction zone may create *mélange* (Marschall and Schumacher 2012), a mechanical mixture of sediment-basalt-peridotite that may favor the formation of distinctive minerals such as chlorite.

At higher temperatures, fluids evolved during the breakdown of lawsonite, amphibole, and mica are more solute rich, containing Si, Al, and alkalis (Manning 2004). If flushed with

water-rich fluids, the top of the plate may melt at $T \geq 700$ °C and $P \geq 3$ GPa (Mann and Schmidt 2015). At pressures higher than 5 GPa, sediments no longer melt at a discrete solidus but instead evolve “supercritical” liquids that span a continuum of compositions (Kessel et al. 2005; Fig. 4) from dilute aqueous liquids with little dissolved silicate to melt-like silicate-rich liquids with dissolved water (Hermann et al. 2006).

The workings within the subduction zone beneath volcanic arcs are of particular interest because they prime the source of arc magmatism. The tracers of the slab include large ion lithophile elements (e.g., alkalis, Ba, Pb) that are thought to be mobile in lower T fluids and high-field strength elements (e.g., Nb, Ta, REE, Th) which are thought to be mobile only in higher T fluids/melts/supercritical liquids (Elliott 2003; Fig. 5). A range of fluid and solid compositions will exist for different subduction zone P-T paths. Young slabs (e.g., Cascadia) follow higher T/P paths than old, fast subducting slabs (e.g., Tonga; Syracuse et al. 2010). Different thermal regimes will lead to different slab fluid compositions that supply different arcs, for example, REE-poor and high Ba/La, U/Th, and B/Be at Tonga and low H₂O/Ce and high Sr/Y at Cascadia (Ruscitto et al. 2012). Sedimentary versus basaltic slab material supply different ¹⁴³Nd/¹⁴⁴Nd, ¹⁰Be/⁹Be, and ²⁰⁵Tl/²⁰³Tl compositions, reflecting greater mean age, cosmogenic contribution, and seawater interaction, respectively (White and Patchett 1984; Morris et al. 2002; Prytulak et al. 2013). Volcanic arcs often inherit the local subducted sedimentary fingerprints in their Th/La (Plank 2005) and ²⁰⁷Pb/²⁰⁴Pb ratios.



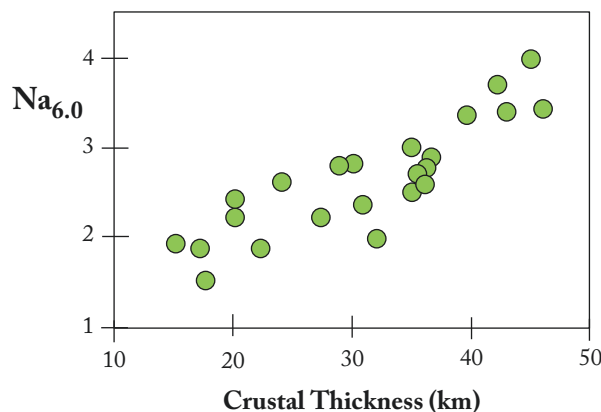
Subduction Zone Geochemistry, Fig. 5 Subduction zones produce arc basalts (green field) that are significantly enriched in Ba/Th compared to mid-ocean ridge basalts (gray field). Line shows expected mixing between low-temperature/alterated oceanic crust fluid (1) and high-temperature/sediment melt (2) from the subduction zone (Mixing calculation and figure from Elliott (2003))

One Man's Trash Is Another Man's...

The progressive removal of water, fluids, melts, supercritical liquids, and buoyant solids leaves behind a dense slab that sinks deeper into the upper mantle, the transition zone, the lower mantle, and potentially as far as the core-mantle boundary. Such processed slab material contributes to mantle heterogeneity. Carbonate and organic carbon are stubborn substances in subduction zones, some destined to become diamonds in the mantle (Walter et al. 2011; Sverjensky et al. 2014). Particularly cold P-T paths can ferry water into the lower mantle in a series of dense hydrous magnesium silicates, leading to a loss of water from the surface hydrosphere (Nishi et al. 2014). The transition zone is capable of containing oceans of water in the mineral ringwoodite, recently discovered as inclusions in high-pressure diamonds (Pearson et al. 2014). The subduction zone can deliver to the deep mantle stable isotope tracers in $^{18}\text{O}/^{16}\text{O}$, $^7\text{Li}/^6\text{Li}$, and $^{34}\text{S}/^{32}\text{S}$ that bear vestiges of their origin in the biosphere, hydrosphere, and atmosphere at Earth's surface (Eiler 2001; Farquhar et al. 2002; Elliott et al. 2006; Sleep et al. 2012). Other radiogenic isotope tracers such as $^{206}\text{Pb}/^{204}\text{Pb}$, $^{187}\text{Hf}/^{186}\text{Hf}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ evolve to anomalous values due to extreme fractionation of parent from daughter isotope in subducting slabs (Chauvel et al. 2008). Such distinctive slab material is thought to surface again in rising mantle plumes, producing volcanism on ocean islands like Hawaii, Galapagos, and Samoa (Blichert-Toft et al. 1999; Jackson et al. 2007; Hofmann 2014).

Or, What Goes Down Must Come Up

Fluids evolved from the subducting plate may rise up the slab interface or into the overlying mantle (Wilson et al. 2014). The



Subduction Zone Geochemistry, Fig. 6 Correlation between the thickness of the crust and the sodium concentration of basaltic magmas, averaged for different volcanic arc segments globally. This relationship is interpreted to reflect lower extents of mantle melting beneath arcs with thick crust, due to the displacement of the hot mantle wedge core to greater depths. Na6.0 is the average Na₂O concentration (wt%) of volcanic rock samples with 5.5 > MgO < 6.5 wt% (Data compilation, figure, and interpretation from Turner and Langmuir (2015a))

exact path of fluid flow from slab to hot core of the mantle wedge and the extent of reaction along the way are poorly known (Pirard and Hermann 2015). Weak, low-density sediment or mélange may become gravitationally unstable and rise as diapirs into the overlying mantle (Behn et al. 2011). These materials may interact with and/or drive melting in the overlying mantle wedge, the source of magmas that feed arc volcanoes.

The mantle wedged between the upper and downgoing plates may melt in two ways: (1) by the addition of slab fluid (s.l.) that lowers the mantle melting temperature or (2) by adiabatic decompression due to an upward component of plate-driven circulation, primarily in the back-arc region (Grove et al. 2002). It has also been proposed that the removal of ice loads during deglaciations may lead to enhanced decompression melting (Huybers and Langmuir 2009). Slab diapirs may also melt as they rise through the mantle wedge and heat up (Castro and Gerya 2008). This sum of processes leads to zonation in the concentration of H₂O and other slab tracers in volcanism at different distances from the trench (Pearce et al. 2005; Kelley et al. 2006; Portnyagin et al. 2007). The mantle melting signal is thought to be best recorded in elements which do not derive primarily from the downgoing plate, such as the high-field strength elements (HFSE: Nb, Ta, Hf, Zr, Ti, and Y) and Na. These elements, in turn, vary with both H₂O (Plank et al. 2013) and crustal thickness (Turner and Langmuir 2015a; Fig. 6), leading to competing models whereby slab H₂O on the one hand and wedge depth on the other control mantle melting (Turner and Langmuir 2015b). Some volcanoes erupt magmas with similar geochemical heritage (e.g., U/Th, Ba/La) for 100,000's year (Wade et al. 2005; Jicha and Singer 2006), while others

erupt an enormous diversity of primary compositions (Patino et al. 2000). The primary melts that rise out of the mantle are thought to be basalts in most cases but in some regions are high Mg/(Mg + Fe) andesites and dacites (Kelemen 1995). Such magmas appear to have been more common in the early Earth (Fig. 7).

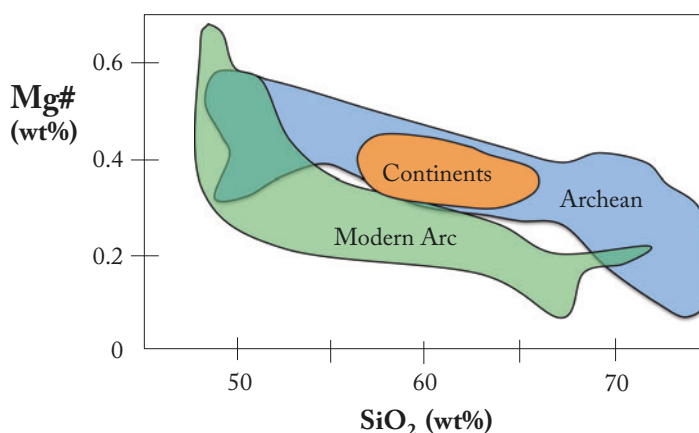
Building Volcanoes and Continents

Magmas continue to be buoyant in the crust, particularly once they begin to exsolve volatile species (e.g., H_2O , CO_2 , SO_2 , halogens) to vapor. Some of the magmas born in the subduction zone will erupt out a volcano, while some will meet their “viscous death” and crystallize in the crust to become a plutonic body (Annen et al. 2006). The magma flux through the crust will affect the extent of cooling, crystallization, and final composition of the erupted or intruded magma. Magmas with short residence time in the crust will remain basaltic

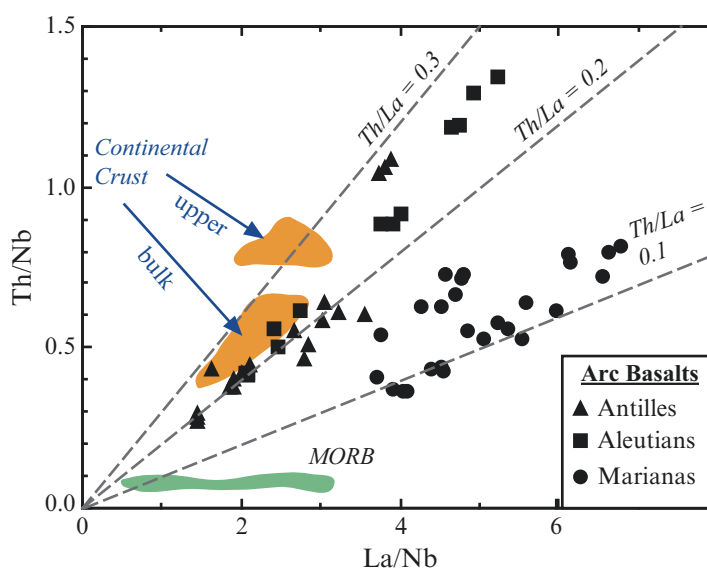
(with high MgO, Ni, Cr), and those with the longest residence time and/or interaction with the crust will evolve to become rhyolites (with high SiO_2 and alkalis). As magmas evolve, they may enrich in Fe (the tholeiitic trend) or deplete in Fe (calc-alkaline). Calc-alkaline trends, predominant at subduction zones and distinctive to Earth, are created from high initial water and oxygen fugacity (Sisson and Grove 1993; Zimmer et al. 2010). Trace elements that are essential constituents to accessory minerals, such as P in apatite and Zr in zircon, will show kinks along crystal fractionation paths as these minerals saturate. Magmas will variably interact, digest, and disrupt the crust they intrude, leading to decreases in $^{143}\text{Nd}/^{144}\text{Nd}$ as magmas evolve to higher SiO_2 (Sisson et al. 2014), isotopic heterogeneity within individual crystals (Davidson et al. 2001), and/or a cargo of foreign crystals (Dungan and Davidson 2004).

The continental crust and arc magmas share geochemical fingerprints, such as low La/Nb and Th/Nb (Fig. 8), which have long provided strong evidence for continent formation at

Subduction Zone Geochemistry, Fig. 7 SiO_2 and Mg# (Mg/[Mg + Fe]) in Archean igneous rocks (dots), bulk continental crust (orange field) and typical modern Aleutian arc lavas (green field). Most modern subduction lavas are not compositionally similar to the continental crust (From Kelemen (1995))



Subduction Zone Geochemistry, Fig. 8 Th/Nb vs. La/Nb in arc basalts from subduction zones, compared to average continental crust (orange field) and mid-ocean ridge and oceanic island basalts (green field). The high Th/Nb (depletion in Nb) is a feature shared by both the continental crust and subduction magmatism. Figure after Plank (2005)



subduction zones (Rudnick 1995; Plank 2005). Few modern arcs, however, provide a good match to the full continental fingerprint (Gazel et al. 2015), and most arc crust is significantly less silicic than bulk continental crust (Rudnick and Gao 2014). This “silica problem” has several proposed solutions (Tatsumi et al. 2008), generally falling into two categories: (a) predominance of high-silica primary magmas in the early Earth or plutonic record (Kelemen 1995; Fig. 7) and (b) subtraction of low-silica crystals by sinking of dense lower crust into the mantle (Jull and Kelemen 2001).

Timescales of Subduction Geochemistry

Radioactive isotopes and diffusion chronometry constrain the timescales of subduction geochemistry, from millions of years to minutes. Geochemical variations and U-Pb zircon geochronology track the evolution and construction of convergent margins over tens of millions of years (Lee et al. 2007). The presence of the cosmogenic and radioactive isotope ^{10}Be in arc volcanic crystals requires Be to travel from shallow sediments on the seafloor down the subduction zone and back to the surface in less than a few Ma (Morris et al. 2002). Disequilibrium in the activity of U-chain isotopes clocks transport from the slab to the surface in less than a few 100,000 years and perhaps as rapidly as a few 1000 years (Turner et al. 2003). Ar-Ar geochronology establishes the lifetime of individual volcanoes to 100–600 ka (Carr et al. 2007). Crystals erupted from volcanoes can endure several freeze-thaw cycles in magma storage regions (Cooper and Kent 2014), recorded in ^{238}U – ^{230}Th crystallization ages on the order of 10,000 years. Diffusion profiles of transition metals (Ni, Fe, Mg, Cr) in primary olivine crystals are speedometers of rapid magma supply from the mantle to some volcanoes in months to years (Ruprecht and Plank 2013). The eruptive process itself may occur in minutes, fueled by the rapid loss of volatiles from melt to vapor and recorded in H_2O diffusion profiles in glass and crystals (Lloyd et al. 2014).

Mass Balances Across the Subduction Zone

Developing meaningful mass balances of different tracers across subduction zones remains an outstanding challenge. An example comes from the rare earth element Nd. The concentration and isotope ratios of Nd in sediments and basaltic crust entering subduction zones are fairly well constrained by drilling. The Nd abundance in subducting peridotite is minor, and Nd is not widely mobilized during the first 700°C of heating in the subduction zone. Its release into slab fluids/melts will be governed largely by the T-dependent solubility of the REE-rich minerals allanite and monazite. A few percent of sediment is generally sufficient to

reproduce the $^{143}\text{Nd}/^{144}\text{Nd}$ composition of arc magmas, but the balance from subducting basaltic crust versus mantle is not currently well constrained. Other unknowns are the contributions of Nd from the preexisting arc crust, especially if it is made of young arc volcanics with similar $^{143}\text{Nd}/^{144}\text{Nd}$ to the intruding magma. The Nd concentrations in arc volcanics are reasonably well known for many volcanoes, but large uncertainties in the magma flux rate at arcs (volcanic and plutonic) lead to minimum uncertainties of a factor of two in the output flux of any magmaphile element. By comparing the volcanic output to the subducted input, it is clear that the Nd contributed from the slab is widely variable from arc to arc. From 0% to 60% of the Nd in volcanic arcs is derived from the slab (Porter and White 2009). Still, the net effect of subduction on the slab is relatively minor for Nd, with 100–70% of the initial slab Nd continuing into the deep mantle.

Even greater uncertainties exist for the mass balance of other chemical species, such as carbon, where current estimates are anywhere from ~0% to 80% C entering subduction zones continuing into the deep mantle (Kelemen and Manning 2015). A similar situation exists for H_2O , although the presence of the surface ocean over most of geological time places maximum constraints on the amount of water that can disappear into the mantle (Parai and Mukhopadhyay 2012). The slow subduction process adds up over geological time; an ocean of water and a mass equivalent to the entire surface pool of organic C have disappeared down subduction zones every few billion years. Variable and inefficient return may have contributed to the unusually high H/C of our planet’s surface (Hirschmann and Dasgupta 2009).

Most mass balance estimates to date are like balancing a checking account that has large uncertainties on the deposits and withdrawals – this leads to an uncomfortable situation! A fundamentally different approach is gaining accuracy. Given a P-T path for a slab, it is possible to calculate where and how much departing fluid is evolved and its elemental composition using thermodynamic and partitioning data from laboratory experiments. With enough accuracy of the underlying chemical reactions, the future will see subduction mass balances predicted from calculation. Such an approach is underway with the arc basalt simulator (Kimura et al. 2009), and geochemical-thermomechanical models (Hebert et al. 2009; Baitsch-Ghirardello et al. 2014).

Summary and Conclusions

Subduction geochemistry is a rich topic, spanning from marine geology to igneous petrology, geodynamics to thermodynamics. Accordingly, diverse and multidisciplinary observations and measurements are needed to understand the full subduction cycle for any geochemical tracer. These

include the study of sediments and serpentinite from the seafloor, study of metamorphic rocks and high-pressure simulations in the laboratory, modeling of magma and mantle movement, and study of plutonic and volcanic rocks, glasses, gases, and crystals. For this reason, subduction geochemistry has generally advanced through coordinated, international programs involving hundreds of scientists, with efforts crossing the shoreline and spanning from megascale drilling to nanoscale chemical analysis. The challenges to our understanding are wide and deep, and the stakes are high – subduction has built the continents, stirred the mantle, and developed our hydrosphere and carbosphere over Earth history.

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Sulfate Minerals

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Definition

Sulfate minerals are mineral species in which the dominant anionic entity is the sulfate anion, $[\text{SO}_4]^{2-}$ (Chang et al. 1996; Alpers et al. 2000). About 380 valid species of sulfate minerals had been described by early 2017 (cf. www.mindat.org), which are often grouped into a broader “sulfate” anion class along with the much small number (ca. 50) of chromates, molybdates, and tungstates. Even rarer related complex anions are the sulfite ion $[\text{S}^{4+}\text{O}_3]^{2-}$ in scotlandite (PbSO_3), fluorsulfonate ion $[\text{SO}_3\text{F}]^-$ in reederite-(Y) ($\text{Na}_{15}\text{Y}_2(\text{CO}_3)_9(\text{SO}_3\text{F})\text{Cl}$), and thiosulfate ($[\text{SO}_3\text{S}]^{2-}$ or $[\text{S}_2\text{O}_3]^{2-}$) in sidpietersite ($\text{Pb}_4(\text{S}_2\text{O}_3)_2(\text{OH})_2$).

Introduction

Sulfur is the commonest element in the Earth that occurs in both negative (S^{2-}) and positive (S^{4+} , S^{6+}) oxidation states. Hexavalent sulfur usually occurs bonded to four oxygen atoms in a tetrahedral arrangement, forming the sulfate anion $[\text{SO}_4]^{2-}$. The complex anion is held together internally by rather strong, covalent S-O bonds (bond valence = 1.5 valence units), but are bound to other cations to form a mineral structure through links that are usually lower in bond valence and more ionic in character. The formation of sulfate anion requires conditions that are oxidizing relative to those found in the deep Earth, so sulfate minerals are characteristic of near-surface environments that are oxygenated, particularly the oxidized zones of sulfide ore bodies, oxidized hydrothermal and fumarole systems and since sulfate is a common anion in the ocean and many other water bodies, in evaporites. Oxidation of sulfides to form sulfuric acid

and hence sulfate minerals is frequently catalyzed by acidophile lithoautotrophic bacteria such as *Thiobacillus* and *Sulfobacillus* in cooperation with iron-oxidizing species (Nordstrom and Southam 1997; Pósfai and Dunin-Borkowski 2006). This process may be exploited for ore processing by bioleaching, and it should be noted that other species utilize the converse reaction of sulfate reduction (Southam 2012). Anhydrite (CaSO_4) may also crystallize as a primary mineral from oxidized, sulfur-rich magmas, although it is may not always be preserved in the geological record since it is sparingly water soluble.

Examples

Sulfate minerals may be simple, anhydrous salts of one or more cations. However, most are more complex, containing additional water, hydroxide anion, or other anionic species such as chloride or carbonate. Sulfate is also an essential but subordinate constituent in some minerals such as nosean ($\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_{24}](\text{SO}_4)\cdot\text{H}_2\text{O}$) which do not fall into the sulfate anion class (nosean is a tectosilicate of the sodalite group). Most of the anhydrous sulfate minerals are uncommon, highly water soluble, ephemeral species of fumaroles, and arid environments. However, baryte (BaSO_4) and celestine (SrSO_4) are extremely insoluble in water and are common hydrothermal gangue minerals of ore deposits, as well as occurring as evaporites. The names of these minerals are as included in the Mineral List of the International Mineralogical Association (2017); the spellings “barite” and “celestite” remain common in American usage. They have an orthorhombic crystal structure in which the large Ba and Sr cations are in 12-fold coordination by oxygen. Anglesite (PbSO_4), which shares the same crystal structure, is a frequent oxidation product of lead sulfide ore minerals such as galena.

Calcium sulfate occurs primarily as orthorhombic anhydrite and also as the common monoclinic dihydrate gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$), as well as the rare, metastable hemihydrate bassanite ($\text{CaSO}_4\cdot \frac{1}{2}\text{H}_2\text{O}$), which is a natural analog of synthetic “plaster of Paris.” Gypsum predominates at the Earth’s surface, but it is readily dehydrated to anhydrite through the increase in pressure and temperature associated with burial, with 21% volume decrease of the solid phase. Conversely, anhydrite crystallizes directly from water above 55 °C, but is readily hydrated to gypsum by the action of water at low temperature and pressure. Gypsum formed some of the largest single crystals known of any mineral (up to 12 m long), discovered in 2000 in the “Cave of Crystals” at Naica, Chihuahua, Mexico (García-Ruiz et al. 2007). Also in Mexico, the abundance of these calcium sulfate minerals in evaporitic sediments at the 65-million-year-old Chicxulub impact site is believed to have filled the atmosphere with sulfate aerosol that caused a prolonged global cooling,

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