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The partitioning behavior of trace elements in subduction zones: Advances and prospects

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Abstract   The partitioning behavior of trace elements is of key importance for understanding the geochemical process and material cycle mechanism in subduction zones. This paper focuses on the advances and prospects on the studies of trace element partitioning in subduction zones from the following four aspects. (1) The properties of fluids derived from subducting slabs and their ability in element transport. How slab-derived solute-rich fluids and supercritical fluids are formed and what the roles and key control factors of these fluids are in transferring of elements (especially the high field strength elements) from slab to wedge are discussed. We point out that the detailed investigations of supercritical fluids may provide a new perspective for the element migration mechanism, material cycle process, arc magma genesis and so on. (2) The behavior of transition elements during mantle wedge melting. The behavior of the first row transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) in the mantle partial melting process is compatible or incompatible, depending on residual mineral assemblage and physicochemical conditions. The partitioning behavior of the elements such as Sc, Ti, Co, Ni and Zn whose valence states do not change in the melting process mainly depends on the residual mineral assemblage and temperature, whereas the partitioning behavior of the multivalent elements such as V and Fe is also the function of oxygen fugacity ($f\mathrm{O}_2$) in addition to mineral assemblage and temperature. Therefore, the partitioning behavior of transition elements has important applications in tracing lithologic inhomogeneity and $f\mathrm{O}_2$ of the mantle wedges. (3) The specificity of element partitioning behavior during arc magma evolution. Garnet has Dy/Yb partitioning behavior different from amphibole, and rutile has Nb/Ta partitioning behavior different from amphibole. Dy/Yb and Nb/Ta partitioning differences for these minerals enable to distinguish the specific evolution process of arc magmas. The Dy/Yb and Nb/Ta generally decrease with the increase of SiO_2 in arc magmas, indicating that amphibole fractionation should be the most important during arc magma differentiation. (4) The behavior of sulfur and chalcophile elements and porphyry metallogeny. In subduction zones, the behavior of chalcophile elements such as Cu and Au is controlled by sulfide and fluid. Therefore, the stability of sulfide, the time at which the fluid exsolves from the melt relative to sulfide saturation, the fluid/sulfide mass ratio and fluid/melt Cu and Au partition coefficients in intermediate-felsic magma-$\mathrm{H}_2\mathrm{O}$ systems are especially important in understanding Cu and Au enrichment in magma-hydrothermal processes. Intermediate-felsic magmas mainly originate from the differentiation of arc magmas at lower crustal reservoirs, and thus the fluid exsolution from the lower crustal reservoirs and the fluid/melt and fluid/sulfide partition coefficients of Cu and Au should be the keys to understanding quantitatively how Cu and Au are migrated from the deep crust to the shallow site of mineralization.

Keywords   Subduction zone, Supercritical fluid, Transition elements, Element partitioning, Ore-forming elements

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1. Introduction

Trace element partition coefficients are the basis for understanding the geochemical processes and material cycle in subduction zones. The processes of material cycle in subduction zones include slab dehydration and fluid release, metasomatism and partial melting in the mantle wedge, arc magma differentiation and continental crust formation and metallogeny (Zheng et al., 2016; Zheng, 2019). Slab dehydration and fluid release involve mineral/fluid element partitioning, and partial melting and magmatic differentiation involve mineral/melt element partitioning. Therefore, the behavior of elements and material cycle in subduction zones are controlled by the element partition coefficients of mineral/fluid and mineral/melt (Kessel et al., 2005a; Xiong et al., 2005; Xiong, 2006). The partition coefficient of an element is not only controlled by the nature of the element itself (ion radius and valence state) and the structure of mineral that it is incorporated into, but also is the function of temperature (T), pressure (P), melt or fluid composition (X), and fO$_2$, so the variation rule of mineral/melt and mineral/fluid partition coefficients with physicochemical parameters (P-T-X-fO$_2$) has important application value for understanding the process of subduction zone material cycle (Xiong et al., 2011; Wang et al., 2019). Currently we have quite clear recognition on the behavior of large ion lithophile elements and rare earth elements in the subduction zone process (Kessel et al., 2005a; Xiong et al., 2011), but are still not very clear for the behavior of high field strength elements, the first row transition elements and S-loving and ore-forming elements, which largely hinders our in-depth understanding of the process of subduction zone material cycle (Xiong et al., 2011; Liu et al., 2014, 2015; Li et al., 2017; Wang et al., 2019). In this paper, we review the partitioning behavior and tracing significance of key trace elements in the subduction zone process, from slab dehydration, mantle metasomatism and partial melting, arc magma evolution to the formation of intermediate-felsic magma and fluid exsolution and mineralization (Figure 1).

2. Fluid property and element transport from slab to wedge

2.1 The properties of fluids derived from subducting slabs

Typical oceanic subduction plate consists of a thin sediment layer on the surface, a 4–7 km basaltic oceanic crust in the middle, and a thick peridotite mantle at the bottom (Poli and Schmidt, 2002). Prior to subduction, the rocks in the plate were hydrated due to the interaction with seawater, forming hydrated plate with hydrous minerals and abundant pore water (Poli and Schmidt, 2002; Zheng et al., 2016; Zheng,
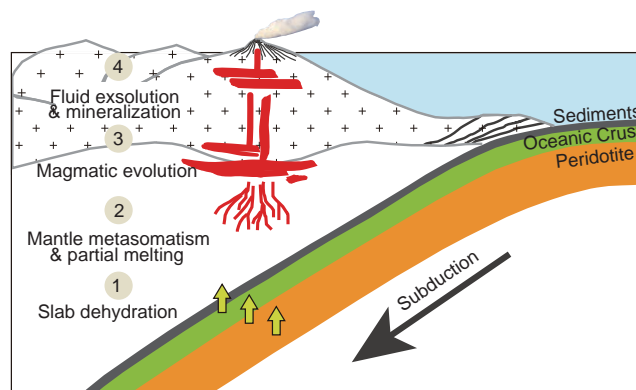

Figure 1   Schematic diagram of material cycle processes in subduction zone, including (1) slab dehydration, (2) mantle metasomatism and partial melting, (3) arc magma evolution and (4) formation of intermediate-felsic magma and fluid exsolution and mineralization. This study focuses on the research advances on the element partitioning behavior in these processes.

2019). During the subduction, the increase of temperature and pressure causes phase transition and formation of a variety of hydrous mineral phases in the hydrated plate. Kawamoto (2006) summarized that there are more than 30 different hydrous minerals possibly formed by the phase transition in the subducted plate. The main hydrous phases in peridotite are serpentine, talc, chlorite, 10-A phase, etc. In addition, wadsleyite and ringwoodite in the mantle transition zone have high water solubility (Ohtani, 2015) and are also important water-bearing minerals. Recently, the ringwoodite encrusted in diamond was found to contain 1.0 wt% water (Pearson et al., 2014), providing strong evidence that the mantle transition zone may be water-rich. The main hydrous phases in the altered oceanic crust and sediments include epidote, chlorite, chloritoid, staurolite, lawsonite and phengite, etc. These hydrous minerals are the necessary basis for water transfer to the deep interior of Earth or fluid formation in subduction zones. Recently, Liu et al. (2018, 2019) discovered that phase-D and phase-H, two important Al-rich hydrous phases of the basalt-H$_2$O system, can be stabilized to the pressures at the lower mantle, providing a key evidence that water could be transported by subducted oceanic crust to the mantle transition zone and lower mantle.

Although the stability of hydrous phases during cold subduction makes the plate capable to transfer water to the deep interior of the earth, the decomposition and dehydration of hydrous phases with increasing slab temperature are still the main process of the water cycle in subduction zone. The most significant effect of the melts and fluids derived from plates is to cause mantle wedge melting and arc magmatism, which is the direct indication of the intense subarc dehydration of the plate. The dehydration of subducting slab may directly form fluids or cause partial melting of the slab itself to form hydrous melts, depending on the thermal structure of subduction zone and the subduction P-T pathway. Partial

melting of subducting oceanic crust produces intermediate-felsic melts with high Sr and low Y, which pass through the mantle wedge to form the so-called adakites (Defant and Drummond, 1990). Such a case is quite rare and occurs only under abnormally hot subduction conditions. Geological, geophysical and geochemical studies and high *T-P* experiments have consistently shown that the fluid released from plate dehydration is the main carrier of material transfer from slab to wedge, that is, the fluid with dissolved silicate components and various trace elements rises into the mantle wedge, causing mantle metasomatism, partial melting and arc magmatism (Poli and Schmidt, 2002; Manning, 2004; Kessel et al., 2005a, 2005b; Hermann et al., 2006; Pommier, 2014; Zheng and Hermann, 2014; Frezzotti and Ferrando, 2015; Wörner et al., 2018). In the past, the media that lead to material transfer from slab to wedge are collectively referred to as fluids, but there is no clear understanding of their nature. Are they mainly water-rich fluids or solute-rich supercritical fluids? So far, the investigations on the formation condition, element migration capacity and key control factors of supercritical fluids are still far from enough, which hinders our understanding of the material cycle process in subduction zones.

The types of liquid phase properties and chemical composition in subduction zones include aqueous fluids, hydrous melts and supercritical fluids. Aqueous fluids tend to dissolve less than 20–30 wt% silicate solute, and hydrous melts tend to dissolve less than 20–30 wt% water, while the contents of solute and water of supercritical fluids are in between (Zheng et al., 2011, 2016; Hermann and Rubatto, 2014; Ni et al., 2017). In a rock-H_2O system, the aqueous fluid is formed at the sub-solidus temperatures, and the hydrous melt±aqueous fluid is formed above the solidus temperatures (whether or not a aqueous fluid in addition to hydrous melt is present depends on the total water content and melting degree of the rock). With the increase of temperature and pressure during subduction, the mutually enhanced solubilities of water in silicate melt and silicate in water result in the formation of a single-phase fluid with composition, density and viscosity between the aqueous fluid and the hydrous melt, namely the supercritical fluid (Shen and Keppler, 1997; Hack et al., 2007; Ni et al., 2017). The *P-T* point where the critical curve of miscibility of aqueous fluid and hydrous melt intersects with the wet solidus of a rock is called the second critical endpoint, which is the end point of the wet solidus. At the pressure conditions above this endpoint, the liquid phase composition continuously change with the increase of temperature, resulting in the formation of supercritical fluid (Ni et al., 2016). The special physicochemical properties of supercritical fluid such as composition, density and viscosity make it has much stronger ability of element migration than aqueous fluid. Supercritical fluid is probably the most effective element migration carrier and its role and effect in

subduction zones have attracted broad attention (Shen and Keppler, 1997; Kessel et al., 2005a; Liu et al., 2009; Zheng et al., 2011, 2016; Kawamoto et al., 2012; Xiao et al., 2015; Ni et al., 2017).

Studies on the thermal structure of subduction zones (e.g., Syracuse et al., 2010) indicate that the depth (pressure) on the top of subduction plates under volcanic arcs is 80–180 km (2.5–6.0 GPa). Experimental studies have shown that the solubility of silicate minerals in fluids increases with the increase of temperature and pressure (Newton and Manning, 2008; Dolejš and Manning, 2010; Cruz and Manning, 2015). At 2.0 GPa, 800–900°C, the solubility of quartz in water can reach 20 wt% (Hunt and Manning, 2012), indicating that at the *P-T* conditions of subducting slab (2.5–6.0 GPa, 700–900°C) water can dissolve more than 20–30 wt% silicate components, forming solute-rich fluid or supercritical fluid. High pressure experiments in combination with synchrotron radiation X-ray imaging studies show that the critical endpoint pressures of peridotite-H_2O system (3.8 GPa, Mibe et al., 2007), basalt-H_2O system (3.2 GPa, Mibe et al., 2011) and sediment-H_2O system (2.5 GPa, Kawamoto et al., 2012) are generally lower than the depth/pressure range (2.5–6.0 GPa) of slab top. These results suggest that most of the fluids produced by plate dehydration below volcanic arcs should be supercritical. As for the composition of solute dissolved in supercritical fluid, analyses of the solute glasses quenched from near-solidus fluids in basalt-H_2O system and sediment-H_2O system in high *T-P* experiment studies showed that the main components are Si, followed by Al and Na and K (Kessel et al., 2005a, 2005b; Hermann et al., 2006; Schmidt, 2015). The *in-situ* Raman spectroscopy of hydrothermal diamond cell experiments shows that polymerization of silicate components in fluid increases with the increase of solute content (Zotov and Keppler, 2002). *In situ* Raman spectroscopy of the $KAlSi_3O_8$-H_2O supercritical fluids shows that the solute structures mostly consist of dimer and trimer (Mibe et al., 2008). The formation of supercritical fluid is believed to be closely related to the polymerization of silicate components in the fluid (Manning, 2004). The composition and structure of supercritical fluid are close to those of hydrous melt, while it can keep the low viscosity close to aqueous fluid (Audétat and Keppler, 2004). These distinct physicochemical properties enable supercritical fluid to dissolve both fluid- and melt-mobile elements, so it has a strong ability to dissolve and migrate elements.

2.2 The key factors controlling element migration ability of supercritical fluid

In shallow subduction conditions, plate dehydration tends to generate dilute aqueous fluids. The ability of dilute fluids to dissolve elements is very weak, and even for large ionic

lithophile elements (LILE), their role is limited (Manning, 2004; Spandler et al., 2004), except for the cases of F- and Cl-rich aqueous fluids (Rapp et al., 2010; Keppler, 2017). Under deep subduction conditions, solute-rich fluids or supercritical fluids are formed by plate dehydration due to the increase of silicate components dissolved in the fluid with temperature and pressure (Kessel et al., 2005b; Hermann et al., 2013). Arc magmas are generally enriched in LILE and supercritical fluids must be more favorable to the migration of these elements compared to aqueous fluids. High field strength elements (HFSE), such as Ti, Nb, Ta, Zr, Hf, are often considered to be "fluid-immobile elements". However, the wide presence of rutile in multiphase inclusions and high-pressure veins in metamorphic rocks of orogenic belts (Gao et al., 2007; Zhang et al., 2008; Huang et al., 2012; Xiao et al., 2014) directly indicates that HFSEs are mobile in fluids, and was considered as strong evidence of supercritical fluid activity during metamorphism. Enrichment of HFSE in some arc magmas (Zheng and Hermann, 2014) as well as presence of zircon and rutile in some orogenic peridotites (Kalfoun et al., 2002; Malaspina et al., 2006; Li et al., 2016; Faithfull et al., 2018; Zheng et al., 2019) also indicate that these so-called fluid-immobile elements can be transferred to the mantle wedge by supercritical fluids. Therefore, supercritical fluid may be an important medium for material migration in subduction zones, and strengthening the study of supercritical fluid may provide a new perspective for the element migration process and the genesis of arc magmas in subduction zones.

It is well known that arc magmas are characterized by the enrichment of LILE, but there are important differences in the enrichment degree among the magmas from different arcs. In addition, the contents of HFSEs in arc magmas are highly variable, although these elements relative to other similar incompatible elements (e.g., LILE) generally depleted. The variability of trace element contents and characteristics in arc magmas indicate that the fluids released by the slabs are not all supercritical fluids, or that the element carrying capacity of supercritical fluids varies with different physicochemical conditions. This raises an important issue: what are the key control factors of element migration ability of supercritical fluid? Except that the migration of multivalent elements is closely related to $f\mathrm{O}_2$, the factors affecting the migration of most trace elements such as LILE, REE and HFSE are temperature, pressure and fluid chemistry (including solute content, composition and volatiles F and Cl, etc.). The dehydration of subducting slabs forms a system of fluid coexisting with residual minerals, so the composition and trace element contents in the fluid are buffered by the residual minerals. Most trace elements have no independent minerals of their own and their contents in the fluid is actually controlled by the partition coefficients between fluid and residual mineral assemblage (residual solid). Ti and Zr

are the exceptions. These two elements in eclogites usually form accessory minerals rutile and zircon, which are highly concentrated in HFSE such as Ti, Nb, Ta, Zr and Hf. Therefore, HFSE migration is mainly controlled by the solubility of rutile and zircon in fluid. Therefore, investigations of the effects of temperature, pressure and fluid chemistry on the partition coefficients of trace elements between fluid and mineral and on the solubility of accessory minerals in fluid are critical to reveal the key control factors of element migration in supercritical fluid.

Due to the difficulty in quenching the fluid and supercritical fluid, experimental investigations on fluid composition and element partition coefficients in coexisting mineral +fluid systems at high pressures are still very limited. With the fluid freezing technique, Kessel et al. (2005b) determined the partition coefficients of trace elements (including LILE, HFSE and REE) between aqueous fluid, supercritical fluid and hydrous melt and residual solid in the eclogite-$\mathrm{H}_2\mathrm{O}$ system at the pressures of 4.0 and 6.0 GPa. They explained that the frozen liquids in the 4.0 GPa experiments were aqueous fluids (700–900°C) or hydrous melts (1000°C), while the frozen liquids in the 6.0 GPa experiments were supercritical fluids (800–1200°C). The following three points are the main results from their experiments. (1) The partition coefficients of trace elements between supercritical fluid and residual solid are close to those between hydrous melt and residual solid, but obviously higher than those between aqueous fluid and residual solid, indicating that supercritical fluid has higher elemental dissolution ability than aqueous fluid (Figure 2). (2) The partition coefficients of HFSEs (Nb, Ta, Ti, Zr, Hf) for aqueous fluid, supercritical fluid and hydrous melt are highly variable, which are controlled by the solubility of rutile and zircon in these liquids. (3) For both aqueous fluid and supercritical fluid, the partition coefficients of trace elements increase with increasing temperature, which seems to indicate that temperature is the most important factor affecting the element partitioning. However, the increase of temperature and pressure could lead to significant changes in solute content and composition in fluids in the eclogite-$\mathrm{H}_2\mathrm{O}$ system, so this result may not be the effect of temperature alone. In order to avoid the change of fluid composition in complex rock composition systems with of the variations of temperature and pressure, the effects of single variables such as temperature, pressure and fluid chemistry on the solubility of the accessory minerals can be investigated in a single accessory mineral+supercritical fluid system with high solute content (or low $\mathrm{H}_2\mathrm{O}$ content). Hayden and Manning (2011) and Chen et al. (2018) conducted experiments in the system of rutile+supercritical fluid (solute content >50 wt% and $\mathrm{H}_2\mathrm{O}$<50 wt%). They used quenching method and mass balance calculation to determine the solubility of rutile (TiO_2) in the supercritical $\mathrm{NaAlSi}_3\mathrm{O}_8$-$\mathrm{H}_2\mathrm{O}$ fluids and supercritical $\mathrm{KAlSi}_3\mathrm{O}_8$-$\mathrm{H}_2\mathrm{O}$
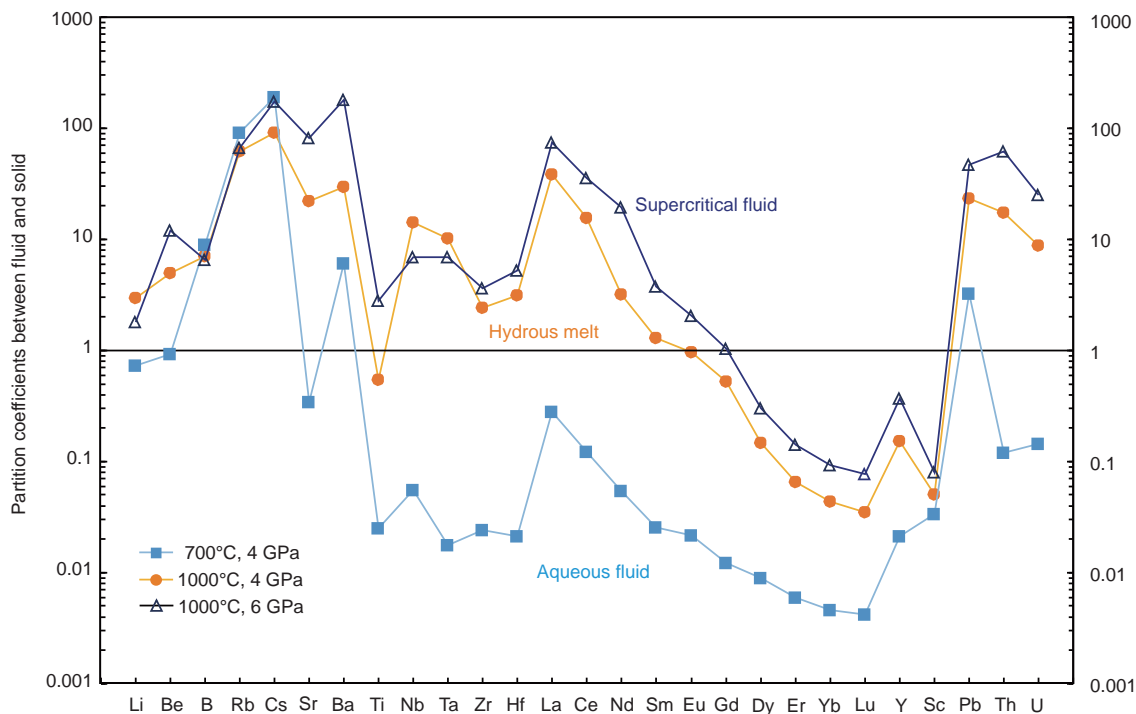
Figure 2   Fluid/solid partition coefficients of trace elements in the eclogite-H_2O system (from Ni et al., 2017, the data in this figure was taken from Kessel et al., 2005a), showing that trace element partition coefficients of supercritical fluid are close to those of hydrous melt, but obviously higher than those of aqueous fluid.

fluids. The results show that the solubility of TiO_2 in these supercritical fluids decreases with the increase of pressure but increases with the increase of temperature and solute content. By compilation of the literature data of TiO_2 solubility in pure water fluid, aqueous fluid, supercritical fluid and hydrous melt (Figure 3), we found that temperature only results in one order of magnitude increase in the TiO_2 solubility, but from pure water fluid, aqueous fluid, supercritical fluid to hydrous melt, TiO_2 solubility increases from ~10 to 10000 ppm with the variation over three orders of magnitude, suggesting that the fluid nature and fluid chemistry (including the solute content and composition) are the key factors controlling TiO_2 solubility. So far there are still few experimental studies on the influence of single variables of temperature, pressure and fluid chemistry on element migration in aqueous fluids and supercritical fluids, except for the systematic results of element Ti. In order to reveal the key factors that control element migration in aqueous fluids and supercritical fluids, investigation of the effects of single variables (fluid chemistry, pressure and temperature) on the solubility and partition coefficients of other elements is a promising direction in the future.

3. The behavior of transition elements during mantle wedge melting

In the last more than 10 years, the first row transition ele-

ments (FRTEs) Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn have attracted important attention in the determination of the lithology and fO_2 of mantle magmas and their source regions. Different from the highly incompatible characteristics of LILEs in the mantle minerals, the partitioning behavior of FRTEs during mantle partial melting vary from compatibility to incompatibility. The partitioning behavior of the elements with single valence state such as Sc, Ti, Mn, Co, Ni, Zn mainly depend on the residual mineral assemblage and temperature, whereas those of multivalent elements such as V and Fe not only depend on mineral assemblage and temperature, but also are the function of fO_2. Therefore, the partitioning behavior of FRTEs are applicable for tracing lithologic heterogeneity and fO_2 of the mantle wedge in subduction zones.

3.1 Partitioning behaviour of FRTEs and lithologic heterogeneity in mantle wedge

The partitioning behavior of divalent elements such as Mn, Fe, Co, Ni and Zn in the mantle melting process are sensitive to mineral assemblage and temperature (Le Roux et al., 2011; Davis et al., 2013). During mantle melting, the partition coefficients of these elements between olivine and mafic melt are always greater than those between pyroxene and mafic melt. Therefore, the abundances of these elements will be different for basaltic melts derived from peridotite compared to those derived from pyroxenite. The variations in the
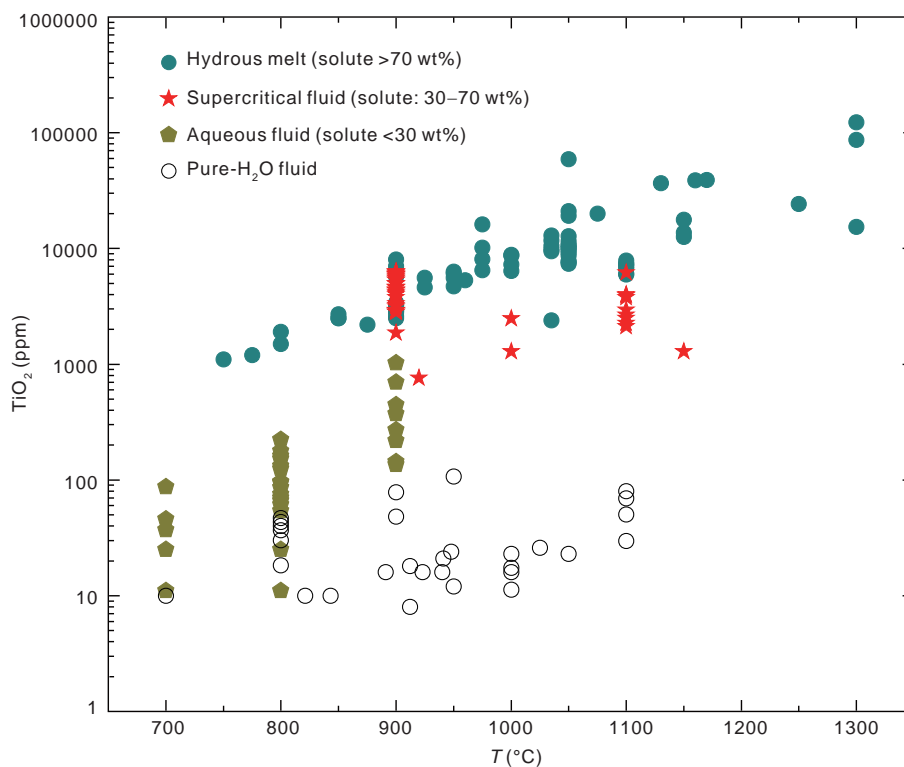
Figure 3 TiO_2 solubilities in pure water fluid, aqueous fluid, supercritical fluid and hydrous melt (data from Chen et al., 2018), showing that temperature only results in one order of magnitude increase in the TiO_2 solubility, but from pure water fluid, aqueous fluid, supercritical fluid to hydrous melt, TiO_2 solubility increases from ~10 to 10000 ppm with variation over three orders of magnitude, suggesting that the nature and chemistry (including the solute content and composition) of fluid are the key factors in control of TiO_2 solubility.

abundances and ratios of these elements in primitive mantle-derived magmas have important applications in defining the mineralogy (or lithology) heterogeneity of OIB and MORB source regions. Humayun et al. (2004) reported the high precision Fe/Mn ratios of MORBs and OIBs (Hawaii basalts and Iceland basalts). The results revealed that Fe/Mn>65 in Hawaii basalts and Fe/Mn<62 in MORBs and Iceland basalts. They therefore speculated that the high Fe/Mn ratios of Hawaii basalts indicated Fe enrichment in their source region due to interaction with the Earth's core, or that their source region may involve the cycled oceanic crust. Sobolev et al. (2005, 2007) further speculated that the source regions of OIB lavas with high Fe/Mn ratios involved cyclic oceanic crust. They showed that the abundances and ratios of transition elements such as Ni, Fe/Mn and Ni/Co in olivine phenocrysts of many intraplate basalts were significantly different from those in olivine of MORBs, and pointed out that these transition elements characteristics in the olivine phenocrysts implied that the source regions of intraplate basalts are more likely to be pyroxenite than peridotite. This is because Ni and Fe partition coefficients of olivine/melt are significantly higher than those of pyroxene/melt, so when pyroxene is the main residual phase, the coexisting melt must be relatively enriched in Fe and Ni. Le Roux et al. (2010, 2011) used Fe, Mn, Co, Ni, Zn to determine the mineralogy

of the OIB source regions. They found that the range of Zn/Fe in OIBs was greater than that in MORBs, and suggested that the high Zn/Fe ratios of OIBs require high proportion of pyroxene or pyroxenite in their source regions. Their experiments demonstrated that residual clinopyroxene can result in Zn/Fe fractionation, but olivine and orthopyroxene cannot (that is, the partition coefficient ratios of Zn/Fe for olivine/melt and orthopyroxene/melt are close to 1.0, whereas the partition coefficient ratio of Zn/Fe for clinopyroxene/melt is significantly less than 1.0). Davis et al. (2013) supplemented the experimental work of Le Roux et al. (2011). They concluded that Fe/Mn and Co/Fe are the best indicators to identify the lithologic heterogeneity in the source region of mantle-derived magmas.

In subduction zones, the metasomatism by hydrous melt and supercritical fluid may lead to lithologic heterogeneity in the mantle wedges. As we know, the mantle melting is water-bearing melting, the generation temperatures for primitive arc basalts are about 100°C on average lower than those for the MORB generation temperatures (Wang et al., 2019), and temperature has an important effect on the partitioning of elements. Therefore, it is important to obtain the partition coefficients of the FRTEs under the melting conditions of mantle wedges, but experimental study in this area is still almost blank. Under the *P-T* condition of subduction zones,

systematic determination of the partition coefficients of FRTEs for minerals (olivine, orthopyroxene, clinopyroxene, spinel, garnet)/melt will be of great significance for identification of the lithologic heterogeneity in the source regions of arc basalts.

3.2 Partitioning behavior of multivalent elements and the fO_2 of mantle wedge

Oxygen fugacity (fO_2) controls the species and behavior of multivalent elements during mantle melting, magma evolution, and volcanic eruption. It thus plays an important role in crust-mantle differentiation and magmatic evolution, migration and enrichment of ore-forming elements, and formation and evolution of the atmosphere. The relative fO_2 of the mantle decreases with depth, but whether or not the fO_2 of the upper mantle varies with the tectonic setting remains a mystery. Subduction zones and mid-ocean ridges are the two largest belts of mantle-derived magmas on Earth. Arc magmas are more oxidizing than MORBs. However, whether the mantle source of arc magmas is also more oxidizing than that of MORBs is strongly debated due to the conflicting results from different approaches of fO_2 estimation. Oxybarometers based on Fe valence states such as the Fe^{3+}-Fe^{2+} mineral equilibrium in mantle xenoliths (e.g., Ballhaus et al., 1994; Parkinson and Arculus, 1999; Evans et al., 2012) and based on Fe^{3+}/Fe_T ratios in basaltic lavas and olivine-hosted melt inclusions (e.g., Kelley and Cottrell, 2009; Kelley et al., 2010) indicate that arc mantle is oxidized relative to the MORB source. These studies suggested that the mantle wedges became relatively oxidized due to the metasomatism by slab-derived fluids and melts.

In contrast, the studies on V/Sc, Zn/Fe and Cu systematics (Lee et al., 2005, 2010, 2012) argued that arc mantle and oceanic mantle are similar in fO_2 based on the seemingly similar V/Sc and Zn/Fe ratios and Cu contents in primitive arc basalts and MORBs. V and Fe are multivalent elements and their mineral/melt partitioning behavior is fO_2-sensitive. Cu is a S-loving element whose partitioning behavior is controlled by sulfide, and both the stability of sulfide and the solubility of S in magma are fO_2-sensitive. Therefore, the use of V/Sc and Zn/Fe ratios and Cu contents to trace the fO_2 of mantle-derived magmas and their source regions may have important applications. Lee et al. (2005, 2010) pointed out that Sc and Zn are homovalent (Sc: 3+ and Zn: 2+) and redox-insensitive, and V and Sc are incompatible and Zn and Fe have similar compatibilities during the early crystallization of olivine. They thus thought that V/Sc and Zn/Fe ratios should preserve a record of fO_2 in the mantle source. Based on the similar Cu contents of MORBs and primitive arc basalts that they collected, Lee et al. (2012) believed that both arc mantle and oceanic mantle were saturated with sulfide during partial melting and they thought that sulfide

saturation provides evidence for similar fO_2 in arc mantle and oceanic mantle. Different from the result of Lee et al. (2005), recent data collection (Stolper and Bucholz, 2019) shows that the V/Sc ratios of arc basalts increase with decreasing magma age, suggesting that younger (<400–800 Ma) arc basalts and arc mantle are more oxidized.

Cu is an economically important element and a geochemical tracer element. Accurate Cu partition coefficient is the key to correctly understanding the geochemical behavior of Cu. However, there are serious problems about the previously obtained Cu partition coefficients between minerals and melts. For example, the Cu partition coefficients between minerals and silicate melts determined by previous phenocryst/matrix methods and by the conventional experiment techniques were mostly inaccurate. This makes it highly uncertain to understand quantitatively the behavior of Cu in magmatic processes. Liu et al. (2014) recently developed a new experimental technique to determine the Cu partition coefficients between mantle minerals (olivine, orthopyroxene, clinopyroxene, spinel) and basaltic melts. They found that Cu is highly incompatible in olivine, orthopyroxene, and clinopyroxene, and the partition coefficients for these minerals increase slightly with the increase of fO_2. The bulk partition coefficient (residual solid/melt) of Cu during mantle melting is 0.05 at relatively reduced conditions (<FMQ+2), whereas it is 0.12 at oxidizing conditions (>FMQ+2). Their mantle melting calculations show that the Cu contents of MORBs cannot be explained by the bulk partition coefficient of 0.05 (sulfide-free mantle mineral assemblage), which requires the presence of sulfide to raise the bulk partition coefficient. MORBs were thus formed at low fO_2 conditions with the presence of residual sulfide. Their calculations also show that the high Cu contents of 30–40% arc basalts can be explained by the bulk partition coefficient of 0.12 at oxidized conditions. Therefore, it cannot be excluded that the 30–40% arc basalts were formed at high fO_2 (>FMQ+2) in the absence of sulfide, so the fO_2 of the subarc mantle may be highly variable.

During mantle melting, the partition coefficients of most trace elements are the function of temperature, pressure and mineral composition. The recent experimental results of Wang et al. (2019) indicate that the partition coefficients of V between mantle minerals (olivine, orthopyroxene, clinopyroxene and spinel) and basaltic melt are not only sensitive to fO_2, but temperature also has an important influence. The mantle melting temperatures at mantle wedges are generally ~100°C lower than those under mid-ocean ridges. If temperature has different effects on the partition coefficients of V, Sc, Zn and Fe, then V/Sc and Zn/Fe ratios cannot be used as the indicators or proxies of fO_2 unless the effect of temperature is calibrated. So far the published V and Zn partition coefficients corresponding to the arc mantle melting conditions are still very rare (Wang et al., 2019). Therefore, in

order to use V/Sc and Zn/Fe to constrain the $f\mathrm{O_2}$ of mantle wedges, the accurate mineral/melt partition coefficients under arc mantle melting conditions are still required, which is the research direction in the future.

4. Elements (Nb/Ta and Dy/Yb) partitioning specificity and arc magma evolution tracer

The andesitic continent crust is mainly formed in subduction zones and is thought to be the result of arc magmatic differentiation (Rudnick and Fountain, 1995). Intermediate-felsic magmas are mainly derived from the differentiation of arc basalts at the reservoirs of the lower crust (Annen et al., 2006). Moreover, the evolution of arc magmas is characterized by Fe depletion, that is, the calcium-alkali evolution trend (e.g., Zimmer et al., 2010). Although magma mixing in subduction zone magmas is common due to continuous melt extraction from the mantle wedge and magma recharge, the variation trends of Zr and P in basalt-andesite-dacite–rhyolite suites indicate that the evolution of arc magmas is dominated by crystal fractionation (Lee and Bachmann, 2014). Early studies suggested that plagioclase was not the early crystal fractionation phase of subduction zone magmas due to the water-rich feature of the magmas, and the fractionation of magnetite and minor plagioclase resulted in the Fe depletion and calcium-alkali evolution tendency (Sisson and Grove, 1993). Recently, Tang et al. (2018, 2019), based on the more oxidizing feature of arc magmas compared with MORBs, pointed out that magnetite was not the cause of arc magma Fe depletion because magnetite could lead to Fe depletion, but at the same time will lead to more reducing in the evolving magmas. Based on the study of garnet pyroxenites (cumulates) from the lower crust at the thick crust regions of Arizona, they believed that the fractionation of Fe-rich and Fe^{3+}/Fe_T-low garnet was the fundamental cause of the Fe depletion and the Fe^{3+}/Fe_T increase (more oxidizing) in evolving arc magmas. However, the crystal fractionation of amphibole can also lead to magma Fe depletion, and the role played by amphibole fractionation in the generation of intermediate-felsic arc magmas has also attracted important attention (Davidson et al., 2007; Li et al., 2017).

   Which, amphibole or garnet, is the more important fractionation phase during the arc magmatic evolution and generation of intermediate-felsic magmas may be traced by the specificity of element partitioning behavior. The partitioning behavior of the rare earth elements Dy/Yb ratio between garnet and amphibole are quite different. Garnet has low Dy/Yb ratio, while amphibole has high Dy/Yb ratio (Figure 4a). Therefore, the fractionation dominated by garnet will lead to an increase of Dy/Yb ratio in the magma, while the fractionation dominated by amphibole will lead to a decrease of Dy/Yb. Data collected by Davidson et al. (2007)

show that Dy/Yb ratios of arc magmas generally decrease with increasing SiO_2, indicating that amphibole is more important in the differentiation process. Tang et al. (2018) used global arc magmas with MgO=4%±1% to plot $[Dy/Yb]_N$ vs. FeO_T/MgO, which shows that $[Dy/Yb]_N$ increases with the decrease of FeO_T/MgO (vice versa, $[Dy/Yb]_N$ decreases with the increase of FeO_T/MgO). They explained that this variation trend of $[Dy/Yb]_N$ vs. FeO_T/MgO in arc magmas is the result of garnet fractionation. However, nearly each of all the mafic silicate minerals has Mg partition coefficient always greater than Fe partition coefficient, and thus the crystal fractionation of mafic minerals will lead to the increase of FeO_T/MgO, that is, the fractional crystallization of magma will not lead to the decrease of FeO_T/MgO, but lead to the increase of FeO_T/MgO. Therefore, if the decrease of $[Dy/Yb]_N$ with the increase of FeO_T/MgO is the result of magmatic evolution, it exactly reflects the fractionation of amphibole.

   Another element tracer for arc magmatic evolution and continental crust formation is the Nb/Ta partitioning specificities of rutile and amphibole. Rutile has low Nb/Ta partition ratio, while amphibole has high Nb/Ta partition ratio (Figure 4b). Therefore, rutile fractionation will lead to the increase of magma Nb/Ta, while amphibole fractionation will lead to the decrease of magma Nb/Ta. The experimental results of Li et al. (2017) show that when the magma water content is less than 6–8%, amphibole/melt Nb/Ta partition coefficient is greater than 1.0, which will lead to the decrease of Nb/Ta in the melt. Since amphibole is the main crystalline phase in the basalt-H_2O system at middle-lower crustal conditions, they argued that the fractionation of amphibole ±biotite can explain the low Nb/Ta characteristics of continental crust. However, Tang et al. (2019) found that rutile and ilmenite in the Arizona garnet pyroxenite cumulates have high Nb/Ta ratios, and argued that rutile-bearing "arclogite" cumulation is the fundamental cause for the low Nb/Ta ratios in the continental crust. They used global arc magmas with SiO_2=70±1% to plot $[Dy/Yb]_N$ vs. Nb/Ta, which shows that Nb/Ta decreases with the increase of $[Dy/Yb]_N$. They thus explained that this trend is the result of crystal fractionation of rutile and garnet. However, when arc magmas evolve to ~70% SiO_2, the fractionation of biotite and zircon is important. Therefore, the fractionation of amphibole+biotite (high Nb/Ta ratios) can explain the low Nb/Ta ratios, while the fractionation of zircon (low Dy/Yb ratio) can explain the high Dy/Yb ratios in highly evolved magmas.

   There are still several key issues about the specific process of arc magma evolution: (1) The Fe depletion (calc-alkali evolution) trend in arc magmas controlled by fractionation of amphibole or garnet should be discussed in detail on the basis of arc-by-arc. (2) Clarification of the essential link between Fe depletion and Dy/Yb (crustal thickness proxy). Crustal thickness affects not only the residual mineral as-
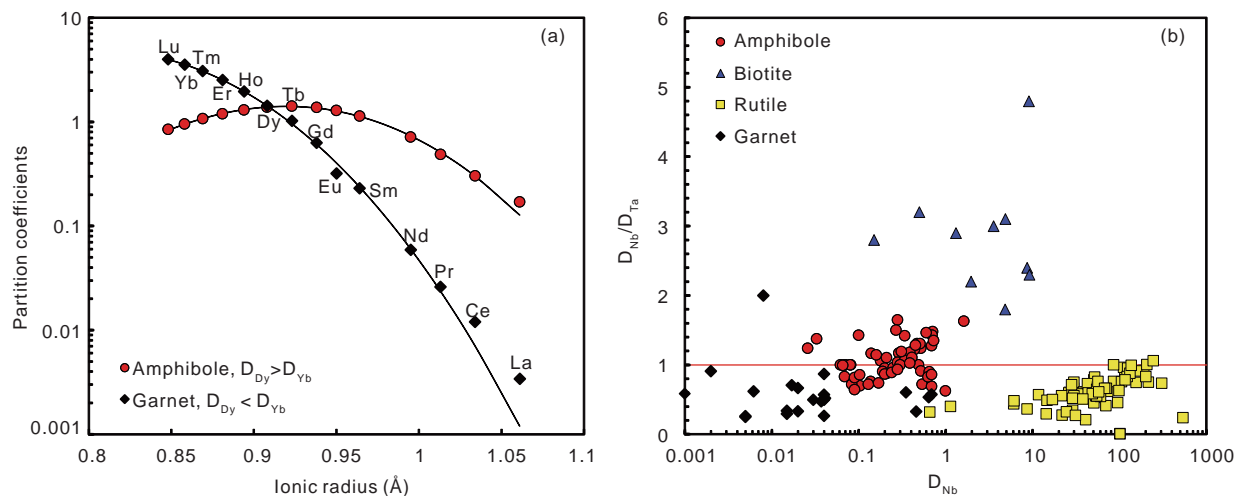
Figure 4   (a) Partition coefficients of REEs for amphibole/melt (Shimizu et al., 2017) and garnet/melt (Suzuki et al., 2012), indicating that amphibole has high Dy/Yb partitioning ratio, whereas garnet has low Dy/Yb partitioning ratio. (b) Partition coefficients of Nb and Ta for minerals (amphibole, biotite, rutile and garnet)/melt (data from Li et al., 2017), showing that amphibole and biotite have high Nb/Ta partition ratio, whereas rutile has low Nb/Ta partition ratio.

semblages and the initial magma Dy/Yb during mantle partial melting, but also the mineral assemblages and the magma Dy/Yb in intra-crustal evolution process. (3) What is the essential meaning of the high Nb/Ta ratios of rutile in the lower crustal cumulates? Magmatic orogeny usually experiences a process from thin crust to thick crust. Just like the transition from amphibolite facies to eclogite facies during slab subduction, is the lower crustal rutile-bearing garnet pyroxenites in the thickened crust regions also the result of the metamorphism of amphibole-rich cumulates? If so, the high Nb/Ta ratios of rutile in the lower crustal cumulates is completely possible to inherit the Nb/Ta ratios of original amphibole-dominated cumulates. (4) Clarification of the essential link between Fe depletion and fO_2 increase during arc magma evolution. For this issue, investigation of Fe^{3+} and Fe^{2+} partitioning behavior between mafic minerals (garnet, clinopyroxene and amphibole) and intermediate-felsic melts is of critical importance. The related results are very helpful not only to understanding whether the Fe depletion results at the same time in higher Fe^{3+}/Fe^{2+} during arc magma evolution, but also to understanding that the oxidizing characteristics of arc magmas is a result of magmatic differentiation, or only reflect high fO_2 in the mantle wedges (arc magma source regions).

5.   Behavior of sulfur and S-loving elements and porphyry deposit formation

Sulfur (S) is an important complexing agent of metallogenic elements. S-loving elements include Cu, Mo, Ag, Au, Pt group elements and some transition elements (Fe, Co, Ni), etc. These elements are also referred chalcophile elements. In the crust-mantle system, S and chalcophile elements always

accompany with each other. Cu, Mo and Au are the most eye-catching metallogenic elements in subduction zones and collision zones. They form porphyry deposits and the proportions of global resources are Cu>70%, Mo>50% and Au~20%. Therefore, porphyry deposits are the largest S and Cu anomalies in Earth's surface. Mantle partial melting leads to the dissolution of sulfide and the formation of mafic magmas containing S and chalcophile elements. Under the water-poor condition, differentiation of mafic magma results in sulfide (enriched with chalcophile elements) over-saturation to form sulfide-bearing cumulates or magmatic sulfide deposits. Under the water-rich condition, mafic magmas evolve to form intermediate-felsic magmas and then fluid saturation and exsolution take place and meantime the fluid dissolves and destroys sulfide, resulting in formation of ore-bearing fluids and porphyry deposits. Volcanic eruptions emit large amounts of S and other volatiles, causing short-term "volcanic winters" and long-term climate change. These processes involve element partitioning between silicate minerals/sulfides/magmatic melts/aqueous fluids, controlling the distribution of S and S-loving elements in each of these phases. Therefore, the partitioning behavior of S and chalcophile elements in magmatic-hydrothermal systems is of great significance for understanding the formation of magmatic sulfide deposits and porphyry deposits and the climate change.

For the formation of porphyry deposits, regardless of the island-arc and continent-margin metallogeny model (e.g., Heinrich et al., 2004) and the collision-setting metallogeny model (Hou et al., 2015), both them involve magma evolution from mafic to intermediate-felsic melts and subsequent fluid exsolution in the magma chamber. The enrichment of metals in ore-forming processes involves the partitioning of Cu, Mo and Au between minerals (silicate minerals, sulfide),

melt and fluid. Liu et al. (2014, 2015, 2018) systematically determined the Cu partition coefficients between silicate minerals (olivine, orthopyroxene, clinopyroxene, garnet, amphibole, plagioclase, Fe-Ti oxides) and mafic to felsic melts (Figure 5), which resolved the debate on the compatibility or incompatibility of Cu in silicate minerals. Cu is highly incompatible in mafic minerals, and the partition coefficients for these minerals are generally less than 0.2, insensitive to temperature, pressure and system composition, but slightly sensitive to fO_2. Cu is moderately incompatible to compatible in Fe-Ti oxides and the partition coefficients are 0.5–2.0. The partition coefficients of Au between mafic minerals, Fe-Ti oxides and melts are still absent due to analytical difficulty, but were estimated to be less than 0.01 (Müller and Groves, 2016). For the partition coefficients of Cu and Au between sulfides and silicate melts, a large number of natural samples and experimental results show that the partition coefficients range from <100 to >10000 (e.g., Rajamani and Naldrett, 1978; Ripley et al., 2002; Li and Audétat, 2012, 2013; Kiseeva and Wood, 2013, 2015; Zajacz et al., 2013; Mungall and Brenan, 2014; Li and Audétat, 2015; Li et al., 2019). The factors influencing Cu and Au partition coefficients are complex, including sulfide properties (solid sulfide or liquid sulfide), melt composition, temperature, fO_2 and fS_2 etc. For the partition coefficients of metal elements between fluids and silicate melts, the Cu partition coefficient is very sensitive to fluid chemistry; the experimental results (Candela and Holland, 1984) showed that the partition coefficient increase to higher than 100 with the increase of fluid [Cl]. While the partition coefficient of Au is not sensitive to fluid chemistry, and does not change with the fluid composition in the systems with and without sulfur ($D^{fluid/melt}$=15–30, Simon et al., 2006). Recently, Audétat (2019) measured the melt-fluid inclusions in natural quartz samples and found that $D^{fluid/melt}$ of Cu is ~50–80 and $D^{fluid/melt}$ of Mo is ~20.

In summary, sulfide and fluid control the behavior of chalcophile elements such as Cu and Au. Therefore, the stability of sulfide and the timing of fluid exsolution relative sulfide saturation, the mass ratio of fluid/sulfide as well as the Cu and Au fluid/melt partition coefficients are particularly important for understanding the enrichment behavior of Cu and Au in the magma-hydrothermal process. Under the condition that both sulfide and fluid are oversaturated, sulfide and fluid compete for Cu, Au and other chalcophile elements, just like tug-of-war or arm-wrestling. Whether the magmatic process leads to the formation of sulfide-bearing cumulates/magmatic sulfide deposits or it leads to the formation of magma-hydrothermal deposits (porphyry deposits) depends on which side (sulfide or fluid) wins. In the settings of rift valley and mantle plume, the magmas are relatively water-poor and fO_2-low, and sulfide wins and sinks due to its high density to form sulfide-bearing cumulates or magmatic
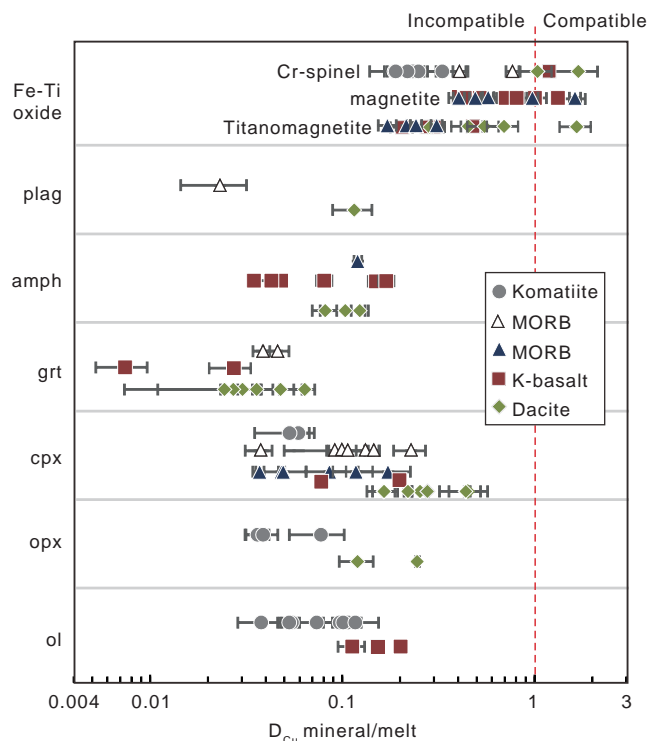

Figure 5   Partition coefficients of Cu between olivine(ol), orthopyroxene (opx), clinopyroxene(cpx), garnet(grt), amphibole(amph), plagioclase (plag), Fe-Ti oxides and mafic-felsic melts (from Liu et al., 2015), indicating that Cu in silicate minerals is highly incompatible (partition coefficients generally less than 0.2), and is incompatible to compatible in Fe-Ti oxides (partition coefficients between 0.2 and 2.0).

sulfide deposits. In the subduction environments, the magmas are water-rich and fO_2-high, and fluid wins, that is, fluids destroy sulfide and suppress sulfide saturation and the fluids float upward to form magma-hydrothermal deposits (porphyry deposits). The viewpoints on key control factors for porphyry deposit formation include: (1) The magmas have high fO_2 and thus sulfide (S^{2-}) cannot be stable; S in the magmas is present as S^{6+} and finally the ore-forming fluid is exsolved from the magmas (e.g., Sun et al., 2011; Lee and Tang, 2020). (2) Magma crystallization results in chalcophile elements enriched in sulfide. Further magma crystallization or decompression leads to fluid exsolution and sulfide is dissolved and destroyed by the fluid, and the resulting fluid is enriched in S and Cu (Wilkinson, 2013; Richards et al., 2015). (3) Beneath the porphyry deposit, there is a big magma chamber that provides a steady flux of ore-forming fluids. For this model, the Cu content in magma does not need to be highly enriched, but exsolution of a large amount of fluid, presence of channels gathering fluid and efficient precipitation mechanism are critical for the deposit formation (Heinrich et al., 2004; Audétat, 2010; Audétat and Pettke, 2003; Audétat, 2019). The former emphasizes the importance of fO_2, while the latter two emphasize the importance of fluid, and point out that fO_2 promotes sulfide dissolution but is not a critical metallogenic factor.

There are still several important unsolved issues about the formation of porphyry deposits in subduction zones and collision zones: (1) How tectonic activity triggers the mineralization burst in a short-term (Cooke et al., 2005). (2) What is the essential link between the formation and crustal thickness (Lee and Tang, 2020). (3) Whether the shallow magma chamber beneath the ore body can supply over 1 billion tons of S for a huge deposit (Audétat and Li, 2017). (4) The depth and timing of fluid exsolution from magma (that is, how Cu and Au migrate from the deep to the shallow) (Matjuschkin et al., 2016). (5) Why Cu/Au ratio is variable among single deposits and why sometimes Cu or Au form independent deposits (Cu or Au mineralization alone) (Cooke et al., 2005). The existence of these unsolved issues is mainly due to the fact that most previous experimental investigations only focused on the metallogenic process and mechanism at the mineralization sites (<5 km), while the deep magmatic process, especially the magmatic-hydrothermal process is rarely studied. The intermediate-felsic magmas mainly derived from the differentiation of mafic magmas at the lower crustal reservoirs (Annen et al., 2006). It is well known that (1) primitive arc magmas contain 2–6 wt% H_2O (Plank et al., 2013), (2) the generation of intermediate-felsic magmas requires >70% fractional crystallization (Farner and Lee, 2017), and (3) the formation of economic deposits is low-probability events (only one in 1000 exploration targets has economic value). It is widely believed that the high water content of magma is a favorable factor for metallogeny. Although the solubility of H_2O under the lower crustal pressures may be as high as 15–20 wt%, it is much possible that a mafic magma with 6 wt% H_2O could evolve into the intermediate-felsic magma containing up to 30% H_2O after undergoing 70% fractional crystallization. Therefore, under the conditions of the lower crust, fluid exsolution from the magmatic reservoir is much possible. The investigations of fluid exsolution and Cu and Au partitioning for fluid/melt and fluid/sulfide under such conditions may be the key to quantitatively understanding how Cu and Au migrate from the deep to the shallow and why Cu/Au ratio varies among deposits. The experimental study should be shifted from the shallow magma-hydrothermal systems to the deeper magma-hydrothermal systems in the future.

6.　Concluding remarks

The issues discussed in this paper includes the properties of fluids derived from subducting slabs and their ability in element transport, the behavior of FRTEs during mantle wedge melting, the specificity of element partitioning behavior during arc magma evolution, and the partitioning behavior of chalcophile elements and porphyry metallogeny. The following conclusions can be drawn.

(1) The element carrying capacity of supercritical fluid is of great significance for the understanding of element transfer from slab to wedge. Detailed investigation of the role of supercritical fluids may provide a new perspective for the element migration mechanism and material cycle process in subduction zones.

(2) Partition coefficients of the first row transition elements may have important application in defining lithologic heterogeneity and fO_2 in the mantle wedges. So far the related experimental investigations are still rare and thus needs to be strengthened.

(3) The specific process of arc magmatic calc-alkali evolution (Fe depletion) trend and its relationship with the variation of fO_2 are still controversial. The specificity of element partitioning (Dy/Yb, Nb/Ta, Fe^{3+}/Fe^{2+}) of amphibole, rutile, clinopyroxene and garnet is an important pathway to solve this controversy.

(4) Arc magma evolution and fluid exsolution at the lower crust magma chamber and the related Cu and Au fluid/melt and fluid/sulfide partitioning are critical to understanding the migration of Cu and Au from the deep reservoir to the shallow mineralization site. Such research should be strengthened in the future.

References

Annen C, Blundy J D, Sparks R S J. 2006. The genesis of intermediate and silicic magmas in deep crustal hot zones. J Petrol, 47: 505–539

Audétat A. 2010. Source and evolution of molybdenum in the porphyry Mo (-Nb) deposit at Cave Peak, Texas. J Petrol, 51: 1739–1760

Audétat A. 2019. The metal content of magmatic-hydrothermal fluids and its relationship to mineralization potential. Econ Geol, 114: 1033–1056

Audétat A, Keppler H. 2004. Viscosity of fluids in subduction zones. Science, 303: 513–516

Audétat A, Li W. 2017. The genesis of Climax-type porphyry Mo deposits: Insights from fluid inclusions and melt inclusions. Ore Geol Rev, 88: 436–460

Audétat A, Pettke T. 2003. The magmatic-hydrothermal evolution of two barren granites: A melt and fluid inclusion study of the Rito del Medio and Cañada Pinabete plutons in northern New Mexico (USA). Geochim Cosmochim Acta, 67: 97–121

Ballhaus C, Berry R F, Green D H. 1994. High-pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: Implications for the oxidation state of the upper mantle. Contrib Mineral Petrol, 118: 109

Candela P A, Holland H D. 1984. The partitioning of copper and molybdenum between silicate melts and aqueous fluids. Geochim Cosmochim Acta, 48: 373–380

Chen W, Xiong X L, Wang J T, Xue S, Li L, Liu X C, Ding X, Song M S. 2018. TiO₂ solubility and Nb and Ta partitioning in rutile-silica-rich supercritical fluid systems: Implications for subduction zone processes. J Geophys Res-Solid Earth, 123: 4765–4782

Cooke D R, Hollings P, Walshe J L. 2005. Giant porphyry deposits: Characteristics, distribution, and tectonic controls. Econ Geol, 100: 801–818

Cruz M F, Manning C E. 2015. Experimental determination of quartz solubility and melting in the system SiO_2-H_2O-NaCl at 15–20 kbar and 900–1100°C: Implications for silica polymerization and the formation of supercritical fluids. Contrib Mineral Petrol, 170: 35

Davidson J, Turner S, Handley H, MacPherson C, Dosseto A. 2007. Amphibole "sponge" in arc crust? Geology, 35: 787–790

Davis F A, Humayun M, Hirschmann M M, Cooper R S. 2013. Experimentally determined mineral/melt partitioning of first-row transition elements (FRTE) during partial melting of peridotite at 3 GPa. Geochim Cosmochim Acta, 104: 232–260

Defant M J, Drummond M S. 1990. Derivation of some modern arc magmas by melting of young subducted lithosphere. Nature, 347: 662–665

Dolejš D, Manning C E. 2010. Thermodynamic model for mineral solubility in aqueous fluids: Theory, calibration and application to model fluid-flow systems. Geofluids, 10: 20–40

Evans K A, Elburg M A, Kamenetsky V S. 2012. Oxidation state of subarc mantle. Geology, 40: 783–786

Faithfull J W, Dempster T J, MacDonald J M, Reilly M. 2018. Metasomatism and the crystallization of zircon megacrysts in Archaean peridotites from the Lewisian complex, NW Scotland. Contrib Mineral Petrol, 173: 99

Farner M J, Lee C T A. 2017. Effects of crustal thickness on magmatic differentiation in subduction zone volcanism: A global study. Earth Planet Sci Lett, 470: 96–107

Frezzotti M L, Ferrando S. 2015. The chemical behavior of fluids released during deep subduction based on fluid inclusions. Am Miner, 100: 352–377

Gao J, John T, Klemd R, Xiong X. 2007. Mobilization of Ti-Nb-Ta during subduction: Evidence from rutile-bearing dehydration segregations and veins hosted in eclogite, Tianshan, NW China. Geochim Cosmochim Acta, 71: 4974–4996

Hack A C, Thompson A B, Aerts M. 2007. Phase relations involving hydrous silicate melts, aqueous fluids, and minerals. Rev Mineral Geochem, 65: 129–185

Hayden L A, Manning C E. 2011. Rutile solubility in supercritical NaAl-Si_3O_8-H_2O fluids. Chem Geol, 284: 74–81

Heinrich C A, Driesner T, Stefánsson A, Seward T M. 2004. Magmatic vapor contraction and the transport of gold from the porphyry environment to epithermal ore deposits. Geology, 32: 761–764

Hermann J, Rubatto D. 2014. Subduction of Continental Crust to Mantle Depth. In: Holland H D, Turekian K, eds. KTreatise on Geochemistry, 2nd ed. Amsterdam: Elsevier. 309–340

Hermann J, Spandler C, Hack A, Korsakov A. 2006. Aqueous fluids and hydrous melts in high-pressure and ultra-high pressure rocks: Implications for element transfer in subduction zones. Lithos, 92: 399–417

Hermann J, Zheng Y F, Rubatto D. 2013. Deep fluids in subducted continental crust. Elements, 9: 281–287

Hou Z Q, Yang Z M, Lu Y J, Kemp A, Zheng Y C, Li Q Y, Tang J X, Yang Z S, Duan L F. 2015. A genetic linkage between subduction- and collision-related porphyry Cu deposits in continental collision zones. Geology, 43: 247–250

Huang J, Xiao Y, Gao Y, Hou Z, Wu W. 2012. Nb-Ta fractionation induced by fluid-rock interaction in subduction-zones: Constraints from UHP eclogite- and vein-hosted rutile from the Dabie orogen, Central-Eastern China. J Metamorph Geol, 30: 821–842

Humayun M, Qin L, Norman M D. 2004. Geochemical evidence for excess iron in the mantle beneath Hawaii. Science, 306: 91–94

Hunt J D, Manning C E. 2012. A thermodynamic model for the system SiO_2-H_2O near the upper critical end point based on quartz solubility experiments at 500–1100°C and 5–20 kbar. Geochim Cosmochim Acta, 86: 196–213

Kalfoun F, Ionov D, Merlet C. 2002. HFSE residence and Nb/Ta ratios in metasomatised, rutile-bearing mantle peridotites. Earth Planet Sci Lett, 199: 49–65

Kawamoto T. 2006. Hydrous phases and water transport in the subducting slab. Rev Mineral Geochem, 62: 273–289

Kawamoto T, Kanzaki M, Mibe K, Matsukage K N, Ono S. 2012. Separation of supercritical slab-fluids to form aqueous fluid and melt components in subduction zone magmatism. Proc Natl Acad Sci USA, 109: 18695–18700

Kelley K A, Plank T, Newman S, Stolper E M, Grove T L, Parman S, Hauri E H. 2010. Mantle melting as a function of water content beneath the Mariana Arc. J Petrol, 51: 1711–1738

Kelley K A, Cottrell E. 2009. Water and the oxidation state of subduction zone magmas. Science, 325: 605–607

Keppler H. 2017. Fluids and trace element transport in subduction zones. Am Miner, 102: 5–20

Kessel R, Schmidt M W, Ulmer P, Pettke T. 2005a. Trace element signature of subduction-zone fluids, melts and supercritical liquids at 120–180 km depth. Nature, 437: 724–727

Kessel R, Ulmer P, Pettke T, Schmidt M W, Thompson A B. 2005b. The water-basalt system at 4 to 6 GPa: Phase relations and second critical endpoint in a K-free eclogite at 700 to 1400°C. Earth Planet Sci Lett, 237: 873–892

Kiseeva E S, Wood B J. 2013. A simple model for chalcophile element partitioning between sulphide and silicate liquids with geochemical applications. Earth Planet Sci Lett, 383: 68–81

Kiseeva E S, Wood B J. 2015. The effects of composition and temperature on chalcophile and lithophile element partitioning into magmatic sulphides. Earth Planet Sci Lett, 424: 280–294

Le Roux V, Dasgupta R, Lee C T A. 2011. Mineralogical heterogeneities in the Earth's mantle: Constraints from Mn, Co, Ni and Zn partitioning during partial melting. Earth Planet Sci Lett, 307: 395–408

Le Roux V, Lee C T A, Turner S J. 2010. Zn/Fe systematics in mafic and ultramafic systems: Implications for detecting major element heterogeneities in the Earth's mantle. Geochim Cosmochim Acta, 74: 2779–2796

Lee C T A, Bachmann O. 2014. How important is the role of crystal fractionation in making intermediate magmas? Insights from Zr and P systematics. Earth Planet Sci Lett, 393: 266–274

Lee C T A, Luffi P, Plank T, Dalton H, Leeman W P. 2009. Constraints on the depths and temperatures of basaltic magma generation on Earth and other terrestrial planets using new thermobarometers for mafic magmas. Earth Planet Sci Lett, 279: 20–33

Lee C T, Luffi P, Le Roux V, Dasgupta R, Albarede F, Leeman W P. 2010. The redox state of arc mantle using Zn/Fe systematics. Nature, 468: 681–685

Lee C T A, Tang M. 2020. How to make porphyry copper deposits. Earth Planet Sci Lett, 529: 115868

Lee C T A, Luffi P, Chin E J, Bouchet R, Dasgupta R, Morton D M, Le Roux V, Yin Q, Jin D. 2012. Copper systematics in arc magmas and implications for crust-mantle differentiation. Science, 336: 64–68

Lee C T A, Leeman W P, Canil D, Li Z X A. 2005. Similar V/Sc systematics in MORB and arc basalts: Implications for the oxygen fugacities of their mantle source regions. J Petrol, 46: 2313–2336

Li H Y, Chen R X, Zheng Y F, Hu Z. 2016. The crust-mantle interaction in continental subduction channels: Zircon evidence from orogenic peridotite in the Sulu orogen. J Geophys Res-Solid Earth, 121: 687–712

Li L, Xiong X L, Liu X C. 2017. Nb/Ta fractionation by amphibole in hydrous basaltic systems: Implications for arc magma evolution and continental crust formation. J Petrol, 58: 3–28

Li Y, Audétat A. 2012. Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and hydrous basanite melt at upper mantle conditions. Earth Planet Sci Lett, 355-356: 327–340

Li Y, Audétat A. 2013. Gold solubility and partitioning between sulfide liquid, monosulfide solid solution and hydrous mantle melts: Implications for the formation of Au-rich magmas and crust-mantle differentiation. Geochim Cosmochim Acta, 118: 247–262

Li Y, Audétat A. 2015. Effects of temperature, silicate melt composition,

and oxygen fugacity on the partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and silicate melt. Geochim Cosmochim Acta, 162: 25–45

Li Y, Feng L, Kiseeva E S, Gao Z, Guo H, Du Z, Wang F, Shi L. 2019. An essential role for sulfur in sulfide-silicate melt partitioning of gold and magmatic gold transport at subduction settings. Earth Planet Sci Lett, 528: 115850

Liu X, Matsukage K N, Li Y, Takahashi E, Suzuki T, Xiong X. 2018. Aqueous fluid connectivity in subducting oceanic crust at the mantle transition zone conditions. J Geophys Res-Solid Earth, 123: 6562–6573

Liu X, Matsukage K N, Nishihara Y, Suzuki T, Takahashi E. 2019. Stability of the hydrous phases of Al-rich phase D and Al-rich phase H in deep subducted oceanic crust. Am Miner, 104: 64–72

Liu X, Xiong X. 2018. Copper. In: White W M, Marty B, Yurimoto H, eds. Encyclopedia of Geochemistry. Cham: Springer Publication. 303–305

Liu X, Xiong X, Audétat A, Li Y, Song M, Li L, Sun W, Ding X. 2014. Partitioning of copper between olivine, orthopyroxene, clinopyroxene, spinel, garnet and silicate melts at upper mantle conditions. Geochim Cosmochim Acta, 125: 1–22

Liu X, Xiong X, Audétat A, Li Y. 2015. Partitioning of Cu between mafic minerals, Fe-Ti oxides and intermediate to felsic melts. Geochim Cosmochim Acta, 151: 86–102

Liu X, Zhang L F, Alistair H C, Zheng H F, Hu X M, Chang L L, He Q. 2009. Effect of water on the partial melting process of some silicate system: Important implication of the second critical endpoint. Acta Petrol Sin, 25: 3407–3421

Malaspina N, Hermann J, Scambelluri M, Compagnoni R. 2006. Polyphase inclusions in garnet-orthopyroxenite (Dabie Shan, China) as monitors for metasomatism and fluid-related trace element transfer in subduction zone peridotite. Earth Planet Sci Lett, 249: 173–187

Manning C E. 2004. The chemistry of subduction-zone fluids. Earth Planet Sci Lett, 223: 1–16

Matjuschkin V, Blundy J D, Brooker R A. 2016. The effect of pressure on sulphur speciation in mid- to deep-crustal arc magmas and implications for the formation of porphyry copper deposits. Contrib Mineral Petrol, 171: 66

Mibe K, Chou I M, Bassett W A. 2008. *In situ* Raman spectroscopic investigation of the structure of subduction-zone fluids. J Geophys Res, 113: B04208

Mibe K, Kanzaki M, Kawamoto T, Matsukage K N, Fei Y, Ono S. 2007. Second critical endpoint in the peridotite-H_2O system. J Geophys Res, 112: B03201

Mibe K, Kawamoto T, Matsukage K N, Fei Y, Ono S. 2011. Slab melting versus slab dehydration in subduction-zone magmatism. Proc Natl Acad Sci USA, 108: 8177–8182

Müller D, Groves D. 2016. Postassic Igneous Rocks and Associated Gold-Copper Mineralization. 4th ed. Berlin: Spring. 1–297

Mungall J E, Brenan J M. 2014. Partitioning of platinum-group elements and Au between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile elements. Geochim Cosmochim Acta, 125: 265–289

Newton R C, Manning C E. 2008. Thermodynamics of SiO_2-H_2O fluid near the upper critical end point from quartz solubility measurements at 10 kbar. Earth Planet Sci Lett, 274: 241–249

Ni H W, Zhang L, Guo X. 2016. Water and partial melting of Earth's mantle. Sci China Earth Sci, 59: 720–730

Ni H, Zhang L, Xiong X, Mao Z, Wang J. 2017. Supercritical fluids at subduction zones: Evidence, formation condition, and physicochemical properties. Earth-Sci Rev, 167: 62–71

Ohtani E. 2015. Hydrous minerals and the storage of water in the deep mantle. Chem Geol, 418: 6–15

Parkinson I J, Arculus R J. 1999. The redox state of subduction zones: Insights from arc-peridotites. Chem Geol, 160: 409–423

Pearson D G, Brenker F E, Nestola F, McNeill J, Nasdala L, Hutchison M T, Matveev S, Mather K, Silversmit G, Schmitz S, Vekemans B, Vincze L. 2014. Hydrous mantle transition zone indicated by ringwoodite included within diamond. Nature, 507: 221–224

Plank T, Kelley K A, Zimmer M M, Hauri E H, Wallace P J. 2013. Why do mafic arc magmas contain ~4 wt% water on average? Earth Planet Sci Lett, 364: 168–179

Poli S, Schmidt M W. 2002. Petrology of subducted slabs. Annu Rev Earth Planet Sci, 30: 207–235

Pommier A. 2014. Geophysical assessment of migration and storage conditions of fluids in subduction zones. Earth Planet Sp, 66: 38

Rajamani V, Naldrett A J. 1978. Partitioning of Fe, Co, Ni, and Cu between sulfide liquid and basaltic melts and the composition of Ni-Cu sulfide deposits. Econ Geol, 73: 82–93

Rapp J F, Klemme S, Butler I B, Harley S L. 2010. Extremely high solubility of rutile in chloride and fluoride-bearing metamorphic fluids: An experimental investigation. Geology, 38: 323–326

Richards J P, Cawood P A, Wyman D, Cassidy K, Hollings P. 2015. The oxidation state, and sulfur and Cu contents of arc magmas: Implications for metallogeny. Lithos, 233: 27–45

Ripley E M, Brophy J G, Li C. 2002. Copper solubility in a basaltic melt and sulfide liquid/silicate melt partition coefficients of Cu and Fe. Geochim Cosmochim Acta, 66: 2791–2800

Rudnick R L, Fountain D M. 1995. Nature and composition of the continental crust: A lower crustal perspective. Rev Geophys, 33: 267–309

Schmidt M W. 2015. Melting of pelitic sediments at subarc depths: 2. Melt chemistry, viscosities and a parameterization of melt composition. Chem Geol, 404: 168–182

Shen A H, Keppler H. 1997. Direct observation of complete miscibility in the albite-H_2O system. Nature, 385: 710–712

Shimizu K, Liang Y, Sun C, Jackson C, Saal A. 2017. Parameterized lattice strain models for REE partitioning between amphibole and silicate melt. Am Mineral, 102: 2254–2267

Simon A C, Pettke T, Candela P A, Piccoli P M, Heinrich C A. 2006. Copper partitioning in a melt-vapor-brine-magnetite-pyrrhotite assemblage. Geochim Cosmochim Acta, 70: 5583–5600

Sisson T W, Grove T L. 1993. Experimental investigations of the role of H_2O in calc-alkaline differentiation and subduction zone magmatism. Contrib Mineral Petrol, 113: 143–166

Sobolev A V, Hofmann A W, Kuzmin D V, Yaxley G M, Arndt N T, Chung S L, Danyushevsky L V, Elliott T, Frey F A, Garcia M O, Gurenko A A, Kamenetsky V S, Kerr A C, Krivolutskaya N A, Matvienkov V V, Nikogosian I K, Rocholl A, Sigurdsson I A, Sushchevskaya N M, Teklay M. 2007. The amount of recycled crust in sources of mantle-derived melts. Science, 316: 412–417

Sobolev A V, Hofmann A W, Sobolev S V, Nikogosian I K. 2005. An olivine-free mantle source of Hawaiian shield basalts. Nature, 434: 590–597

Spandler C, Hermann J, Arculus R, Mavrogenes J. 2004. Geochemical heterogeneity and element mobility in deeply subducted oceanic crust; insights from high-pressure mafic rocks from New Caledonia. Chem Geol, 206: 21–42

Stolper D A, Bucholz C E. 2019. Neoproterozoic to early Phanerozoic rise in island arc redox state due to deep ocean oxygenation and increased marine sulfate levels. Proc Natl Acad Sci USA, 116: 8746–8755

Sun W, Zhang H, Ling M X, Ding X, Chung S L, Zhou J, Yang X Y, Fan W. 2011. The genetic association of adakites and Cu-Au ore deposits. Int Geol Rev, 53: 691–703

Suzuki T, Hirata T, Yokoyama T D, Imai T, Takahashi E. 2012. Pressure effect on element partitioning between minerals and silicate melt: Melting experiments on basalt up to 20 GPa. Phys Earth Planet Inter, 208-209: 59–73

Syracuse E M, van Keken P E, Abers G A, Suetsugu D, Bina C, Inoue T, Wiens D, Jellinek M. 2010. The global range of subduction zone thermal models. Phys Earth Planet Inter, 183: 73–90

Tang M, Erdman M, Eldridge G, Lee C T A. 2018. The redox "filter" beneath magmatic orogens and the formation of continental crust. Sci Adv, 4: eaar4444

Tang M, Lee C T A, Chen K, Erdman M, Costin G, Jiang H. 2019. Nb/Ta systematics in arc magma differentiation and the role of arclogites in continent formation. Nat Commun, 10: 235

Wang J, Xiong X, Takahashi E, Zhang L, Li L, Liu X. 2019. Oxidation state of arc mantle revealed by partitioning of V, Sc, and Ti between mantle minerals and basaltic melts. J Geophys Res-Solid Earth, 124: 4617–4638

Wilkinson J J. 2013. Triggers for the formation of porphyry ore deposits in magmatic arcs. Nat Geosci, 6: 917–925

Wörner G, Mamani M, Blum-Oeste M. 2018. Magmatism in the central andes. Elements, 14: 237–244

Xiao Y, Niu Y, Li H, Wang H, Liu X, Davidson J. 2014. Trace element budgets and (re-)distribution during subduction-zone ultrahigh pressure metamorphism: Evidence from Western Tianshan, China. Chem Geol, 365: 54–68

Xiao Y L, Sun H, Gu H O, Huang J, Li W Y, Liu L. 2015. Fluid/melt in continental deep subduction zones: Compositions and related geochemical fractionations. Sci China Earth Sci, 58: 1457–1476

Xiong X L. 2006. Trace element evidence for growth of early continental crust by melting of rutile-bearing hydrous eclogite. Geology, 34: 945–948

Xiong X L, Adam J, Green T H. 2005. Rutile stability and rutile/melt HFSE partitioning during partial melting of hydrous basalt: Implications for TTG genesis. Chem Geol, 218: 339–359

Xiong X, Keppler H, Audétat A, Ni H, Sun W, Li Y. 2011. Partitioning of Nb and Ta between rutile and felsic melt and the fractionation of Nb/Ta during partial melting of hydrous metabasalt. Geochim Cosmochim Acta, 75: 1673–1692

Zajacz Z, Candela P A, Piccoli P M, Sanchez-Valle C, Wälle M. 2013. Solubility and partitioning behavior of Au, Cu, Ag and reduced S in magmas. Geochim Cosmochim Acta, 112: 288–304

Zhang Z M, Shen K, Sun W D, Liu Y S, Liou J G, Shi C, Wang J L. 2008. Fluids in deeply subducted continental crust: Petrology, mineral chemistry and fluid inclusion of UHP metamorphic veins from the Sulu orogen, eastern China. Geochim Cosmochim Acta, 72: 3200–3228

Zheng J, Xiong Q, Zhao Y, Li W. 2019. Subduction-zone peridotites and their records of crust-mantle interaction. Sci China Earth Sci, 62: 1033–1052

Zheng Y F, Chen R X, Xu Z, Zhang S B. 2016. The transport of water in subduction zones. Sci China Earth Sci, 59: 651–682

Zheng Y F. 2019. Subduction zone geochemistry. Geosci Front, 10: 1223–1254

Zheng Y F, Hermann J. 2014. Geochemistry of continental subduction-zone fluids. Earth Planet Sp, 66: 93

Zheng Y F, Xia Q X, Chen R X, Gao X Y. 2011. Partial melting, fluid supercriticality and element mobility in ultrahigh-pressure metamorphic rocks during continental collision. Earth-Sci Rev, 107: 342–374

Zimmer M M, Plank T, Hauri E H, Yogodzinski G M, Stelling P, Larsen J, Singer B, Jicha B, Mandeville C, Nye C J. 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: 2411–2444

Zotov N, Keppler H. 2002. Silica speciation in aqueous fluids at high pressures and high temperatures. Chem Geol, 184: 71–82

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