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SOURCES AND PROCESSES IN ARC MAGMATISM: THE CRUCIAL ROLE OF WATER

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(12 figures)

ABSTRACT Arc magmatism distinguishes itself from magmatism in other tectonic settings by the crucial role that water plays in its petrogenesis. Water influences the geochemistry of the sub-arc mantle, by transferring fluid-soluble elements from the slab into the mantle. Water probably also carries the oxidised signature from the slab into the mantle wedge. The ubiquitous negative Ti-anomaly in arc magmas may reflect an increase of the compatibility of titanium in the solid residue during partial melting in water-bearing peridotite. Finally, water also has a strong influence on the identity of minerals involved in crystal fractionation processes, and gives rise to the low-Fe (calc-alkaline) fractionation trend by lowering the temperature at which the silicates start crystallising, without influencing the crystallisation temperature of iron-oxides.

KEYWORDS: subduction, partial melting, crystal fractionation, volcanism

1. Introduction

Subduction is one of the fundamental processes on our planet, the necessary counterpart of spreading at mid-ocean ridges, and the link between the Earth’s interior and surface. Oceanic lithosphere is created at divergent plate margins, due to adiabatic upwelling of the asthenospheric mantle, leading to partial melting, the formation of basalts and thereby the creation of oceanic crust. The residue of this melting process, together with intrusives and ultramafic cumulates, forms the lower part of the oceanic lithosphere. Contact with the 2°C “boundary condition” of the ocean causes the newly formed lithosphere to cool down, increasing both in thickness and density with time. Interaction with seawater, both during the early high-temperature hydrothermal and the later halmyrolytic stage of weathering, changes the original anhydrous mineralogy of basalt and peridotite to a hydrous assemblage of ferri-oxihydroxides, chlorite and serpentine. While the newly created oceanic lithosphere moves away from the mid-ocean ridge, it will become covered by sediment, of either pelagic or continental origin. After a time interval that varies from a few to 180 million years, the whole package of partially altered oceanic lithosphere with or without its sedimentary cover will be subducted. During its journey into the earth’s interior, it will undergo a series of mineralogical reactions, among which the devolatilisation reactions that cause partial melting of the mantle, and thereby arc magmatism (Hacker, 2008). Ultimately, the subducted slab may end up at the core-mantle boundary (van der Hilst et al., 1997), where it might become part of a deep-seated mantle plume that feeds intraplate volcanoes such as Hawaii (Zhao, 2001). Apart from the information provided by seismicity, we cannot observe directly what happens in subduction zones and we must rely on messengers that return from this, for us inaccessible, realm. Magma is one of these messengers. In this contribution, I will give an elementary overview of the geochemical tools used to determine the geochemical input from different sources into the arc, and the processes that operate during the formation and differentiation of the magma, and how these determine the final geochemical and petrological signature of arc magmas. The interaction of these two parameters, sources and processes, will be shown to be of importance by a discussion of the cause for the commonly observed lack of iron enrichment in arc magmas during differentiation, also known as the calc-alkaline trend (Miyashiro, 1974), which sets arc magmas apart from magmas generated in other tectonic settings such as mid-ocean ridges or hot spots. Water appears to play a crucial role in providing arc magmas with their unique geochemical and petrological signature.

2. Identification of sources and processes: the geochemical tools

Magmatic geochemists rely heavily on three tools for the identification of sources and processes: bivariate (x-y) diagrams, normalised trace element diagrams (“spidergrams”) and ratios of (heavy) radiogenic isotopes. The importance of the radiogenic isotope ratios is that they only reflect sources, not processes; normalised trace
element diagrams show both influences and bivariate diagrams mainly reflect processes acting upon the magma.

In its simplest form, a normalised trace element diagram, also called a “spidergram” or extended Corryell-Masuda diagram (Hofmann et al., 1986), shows the concentration of trace elements for a single sample (typically a basalt), divided by the concentrations of these elements in a “model” rock, such as normal-Mid-Ocean-Ridge Basalt (N-MORB), or primitive mantle (Sun & McDonough, 1989). Trace elements are typically ordered by their preference for entering the melt phase during partial melting of a dry peridotitic mantle source. If elements prefer the melt phase, they are called “incompatible”, if they prefer the residual solid phase, they are compatible. In Fig. 1, the most incompatible element is Cs, the least incompatible Lu. This type of diagram will reflect both the input of different source materials in a single magma (MORB has a completely different trace element signature than upper continental crust or subducting sediments, Fig. 1), but also partial melting processes: a very small degree of partial melting will cause a greater enrichment of the most incompatible elements than of the less incompatible elements. If the mantle source were represented by a straight line in this type of diagram, then a small % of melt from this source would show a pattern that is sloping downwards from left to right; larger degrees of melting would cause the pattern to become flatter, until, at 100% melting, it would of...
course be horizontal again, as it needs to have the same composition as the original source. The percentage melting that takes place in arcs is generally estimated to lie between 5 and 20% (Stolper & Newman, 1994). In order to correctly interpret processes occurring in the mantle, such as partial melting or the addition of sedimentary material from the subducting plate, one should only plot the composition of magmas which have undergone minimal modification since leaving the mantle, i.e. primary magmas, typically basalts. More evolved (and thereby more felsic) magmas will generally have been affected by processes such as fractional crystallisation, whereby crystals have formed and have become separated from the remaining silicate liquid. This will deplete the magma in the elements that are compatible in fractionating mineral phases, such as Ti and Sr, which partition into magnetite and plagioclase respectively.

Ratios of radiogenic isotopes reflect the parent/daughter element ratios and the time elapsed since the parent/daughter ratio was changed, or, in one phrase: the time-integrated parent/daughter ratio. As can be learned from Fig. 2, the primitive mantle has a lower Rb/Sr ratio than average subducting sediment. As $^{87}$Rb decays to $^{87}$Sr, whereas $^{86}$Sr is a stable isotope, not produced by radioactive decay, sediment will, over time develop a higher $^{87}$Sr/$^{86}$Sr ratio than the primitive mantle. In principle, these isotope ratios do not change during partial melting or fractional crystallisation: if the mantle source that melts has a $^{87}$Sr/$^{86}$Sr ratio of 0.702, then both a 5% and a 20% partial melt will have an isotope ratio of 0.702, even though the Rb/Sr ratios of these two partial melts will be different, as Rb is more incompatible than Sr. Of course, over millions of years, the 5% and the 20% melt will develop different $^{87}$Sr/$^{86}$Sr ratios. Apart from $^{87}$Sr/$^{86}$Sr commonly used “tracers” are $^{143}$Nd/$^{144}$Nd, $^{176}$Hf/$^{177}$Hf (both high in mantle sources, low in sediments and continental crust: Fig. 2) and $^{206}$Pb/$^{204}$Pb ratios (like $^{87}$Sr/$^{86}$Sr, high in sediment and continental crust, lower in mantle sources).

Differentiation processes such as crystal fractionation, tend to cause, among other changes, a major increase in the magma’s silica and decrease in its magnesium content, causing low-silica basalt to differentiate into andesite, dacite and high-silica rhyodacite and rhyolite. Differentiation processes are generally studied with the help of bivariate diagrams, especially Harker variation diagrams, where an element or oxide is plotted against the SiO$_2$ content of the magma (Fig. 3). Crystal fractionation tends to result in curved or kinked trends (Fig. 3A), reflecting a change in an element’s degree of (in)compatibility, because of a change in the fractionating mineral assemblage and/or changes in temperature or melt structure during differentiation (Allègre & Minster, 1978). Mixing between two components, such as two magmas, or a batch of magma and a batch of cumulate crystals, should always produce straight lines on these diagrams (Fig. 3B).

3. Sources and processes involved in magma generation

3.1. Sources and processes in the sub-arc mantle

Arc magmatism occurs where an oceanic plate is subducted underneath another oceanic or continental plate, creating an island arc or a continental arc, respectively. During the 1960’s and 70’s, debate raged about what actually melted to create arc magmas (Green, 1972): the subducted slab or

![Figure 3: Harker variation diagrams (= bivariate diagrams with SiO$_2$ on x-axis) for volcanic whole rock analyses. A: TiO$_2$ versus SiO$_2$ for arc volcano Rinjani (Lombok, Indonesia; database M. Elburg and J. Foden) illustrating incompatible behaviour of titanium in mafic (basaltic) rocks, and compatible behaviour in intermediate to felsic samples, in which titaniferous magnetite was a fractionating mineral. B: Cr versus SiO$_2$ for two suites from Santorini (Skaros and Minoan; GeoRoc database) and samples from the western Aegean arc (Aegina, Methana and Poros; Elburg & Smet, unpublished data). The very rapid decrease of Cr with SiO$_2$ content for the combined Skaros-Minoan trend reflects fractionation of Cr-rich minerals such as spinel and clinopyroxene. The straight Methana-Poros trend is likely to be caused by mixing between felsic and mafic components.](image-url)
the mantle. This debate was largely fed by the idea that arc magmas have an andesitic composition, and can therefore not be formed by partial melting of the earth’s mantle. Although arc lavas may be, on average, andesitic in composition, trace element patterns indicate that they are typically differentiation products of basaltic magma, formed by partial melting of the mantle wedge, and not slab melts (Nicholls & Whitford, 1976). Geophysical models indicate that partial melting of the subducted slab is limited to its very top, except in the case of very young and therefore hot slabs (Peacock, 2003).

The paradoxical situation that partial melting of the mantle occurs in an area where the mantle is cooled down by the introduction of a subducted slab can be explained by the fact that this slab is not just cold, but also wet. Water is liberated from the slab during a series of both pressure- and temperature-dependent mineral reactions (Schmidt & Poli, 1998). Part of this water will be lost in the fore-arc, and may cause the formation of mud volcanoes (Martin et al., 1996). However, a significant amount of fluid will not escape along the detachment, and will react with overlying lithologies. At shallow depths, where temperatures are low, this will only cause hydration of ultramafic rocks to serpentinites. When fluids end up in parts of the mantle that are deeper and therefore hotter, they will cause partial melting. The exact mechanism by which fluids are transported, from the relatively cool slab-mantle interface to the hot core of the mantle wedge where melting takes place, is poorly understood. However, evidence from U-Th disequilibrium series of isotopes suggests that, whatever the mechanism may be, it is quick: less than a few hundred years seem to elapse between the last addition of fluids to the mantle and volcanic eruptions (Turner et al., 2001).

The mantle underlying arcs is generally thought to have a composition that is similar to the mantle underlying mid-ocean ridges (Pearce & Parkinson, 1993), i.e. depleted mantle (Hofmann, 2003). This is reflected in relatively low concentrations of water-insoluble elements such as the High Field Strength Elements (HFSE), Nb, Ta, Zr, Hf and Ti. Other incompatible trace elements, such as the Large Ion Lithophile Elements (LILE) like Sr or K, are present in far higher concentrations (Fig. 1) than in mid-ocean ridge basalts (MORB), as they are added to the magma source by a component coming off the subducted slab, either a fluid or a melt (Elliott et al., 1997). This leads to typically high ratios of LILE/HFSE. When arc magmas have relatively low ratios of e.g. K/Nb, it has been proposed that the unmodified mantle resembles the source of ocean island basalts (OIB) rather than a MORB-source (Reagan & Gill, 1989). Many workers have stressed the importance of fluids as the dominant carrier of elements from the slab into the wedge (Elliott et al., 1997), and it has been argued that fluid and melt components from the slab can be distinguished in diagrams of Ba/Th versus $^{87}\text{Sr}/^{86}\text{Sr}$ (Turner et al., 1997). Ba/Th ratios are low in MORB or OIB-type mantle, altered basalt and sediments; however, as Ba is a fluid-soluble element, whereas Th is fluid-insoluble, any aqueous fluid coming off the subducted slab will have high Ba/Th ratios. As arc lavas with high Ba/Th ratios typically have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, the fluid component is thought to have been in equilibrium with the altered oceanic slab, rather than sediments on top of the slab. Magmas with low Ba/Th ratios can have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and this is thought to reflect a signature from subducted sediments. This sediment signature is likely to have been added to the mantle source as a melt, since Th/Nb ratios of the resulting magmas are higher than those of MORB or sediment, suggesting that Nb has been held back in rutile during this partial melting process on top of the subducted slab (Elliott et al., 1997; Elburg et al., 2002).

Recent experimental work points towards a more important role for partial melts of subducted sediments than previously thought, as it is a far more effective carrier of potassium, an element typically enriched in arc magmas, than fluid (Hermann & Spandler, 2008). Another point of interest is the role that altered ultramafic lithologies (i.e. serpentinites) play as a carrier of water (Ulmer & Trommsdorff, 1995) into the sub-arc mantle. As serpentinites only lose their water at relatively elevated temperatures, they could carry fluids to greater depths than metabasalts. It is possible that the dehydration of these serpentinites would add water to overlying lithologies in the subducting slab (such as metabasalts or metasediments), which find themselves at more elevated temperatures than the serpentinites deeper in the slab. This water addition would induce partial melting in these lithologies, resulting in mixing between the serpentinite-derived fluid and the melt from oceanic crust or pelagic sediments. This explains that we seldom see the unmodified serpentinite-dehydration signature in arc lavas further removed from the trench. This is not the only way in which serpentinites may contribute components to arc magma: it is also possible that the dehydrating serpentinites belong to the entrained overlying mantle wedge, which became hydrated at shallower depths (Straub and Layne, 2002). In that case, there is a greater chance that we might encounter the pure “serpentinite” signature, which should be characterised by high concentrations of B, As, Cs and Li (Tentherey & Hermann, 2004). Deserpentisation reactions may also be the reason why arc magmas are relatively oxidised, compared to MORB (Elburg & Kamenetsky, 2007).

The concentrations of trace elements in a primary magma, which comes from the mantle without having undergone differentiation processes such as fractional crystallisation, magma mixing or crustal contamination, are determined by the relative contributions of sources (mantle, slab-derived fluid or melt) and their exact compositions, in combination with the degree of partial melting of the metasomatised mantle source. The composition of the mantle is mainly a result of previous depletion or enrichment events. In some arcs, there is evidence that the mantle source is more depleted than a “typical” MORB-source (McCulloch & Gamble, 1991), although other workers stress that there is no such thing as a “typical” MORB-source (Hofmann, 2003). Therefore,
it is not clear whether prior depletion of the sub-arc mantle, for instance during melting in a back-arc position, is necessary to explain the relative depletion in the most incompatible elements, reflected in the low Nb/Zr ratios seen in some arcs (McCulloch & Gamble, 1991).

For the “subduction component”, its composition is determined by its identity as a fluid or a melt, and by the specific dehydration and/or melting reactions responsible for its generation. There is increasing recognition that the amount of “subduction component” may be correlated with the degree of partial melting that takes place in the metasomatized mantle source: the more of the subduction component is added to the source, the higher the degree of melting. This process, otherwise known as “flux melting”, has also been shown to be operative in back-arcs (Kelley et al., 2006). If a negative feedback is added to this model, whereby the first increment of subduction component added to the mantle wedge has a larger influence on the degree of melting than subsequent additions, the process can be described as isenthalpic flux melting (Reiners et al., 2000). The small degree of melting that takes place when a very small amount of subduction component is added to the (MORB-type) mantle may explain the apparent OIB-like incompatible trace element ratios observed in some lavas, without having to invoke a plume-like mantle source.

That the type of subducted material exerts an influence on the composition of erupting magmas has been shown by the global correlations between the composition of subducted sediments and erupted products on an arc-by-arc basis (Plank & Langmuir, 1993). That it also holds on the scale of a single arc is suggested by along-arc trends, where the nature or amount of subducted material shows regular variations with position along the arc (Vroon et al., 1993). Across-arc trends have been known for a long time as the K-depth or K-h relationship (Dickinson & Hatherton, 1975), where the amount of potassium in the magma increases with vertical distance to the subducting plate, i.e. with increasing distance from the trench (Fig. 4). This can be a result of a decreasing percentage of partial melting towards the rear of the arc and/or a reflection of the amount or nature of the subduction component added to the mantle source (Elburg et al., 2002). Again these two parameters may be coupled, as it is likely that the slab-derived component will be more similar to an aqueous fluid at shallower depths (lower temperatures) and more melt-like further from the trench, with the fluid-component inducing higher degrees of melting in the metasomatised mantle source than the melt-like addition.

Figure 4: Example of the K-h relationship (Dickinson & Hatherton, 1975), where the potassium content (K) at a given SiO₂-content increases with height (h) above the subducting slab. The four Pantar Strait volcanoes (Treweg, Pura Besar, Ternate and Kisu) in the Indonesian arc are located between the islands of Pantar and Alor, and potassium contents increase from <1.5% to >4% for intermediate compositions with slab depths increasing from ~125 to 180 km. After Elburg et al. (2002).
3.1.2. The negative Ti-anomaly

One of the enduring mysteries in arc magmatism is the low titanium content of the lavas. For fractionated magmas, this is likely related to the crystallisation of titano-magnetite, but it is also observed in near-primary magmas. It used to be thought that a titanium-bearing phase such as rutile was stable in the mantle wedge during partial melting, but experimental work has shown that partial melts from ultramafic lithologies in which rutile is stable actually must have very high titanium contents (Ryerson & Watson, 1987). The current paradigm is that TiO$_2$ is simply not added to the mantle wedge by fluids or melts coming off the subducted slab. However, other high-field strength elements, that are similarly incompatible during mantle melting and supposedly equally immobile in fluids, such as Zr or Hf (Kessel et al., 2005), are always more enriched in arc basalts than Ti. This even holds when the basalts appear to be near-primary (magnesium number (=molecular Mg/(Mg+Fe$_{total}$)*100 >65; MgO > 6 wt.%) and when there is no evidence from Nd- and Hf-isotope data for the addition of any slab-derived REE and Hf (and by inference Zr) to the mantle source, as in the example given in Fig. 5, taken from Reagan et al. (2008). It is therefore likely that Ti is more compatible in the solid residue when the sub-arc mantle melts, than when melting occurs in other tectonic settings. This is unlikely to be related to increasing compatibility of titanium in clinopyroxene with decreasing temperature (Prytulak & Elliott, 2007), as this temperature effect is likely to affect Zr in much the same way as Ti. Residual amphibole could retain Ti, but this would also result in relative depletions of the middle rare earth elements, which is not observed (Fig. 5; Reagan et al., 2008). Although fractionation of Cr-spinel can in principle deplete the magma in Ti compared to neighbouring elements in normalised trace element diagrams, such as Fig. 5, it is a highly inefficient process, as Cr-spinel in arc magmas typically contains less TiO$_2$ than the melt from which it crystallises (Kamenetsky et al., 2001). The magma that is used as an example in Fig. 5 needs about 0.5 wt.% Cr-spinel addition to bring its Cr-contents up to 2000 ppm, which is typical for primary basalts. Addition of this amount of Cr-spinel would increase the magma’s TiO$_2$-contents by less than 0.01%, whereas it needs to increase by ~0.25% to avoid it displaying a negative Ti-anomaly.

It is possible that the high water contents of the sub-arc mantle lead to hydrogen-bearing defects in olivine, which are stabilised by the presence of Ti in the olivine lattice, also known as Ti-clinohumite-type defects (Berry et al., 2005). Already a small increase in the compatibility of Ti in olivine may have a noticeable effect on the titanium contents of the liquid, as olivine is the most abundant phase in the residual mantle. So I propose that this explains the almost ubiquitous negative Ti-anomaly in arc lavas, on which several discriminant functions are based (Winchester & Floyd, 1977; Pearce, 1982).

3.2 Sources and processes involved in differentiation

Primary arc magmas are already formed by contributions from several sources, such as the mantle and materials from the subducted slab. After their formation, on their journey towards the earth’s surface, the magmas undergo chemical changes due to the removal as well as the addition of material: crystal fractionation, crystal accumulation, degassing, crustal contamination, magma mixing. These processes can have a pronounced influence on the magma’s geochemistry, and can cause severe problems in trying to determine the identity of the primary magma, and thereby the sources and processes involved in its petrogenesis in the sub-arc mantle.

It is an often quoted fact that volcanic rocks from convergent margins have compositions that are closer to andesites than basalts. The average SiO$_2$-content of magmas varies between arcs, with continental arcs generally showing both higher SiO$_2$-contents and higher potassium contents for a given SiO$_2$-content. Part of this variation is likely to result from fractional crystallisation.
of minerals such as olivine, clinopyroxene and titanomagnetite, which depletes the melt in MgO and increases its SiO₂-content.

Increasing 87Sr/86Sr ratios with increasing SiO₂ contents (Fig. 6) suggest a role for crustal contamination. The effects of crustal contamination are detected more easily when the arc is built on (old) continental crust, where a pronounced isotopic distinction exists between the primary magma and the overlying plate. The role of crustal contamination in island arcs, where the overlying plate consists of basaltic crust, is more difficult to detect, as it will leave fewer tell-tale geochemical traces; it is, on the other hand, also less likely to occur, as assimilation of continental crust, with an average granitic composition, requires less energy than assimilation of MOR-like basalts and gabbros.

Chemical variation in arc magmas can also be caused by mixing processes. One example thereof is the mixing between two magmas, which may or may not contain crystals. The two magmas will only fully mix if their temperatures and viscosities are similar. This is the case if the two magmas have similar compositions, or if the hotter more mafic magma is volumetrically dominant, causing superheating of the more felsic magma. If the mafic magma is a minor component in the system, globules of this magma will cool against the more felsic magma, leading to dispersed drops of semi-solidified mafic magma, i.e. mafic enclaves, in the felsic magma (e.g. Bacon, 1986). “Mixing” can also take place between magma and crystals, which may be cumulates from previous batches of magma that have passed through the volcanic plumbing system (Charlier et al., 2005). This process can be difficult to identify if the compositions of the magmas passing through the system have not changed significantly through time. It may result in magmas that are suspiciously crystal-rich, and also show signs of accumulative processes in variation diagrams, e.g. very high Mg/Fe ratios for magmas with olivine accumulation.

Mixing of two components can be distinguished from crystal fractionation processes on bivariate diagrams, such as Harker variation diagrams, as it will produce straight mixing lines, whereas crystal fractionation can give rise to curved trends (Allègre & Minster, 1978). Mixing of components should also lead to disequilibrium between minerals and melt, resorption features or “reversed” zoning patterns, where cores of crystals have a composition in equilibrium with a more felsic magma than the rims of the crystals. These features can be detected by thin section studies, and further supported by SEM-EDS or electron microprobe chemical analyses of growth zones within minerals (Sakuyama, 1981), and surrounding glass.

4. “Calc-alkaline” (low-Fe) versus “tholeiitic” (high-Fe) differentiation trends

4.1 A confusion of classifications

The importance of both sources and processes on magmatic evolution is illustrated with a discussion on the “calc-alkaline” differentiation trend, as contrasted to the tholeiitic trend. The term “calc-alkaline” is put in quotation marks, as the definitions of this trend vary. As pointed out by Arculus (2003) and again by Tatsumi et al. (2008), the original definition by Peacock (1931), where the behaviour of CaO versus Na₂O+K₂O determined whether a series was alkalic, alkali-calcic, calc-alkalic or alkalic, is hardly ever used anymore for arc volcanics (although it has been revived for the classification of granites by Frost et al., 2001). Nowadays, it is generally used following Miyashiro (1974), where a rock series that shows increasing FeO*/MgO ratios with increasing SiO₂ is classified as tholeiitic, and one that does not as calc-alkaline (FeO* here means “all iron expressed as FeO†”). The definition by Irvine & Baragar (1971), where tholeiitic and calc-alkaline trends are defined on a triangular diagram of MgO, FeO* and Na₂O+K₂O (alkalis, hence AFM diagram) generally classifies the same series as calc-alkaline and tholeiitic as the Miyashiro (1974) diagram does. Confusion has started from the introduction of the K₂O versus SiO₂ diagram for arc rocks, on which low-K rocks were classified as tholeiitic and medium-K to high-K as calc-alkaline (Pecceirillo & Taylor, 1976). As Fig. 7 illustrates, samples from the volcano Ambae in Vanuatu (data mainly from Eggins, 1993) plot as a tholeiitic series on the diagrams by Miyashiro (1974) and Irvine & Baragar (1971), but not on the diagram after Pecceirillo & Taylor (1976). The latter diagram is also the cause of the misconception that the K-h relationship, where volcanoes tend to have higher potassium contents towards the rear of the arc, tells us that calc-alkaline volcanoes occur towards the rear of the arc. Although the K-h relationship generally holds, medium-
to high-K volcanoes are not necessarily calc-alkaline according to the definitions by Miyashiro (1974) and Irvine & Baragar (1971).

4.2 Role of oxygen fugacity and water

It is, however, a fact that some arc magma series show a trend of increasing FeO*/MgO with SiO$_2$ (“tholeiitic”), which I will call the high-Fe trend, following Arculus (2003), whereas others do not show this FeO*/MgO enrichment (“calc-alkaline”, or low-Fe trend). Fractionation of Mg-Fe silicates causes the high-Fe trend, as olivine and pyroxene crystals always have higher Mg/Fe ratios than the melt from which they crystallise. The easiest way to avoid this high-Fe differentiation trend is the fractionation of a mineral that contains more iron than magnesium, such as an iron oxide like (Ti-bearing) magnetite. Magnetite can only be formed in environments that are rather oxidised, as is typical for arc environments (Brandon & Draper, 1996; Parkinson & Arculus, 1999; Elburg & Kamenetsky, 2007). The oxidation state of a magma can be assessed by different methods, of which the most popular are the analysis of co-existing spinel and olivine crystals (Ballhaus et al., 1991), the analysis of co-existing Fe-Ti-oxides (Sauerzapf et al., 2008 and references therein) or the determination of sulfur speciation by electron microprobe (Wallace & Carmichael, 1992). Although the different methods sometimes give different results, discrepancies are mainly observed at low, rather than high oxidation states. As the absolute oxygen fugacity of a system depends on its temperature, it is often given as log units difference from a well-known oxygen buffer, such as fayalite-magnetite-quartz (FMQ) or nickel – nickel-oxide (NNO). In this shorthand notation, the oxygen fugacity of the NNO buffer would be expressed as being $\Delta$FMQ +1, i.e. the nickel – nickel-oxide buffer defines an oxygen fugacity roughly one log unit higher than the FMQ buffer, and materials equilibrated under the conditions of the NNO buffer are therefore more oxidised than those equilibrated under the FMQ buffer.

If we apply these oxybarometers to arc magmas, it

Figure 7: Whole rock samples from different arc volcanoes (data from GeoRoc database, and own unpublished results), plotted in contrasting classification diagrams. A: Scheme by Irvine & Baragar (1971) based on contents of MgO, FeO* (=all iron expressed as FeO) and the alkalis, Na$_2$O+K$_2$O. Enrichment in FeO* during the early stages of differentiation is called the tholeiitic trend; early enrichment of alkalis the calc-alkaline trend. The dashed arrows give idealised paths for these two fractionation trends. This classification scheme generally gives the same result as that proposed by Miyashiro (1974), shown in B. The correlation with the scheme based on Al$_2$O$_3$ versus normative anorthite content (C) is not always as good. The scheme by Peccerillo & Taylor (1976) (D), referring to medium- to high-K series as calc-alkaline seldom gives the same results as the classification involving Fe/Mg ratios. This confusion has led to the suggestion to abandon the terms tholeiitic and calc-alkaline, and refer to high- or low-Fe trends instead when referring to diagram B (Arculus, 2003).
becomes obvious that magma series that differ very little in their oxidation state (Fig. 8), such as Montserrat (Devine et al., 1998), Ambae (Eggins, 1993) and Pinatubo (de Hoog et al., 2004) can show pronounced differences in their FeO*/MgO trends, while some low-Fe suites (Pico de Orizabo, Righter et al., 2002) have lower oxygen fugacities than some high-Fe suites. So it is unlikely that this is the sole influence on the development of the calc-alkaline trend.

The water contents of arc magmas are typically determined by ion microprobe analyses of glass inclusions within phenocrysts (Sobolev & Chaussidon, 1996). A problem here is that magmas may degas during evolution, and that therefore inclusions in early-crystallised minerals are likely to give the best estimate of the initial H₂O-content. At first sight, the water contents do not seem to be the determining influence on the high- or low-Fe trends either; H₂O typically behaves as an incompatible content and thus increases with differentiation. Therefore the difference in H₂O contents between the Cerro Negro basalts (5%, Sadofsky et al., 2008) and Pinatubo dacites (9%, Borisova et al., 2006), as representatives of the tholeiitic and calc-alkaline differentiation trends respectively, do not seem to be significantly different; both are very water-rich magmas. Neither is it likely that the composition of the subducted materials plays an important role, as calc-alkaline and tholeiitic series of rocks can be found in a single volcano (Tatsumi et al., 2008).

Figure 8: Miyashiro’s (1974) classification diagram with several magmatic suites from the GeoRoc database. Ambae, Cerro Negro and Anatahan are typically “tholeiitic”; Montserrat, West Aegean, Pinatubo and Pico de Orizaba are “calc-alkaline”. Neither initial water content nor oxidation state appears to be determining whether samples belong to either trend.

4.3 Role of magma mixing and crustal contamination

If one delves into the scientific literature, and compares descriptions of “tholeiitic” and “calc-alkaline” series of rocks, it is striking how often terms like “mixing”, “disequilibrium” and “contamination” are applied to calc-alkaline samples (some recent examples are: Zellmer et al., 2003; de Hoog et al., 2004; Zellmer & Turner, 2007; Feeley et al., 2008; Pe-Piper & Moulton, 2008), which is all the more noticeable when authors compare the two rock series in a single arc (George et al., 2004), and sometimes even within a single volcano (Tatsumi et al., 2008). In Japan, the calc-alkaline series of rocks are even defined by their disequilibrium textures, such as reversed zoning in crystals (hence the term R-series, Sakuyama, 1981), as contrasted by the normal zoning seen in the N-series, or tholeiitic rocks.

It is therefore tempting to think that magma mixing or crustal contamination may be the underlying reason for the existence of the low-Fe (calc-alkaline) trend. Viewed in an AFM diagram, the classic tholeiitic differentiation trend is defined by a strong increase in Fe/Mg ratios, followed by an increase in alkali contents, whereas the calc-alkaline trend goes straight towards the alkali corner.
of the diagram (dashed arrows in Fig. 7). Mixing between mafic and felsic (glass) materials from Montserrat, indicating that the calc-alkaline whole rock trend could be generated by mixing. The two curves represent mixing with two different felsic end members, indicating that the exact choice of end members has little effect on the shape of the mixing curve. The straight line is the calc-alkaline/tholeiitic division line after Miyashiro (1974).

Figure 9: Simple mixing models (curved lines) between mafic and felsic (glass) materials from Montserrat, indicating that the calc-alkaline whole rock trend could be generated by mixing. The two curves represent mixing with two different felsic end members, indicating that the exact choice of end members has little effect on the shape of the mixing curve. The straight line is the calc-alkaline/tholeiitic division line after Miyashiro (1974).

4.4 Role of amphibole

Although magma mixing might be the reason for the low-Fe trend in some volcanic suites, the diagram of the element dysprosium (Dy) versus SiO$_2$ (Fig. 10) shows that this cannot be the whole story. The high-Fe series from Cerro Negro (Nicaragua) and Anatahan (Marianas) show increasing Dy with increasing SiO$_2$ contents; the western Aegean islands and Pinatubo (Philippines), which belong to the low-Fe trend, show decreasing Dy contents; Soufrière Hills on Montserrat (Lesser Antilles), which is also a low-Fe volcano, shows first increasing, then decreasing Dy contents. Although the trends for the west Aegean and Pinatubo could be explained by mixing between a more mafic magma with higher Dy contents than the felsic end member, the curved trend for Soufrière Hills cannot be explained by magma mixing (as mixing results in straight trends on all element-element plots) but must be the result of crystal fractionation. During fractionation the mineral assemblage must have changed from one in which the element dysprosium was incompatible to one in which it was compatible. Dy belongs to the middle rare earth elements (MREE), and the only major mineral phase in which these are compatible is amphibole (Davidson et al., 2007). So, if fractionation, rather than magma mixing explains the SiO$_2$-Dy trends for all three low-Fe volcanoes in this diagram, then amphibole must have played a role.

Is amphibole fractionation then the underlying reason of the low-Fe trend? Amphibole indeed has a Mg/Fe ratio (Langmuir et al., 1978). As Fig. 9 shows, the very low FeO* and MgO contents in felsic magmas compared to mafic ones results in a strongly curved trend that reproduces the calc-alkaline trend, as seen in e.g. Soufrière Hills volcano (Montserrat, West-Indies).

Figure 10: Diagram of dysprosium versus SiO$_2$ contents showing that mixing cannot be responsible for the Montserrat whole rock trend, as there is a clear kink in the curve. This reflects the onset of amphibole fractionation, in which Dy is a compatible element. Significantly, all calc-alkaline suites show decreasing Dy contents, whereas the tholeiitic suite for which data are available for felsic samples (Anatahan) shows continuing incompatibility of dysprosium, and thereby no role for amphibole fractionation.
more similar to the melt from which it crystallised than olivine or clinopyroxene (Sisson & Grove, 1993), so its fractionation would indeed lead to a lack of iron-enrichment, as also argued by Boettcher (1977) and Ringwood (1977). Amphibole fractionation could therefore be the cause for the low-Fe trend, but I propose that the low-Fe trend and amphibole fractionation are caused by the same intensive and extensive parameters of the magmatic system, but are not causally related to each other.

4.5 Role of fractionation depth in combination with water

Several experimental studies have investigated the stability of amphibole in arc magmas (Foden & Green, 1992; Moore & Carmichael, 1998; Barclay & Carmichael, 2004). These have shown that its stability field increases with pressure in water-saturated magmas, as the maximum amount of water that can be dissolved in a magma increases with increasing pressure (Fig. 11). Water plays an important role in the stability of other mineral phases too. In general, the presence of water shifts the liquidus of basaltic melts to lower temperatures (Médard & Grove, 2008). It not only retards the onset of plagioclase crystallisation but also increases its anorthite content (Grove & Baker, 1984). Actually, it delays the crystallisation of all the silicate minerals, but it doesn’t significantly shift the appearance of magnetite to lower temperatures (Sisson & Grove, 1993; Berndt et al., 2005). This leads to magnetite being one of the first minerals to crystallise in oxidised, water-rich systems at intermediate pressures, whereas it occurs far later in the fractionation sequence in water-poor systems, i.e. those that started out with low levels of H$_2$O (such as OIB or MORB) or those that lost their water during degassing at shallow levels (such as arc magmas that fractionate in shallow magma chambers). So the same conditions that stabilise amphibole also promote the early fractionation of magnetite – and promote alkali-enrichment by later fractionation of plagioclase, and its higher anorthite (and therefore lower albite) content. The lack of plagioclase fractionation for calc-alkaline rocks also results in higher Al$_2$O$_3$ contents compared to tholeiitic rocks – which is why the tholeiitic/calc-alkaline classification scheme in Fig. 7C can give the same result as the schemes of Figs 7A and B. As enrichment in potassium is more closely related to sources and processes occurring during magma generation (addition of material from the subducting slab, degree of partial melting) rather than during fractionation, the tholeiitic/calc-alkaline classification scheme by Peccerillo & Taylor...
amphibole only starts crystallising at ~55% SiO$_2$ chamber that is heated from below (Couch et al., 2001). Turners (2007), or as a result of “self-mixing” in a magma material with the new batch of mafic magma (Zellmer & mixing of the partially remolten amphibole-bearing to disequilibrium textures, either as a result of the physical intrusion of hotter, more mafic magma. This will then lead to disequilibrium textures, either as a result of the physical mixing of the partially remolten amphibole-bearing material with the new batch of mafic magma (Zellmer & Turner, 2007), or as a result of “self-mixing” in a magma chamber that is heated from below (Couch et al., 2001).

5. Conclusions

The geochemistry and petrology of arc magmas is determined by the interaction of sources and processes. Primary basaltic liquids reflect the composition of the pre-metasomatic mantle composition (generally similar to the source of mid-ocean ridge basalts); the metasomatic addition of material from the subducting slab with or without entrained sediments, of which water is the most important component; and the degree of partial melting of the metasomatised mantle wedge. These melts are subsequently modified by processes operating at crustal levels, such as crystal fractionation and magma mixing; additional material may be added to the magma by assimilation of (continental) crust.

Arc magmas are characterised by a relative depletion in titanium, which has been ascribed to a relative enrichment in other elements by fluids or melts from the subducting plate. Recent geochemical data show that this proposition is untenable, and it seems likely that titanium is more compatible during hydrous partial melting of the mantle wedge than during dry melting, perhaps because of the presence of titanomagnetite-type defects in residual mantle olivine.

Water also plays a crucial role in the lack of iron-enrichment during differentiation seen in many arc suites, which is also known as the “calc-alkaline” trend. Water-bearing magmas start crystallising silicates such as olivine and plagioclase at lower temperatures than dry magmas. As the solubility of water decreases with decreasing pressure, this effect only plays a role when crystal fractionation takes place at intermediate crustal pressures. Water does not delay the fractionation of iron-oxides, such as titanomagnetite, so water-bearing magmas will start fractionating oxides early, causing a depletion of iron in the residual magma. Hydrous magma at intermediate pressures also fractionates amphibole at a relatively early stage, whereas this mineral is not stable at lower pressures. Crystallisation of amphibole is responsible for a sudden increase of crystallinity of the magma. It also depletes the remaining silicate liquid in water. Both effects cause an increase in the effective viscosity of the magma, which may cause it to stall and become “uneruptable” until heating by a new, more mafic batch of magma remobilises the material. Erupted “calc-alkaline” magmas will therefore often show signs of magma mixing. However, magma mixing and the presence of amphibole are not the causes of the low-Fe, “calc-alkaline” trend, but side-effects of fractionation at intermediate pressures, which promotes fractionation of iron-oxides relative to silicate minerals.

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