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Miocene Gangotri-Bhagirathi High Himalayan leuco-granite lense, about 1 km thick, intruding into black schist. IMAGE CREDIT: BRUNO SCAILLET

A rich history of experimental petrology has revealed the paths by which silicic igneous rocks follow mineral–melt equilibria during differentiation. Subdividing these rocks by 'molar Al versus Ca + Na + K' illustrates first-order differences in mineralogy and gives insight into formation mechanisms. Peraluminous magmas, formed by partial melting of sediments, largely owe their attributes and compositions to melting reactions in the protoliths, whereas most metaluminous felsic magmas record both continental and mantle inputs. Peralkaline rhyolites are mainly derived from either protracted crystallization or small degrees of partial melting of basalt, with only a marginal crustal contribution. Most silicic magmas hold 3–7 wt% H_2O_{melt}, which is inversely correlated with pre-eruptive temperature (700 °C to >950 °C) but unrelated to their reduced/oxidized state.

KEYWORDS: granite, rhyolite, phase equilibria, water, redox state, metaluminous, peraluminous, peralkaline, viscosity

INTRODUCTION

Silicic magmas (SiO_2 > 65 wt%) may originate from either partial melting of crustal material or protracted crystallization of parental basaltic (mafic) magmas. Hence, modern experiments have tackled the origin of natural silicic rocks by either establishing phase equilibria of natural granites/rhyolites to understand magma storage and differentiation conditions (e.g. Scaillet et al. 1995; Clemens and Birch 2012) or by performing partial melting experiments on their putative source rocks (e.g. Patiño Douce and Harris 1998; Sisson et al. 2005). Such experiments have offered a range of P–T–H_2O–fO_2 conditions thought to be present during magma production or storage, and these are summarized below. Comparing studies performed either on plutonic or on volcanic rocks allows us to address the question of whether there is, in fact, a plutonic–volcanic connection.

Classification of silicic rocks, whether extrusive or intrusive, has been the subject of countless studies and has been mainly used to constrain the origin (mantle vs. crustal sources) or geodynamic settings of felsic melts. Granitic magmas are widely classified as S- (sedimentary protolith) or I- (igneous protolith) type (e.g. Chappell and White 1974). A further category is the A-type, which corresponds to alkali-rich granites. In this article, we summarize experimental studies bearing on the origin of silicic magmas and employ the compositional parameter A/CNK, i.e.

molar Al/(2Ca + Na + K), which is used to define magmas/silicic rocks that are either peraluminous (A/CNK > 1), metaluminous (1.1 > A/CNK > 1 and A/NK > 1), or peralkaline (A/NK < 1). The A/CNK ratio fundamentally reflects the fact that, in addition to quartz, felsic rocks are made of feldspar, typically having 60 wt% feldspar and 30 wt% quartz, in which Al is stoichiometrically balanced by the Na, K and Ca cations. As we will show, A/CNK exerts a strong control on the nature of rock-forming minerals other than the quartzo-feldspathic component.

We first present a brief historical perspective, as well as the current state of knowledge, concerning the modes of production of silicic magmas. We then discuss the available experimental constraints that seem to govern the emplacement conditions of peraluminous, metaluminous and peralkaline silicic magmas.

ORIGINS

Progress in our understanding of the origin of granite (petrogenesis) via the experimental approach has been marked by several major technical and conceptual milestones. Tuttle and Bowen (1958) laid the foundations for an impressive number of subsequent studies and provided the first quantitative evaluation of P–T–H_2O conditions of granite production. Following this seminal work, which was limited to low pressures (<5 kb), the magmatic origin of granites, sensu lato, was widely accepted. The advent of the modern piston-cylinder apparatus in 1960 represents a second milestone, one that allowed the systematic exploration of the phase equilibria to upper-mantle pressures (e.g. Stern and Wyllie 1981), demonstrating that magmas with more than 60–65 wt% SiO_2 and less than 4–5 wt% MgO, i.e. granites sensu lato, cannot be produced by direct mantle melting. The origin of granite must lie either in the crystal fractionation of mafic magmas or in the partial melting of crustal rocks with mafic, silicic or Al-rich compositions (e.g. amphibolites, gneisses, schists). High-pressure experiments have also shown that the Archean tonalite–trondhjemite–granite (TTG) association requires partial melting of basaltic lithologies in equilibrium with garnet at pressures of 10–30 kb.

Silicic magma production by crystallization of mafic magmas has been achieved in various laboratory studies, which have shown that, regardless of the detail of bulk compositions, rhyolitic derivatives require at least 80 wt%

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crystallization of basalt magma, whereas the production of andesite–dacite liquids requires 40–60 wt% crystallization (e.g. Pichavant et al. 2002; Berndt et al. 2005; Sisson et al. 2005) with higher oxygen fugacities, fO_2, promoting higher SiO_2 (e.g. Berndt et al. 2005).

Because of the compositional and mineralogical diversity of crustal lithologies, the origin of silicic melts by partial melting of the crust has also been the subject of numerous studies. These have shown that fluid-absent partial melting of crustal rocks produces melts with compositions similar to natural granites up to temperatures approaching 1,000°C (Montel and Vielzeuf 1997). Such studies also provide quantitative data for the parameterization of melt productivity with intensive variables such as temperature (e.g. 10 wt% melt at 800°C and 20 wt% at 900°C for an amphibolite). Dehydration (i.e. fluid-absent) melting of the continental crust without mantle input is a viable process in continental collision zones, such as the Himalayas; but in many geotectonic settings, crustal melting seems to be fundamentally driven by basaltic magmatism (Hildreth 1981). In this case, fluid-absent melting would imply either that the intruding basaltic magmas are volatile-poor or that their contribution is limited to heat supply. In subduction zone settings, however, studies have shown that arc basalts, even primitive ones, can be quite H_2O-rich (e.g. Pichavant et al. 2002). Hence, intrusion of arc basaltic magma at the crust–mantle interface or in the lower crust – a process widely believed to be the main source of silicic magmatism and crust production (Hildreth 1981; Annen et al. 2006) – must produce, at least locally, H_2O-rich environments during basalt crystallization. The fate of such H_2O-rich fluid in the lower crust of active arc settings is unclear, but it opens up the possibility of fluid-present conditions during melting of the base of the crust.

Lastly, silicic magma petrogenesis probably also involves mixing, in particular for explaining crystal-rich magmas with intermediate compositions, such as andesite. Although andesitic liquids do erupt in various volcanic centers (e.g. Ownby et al. 2011), petrological and geochemical observations have shown that intermediate rocks occurring in arc settings result from mixing/mingling between mafic and felsic magmas as well, in particular when end-members are broadly in equal proportions and iso-viscous (e.g. Laumonier et al. 2014).

EVOLUTION AND MAGMA STORAGE

Phase equilibrium experiments carried out directly on magmatic rocks provide quantitative constraints on the evolution and storage conditions of felsic magmas. Below, we use selected examples to illustrate the main differences between the phases (minerals) that crystallize in peraluminous, metaluminous or peralkaline silicic magmas. The experimentally determined phase diagrams presented here were all derived under fluid-present conditions, but at various water activities. In each diagram (FIGS. 1, 2 AND 3), the water activity is directly related to the water content of the melt, which is reported either in the x-axis or as isopleths. The maximum water content that can be reached at water-saturated conditions (i.e. a water activity of 1) depends on pressure and is marked by the near-vertical curves, limiting the phase diagrams on the right side in FIGURES 1, 2 and 3. The left-most boundary in each phase diagram is the solidus curve.

Peraluminous Silicic Magmas

Representative compositions used in these phase-relation experiments are listed in TABLE 1. Peraluminous silicic rocks occur in three general types of geological environment: first, in continental areas that have a thick crust, the result of continental collisional tectonics as has occurred in the Himalayas or in the Hercynian belt across Europe; second, in areas of active oceanic subduction beneath overthick-ened continental crust, such as in the Peruvian Andes; third in post-orogenic settings, such as in the Devonian terranes of eastern Australia. Minerals typifying the peraluminous character of felsic rocks include cordierite, garnet, muscovite, tourmaline, hercynite, and the aluminosilicates of andalusite or sillimanite. In reduced felsic and iron-rich (>1.5 wt% FeO_{tot}) magmas and at pressures above 4–5 kbar, garnet crystallizes at near-liquidus conditions; the same magmatic conditions restrict cordierite formation to near-solidus conditions (Clemens and Birch 2012) (FIG. 1B). In contrast, near-liquidus cordierite only occurs at or below 2 kb (FIG. 1C). In felsic leucogranites (e.g. iron-poor with FeO_{tot}< 1.5 wt%), Mn-rich garnet (spessartine) occurs only in late-stage derivatives; this contrasts with higher temperature almandine-type garnet occurring in more mafic peraluminous granites. In felsic end-member leucogranites of S-type affinity, muscovite is the diagnostic phase of a strongly peraluminous magma, but magmatic muscovite is only expected at pressures higher than 3.5 kbar. Muscovite is also a late-crystallizing mineral (FIG. 1A) except when fO_2

TABLE 1	COMPOSITIONS USED IN PHASE EQUILIBRIUM EXPERIMENTS ON PERALUMINOUS (1–5), METALUMINOUS (6–13), AND PERALKALINE (14–17) FELSIC ROCKS. Sources listed below.

Felsic Rock	Peraluminous					Metaluminous								Peralkaline			
Composition (wt%)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
SiO_2	75.77	69.83	70.46	73.04	72.94	72.1	73.6	70.77	73.74	63.83	66.30	75.65	77.56	75.2	72.64	74.17	71.25
TiO_2	0.11	0.65	0.69	0.13	0.06	0.8	0.34	0.65	0.46	0.61	0.52	0.17	0.1	0.17	0.18	0.17	0.3
Al_2O_3	13.54	14.75	14.92	15.32	15.57	13.4	12.44	13.22	11.96	18.18	16.24	13.04	12.39	12.11	10.3	10.89	8.03
FeO_{tot}	1.69	4.21	3.51	0.89	0.76	3.7	3	3.98	4	3.97	3.90	1.71	1.13	1.81	4	3.98	6.93
MnO	0.01	0.05	—	0.01	0.01	0.07	0.08	0.06	0.01	0.07	0.10	0.06	0.06	0.04	0.06	0.06	0.21
MgO	0.31	1.5	1.54	0.2	0.14	0.7	0.27	0.62	0.24	1 .72	1.71	0.19	0.04	0.07	0.04	0	0.01
CaO	0.65	2.76	1.92	0.85	0.57	2.2	1.24	2.08	1.13	5.77	4.05	0.96	0.51	0.44	0.1	0.29	0.33
Na_2O	2.64	2.45	2.5	3.85	4.56	3.8	3.53	2.96	2.22	4.96	4.21	3.4	3.45	4.59	5.68	5.81	6.54
K_2O	5.27	3.79	4.53	4.96	4.14	3.4	4.23	5.41	5.93	1.31	2.76	4.8	4.76	4.73	4.35	4.68	4.6
P_2O_5	—	—	—	0.14	0.19	0.3	0.07	0.11	0.08	—	0.16	0.05	0.01	—	—	—	—
A/CNK	1.21	1.12	1.19	1.16	1.20	0.96	0.98	0.91	0.99	0.91	0.94	1.04	1.05	0.90	0.72	0.72	0.49

SOURCES: 1, 2 (Clemens and Birch 2012); 3 (Clemens and Wall 1981); 4, 5 (Scaillet et al. 1995); 6 (Dall'Agnol et al. 1999); 7 (Clemens et al. 1986); 8, 9 (Almeev et al. 2012); 10 (Rutherford et al. 1985); 11 (Costa et al. 2004); 12, 13 (Klimm et al. 2008); 14, 15, 16 (Scaillet and Macdonald 2001); 17 (Scaillet and Macdonald 2006)

is high, with crystallization temperatures generally lower than 680°C. Contrary to common belief, muscovite is not restricted to water-saturated conditions (Fig. 1A).

The conditions of magma emplacement, derived by comparing crystallization sequence inferred from petrographic observations with known phase equilibria, are characterized by having elevated water contents of the melt (H_2O_{melt}) of between 4 and 7 wt% H_2O and temperatures that range between 750°C and 900°C, the water content and temperature being (roughly) inversely correlated. In the selected examples (Himalayas and Australia), the pressure of magma storage either prior to eruption or during crystallization is up to 4–5 kbar. The depth of magma production is generally a poorly constrained parameter and likely varies depending on the structural location of favorable lithologies. In some circumstances, such as in the Himalayas, granites and their likely sources are well exposed. In this representative case of crustal melting during continental collision, experiments that examined dehydration melting of muscovite-bearing Himalayan metapelites produced melt compositions identical to granite plutons intruded at higher levels, i.e. with 5–6 wt% H_2O_{melt} at 750–800°C (Patiño Douce and Harris 1998). These temperature–H_2O constraints are essentially identical to those based on phase equilibria experiments carried out on the granite itself (Scaillet et al. 1995). The production of more mafic peraluminous magmas (i.e. compositions 2 and 3 in TABLE 1) requires higher temperatures, which should involve biotite breaking down in the source region to form orthopyroxene and/or garnet in the residue. The available data indicate that felsic volcanic and plutonic peraluminous rocks share common P–T–H_2O–fO_2 conditions. As for other silicic categories, there is no experimental basis to support the claim that rhyolitic melts crystallizing at depth to form plutonic magmas are drier, and, hence, more viscous and less mobile than melts from volcanic systems with equivalent whole-rock compositions.

Metaluminous Silicic Magmas

The dominant type of silicic magma found in subduction zone settings is metaluminous, but this category also occurs in anorogenic zones and hot-spots. Compared to peraluminous and peralkaline varieties, the SiO_2 content of common metaluminous silicic rocks goes down to values as low as 60 wt%: these are andesites and dacites, which are of so-called intermediate compositions and which dominate in arc settings. When hydrous, the mafic mineralogy of andesites and dacites is dominated by biotite and by calcic amphibole (hornblende). These magmas are typically considered to have originated from igneous sources, either via fractional crystallization of mafic magmas or by partial melting of older, crustal metaluminous intrusive during which biotite and amphibole breakdown takes place. Mixing processes may also act at any stage during magma evolution. The range of temperatures of metaluminous magmas is broadly similar to that of peraluminous ones, though temperatures of 1,000°C or higher have been recorded. This is, in part, related to the greater compositional range covered (i.e. greater mafic character) and to the local remelting of dehydrated crust.

The Tuttle and Bowen (1958) work primarily applies to evolved metaluminous magmas. Phase equilibria at H_2O-saturation in the system quartz–albite–orthoclase have shown that the minimum composition, or eutectic, trends toward more sodic compositions with increasing pressure (Luth et al. 1964). The experimental constraints observed at H_2O-saturation in this system have been used to infer P–T conditions for the emplacement of relatively felsic granites in the crust, and, more recently, of magma ascent to the surface from shallow reservoirs (Blundy and Cashman 2008). However, the quantitative application of experimental results obtained in this synthetic system to natural cases is hampered by the incomplete understanding of the effect of small amounts of Ca on the haplogranite phase relationships. Similarly, investigation of the role of CO_2 (Holtz et al. 1992) has shown that a decrease in H_2O_{melt} at constant total pressure displaces the minimum (eutectic) toward more potassic melts at constant normative quartz content. This effect is not yet fully accounted for in current thermodynamic models.

The compositions of representative natural metaluminous silicic magmas used in experiments are listed in TABLE 1, and representative phase relationships are shown in FIGURE 2. The results obtained on ferroan metaluminous granites outcropping in anorogenic settings show that they have 4–5 wt% H_2O_{melt} at temperatures up to 950°C for the more mafic varieties (e.g. Clemens et al. 1986;
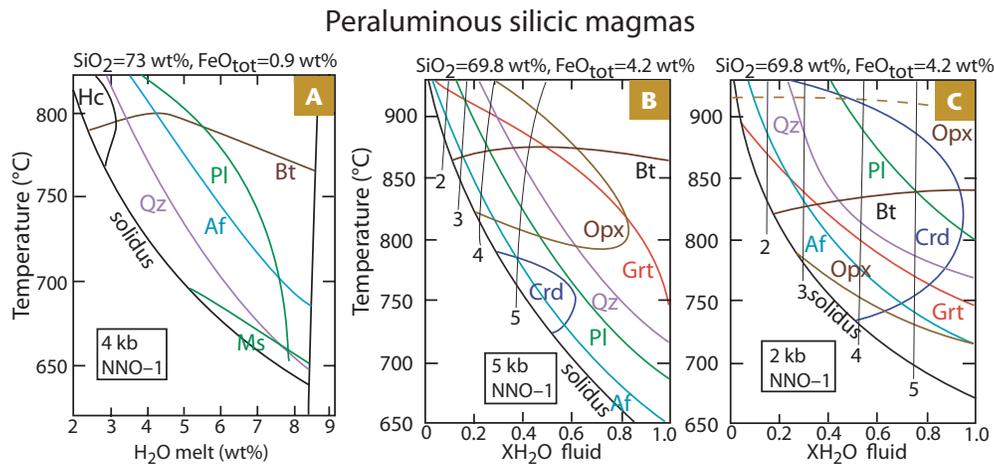
Peraluminous silicic magmas

FIGURE 1 Isobaric T–H_2O_{melt} phase relationships of peraluminous silicic magmas (NNO–1 means an fO_2 one log unit below the NNO solid buffer). (A) Fe-poor leucogranite from the High Himalayas (composition 4 in TABLE 1; Scaillet et al. 1995). (B) and (C) Fe-rich granite from SE Australia (Clemens and Birch 2012; composition 2 in TABLE 1). In (B) and (C), the H_2O_{melt} is shown as isopleths labeled as 2, 3, 4 and 5. The black near-vertical curve at high H_2O_{melt} in (A) is the water solubility curve. The black curve on the left of all three diagrams is the solidus curve. In these and all subsequent phase diagrams (see Figs. 2 and 3), a fluid phase composed of H_2O and CO_2 coexists with the melt and solid phases. The solidus temperature, as well as H_2O_{melt}, depend on the proportion of H_2O and CO_2 in the fluid phase. Phase abbreviations are Af (alkali feldspar), Bt (biotite), Crd (cordierite), Grt (garnet), Hc (hercynite), Ms (muscovite), Opx (orthopyroxene), Pl (plagioclase), Qz (quartz).

Dall'Agnol et al. 1999; Klimm et al. 2008). The comparison of phase equilibria and petrologic observations provides a constraint on the pressure of magma emplacement to be around 1–3 kbar, with redox states in the range of fO_2 that corresponds to the fayalite–magnetite–quartz (FMQ) and Ni–NiO (NNO) buffers. Most metaluminous magmas, notably the more mafic (i.e. intermediate) ones – with H_2O_{melt} >4 wt%; compare FIGURES 2A and 2B – contain hornblende at pressures higher than 1 kbar. Hornblende is, however, not stable in the most felsic (i.e. Ca-poor) metaluminous granites, these normally being the most K-rich (Klimm et al. 2008) and having biotite as the dominant hydrous mineral. The most fractionated examples of A-type metaluminous magmas have concentrations of F reaching or exceeding 1 wt%, something also observed in peraluminous rhyolites. Phase equilibria of these particular metaluminous magmas indicate emplacement temperatures in the range 675–720 °C and a H_2O_{melt} of 4–5 wt% (Webster et al. 1987). The low liquidus temperatures are due to the near-eutectic compositions and to the fluxing effect of F on silicate systems.

Although metaluminous rhyolites are not as abundant as intermediate magmas (dacite/ andesite or granodiorite) in arc settings, they sometimes erupt as single entities or as a part of a zoned eruption (e.g. Castro and Dingwell 2009), and when this happens, they display the same phase assemblages as anorogenic granites. The available phase relationships for metaluminous rhyolites point to pre-eruptive temperatures of around 800–850 °C, with H_2O_{melt} >4 wt%, storage pressures of 1.5–2 kbar, and fO_2 somewhat higher than anorogenic equivalents (from NNO up to 1.6 log units above it, or NNO+1.6). Except for the redox state, these conditions are essentially identical to those inferred for anorogenic granites.

Metaluminous rhyolites may also occur as the products of large-volume eruptions in hot spot settings. Amphibole is very often absent from such rhyolites, which instead contain pyroxenes in addition to fayalite. Detailed phase equilibria by Almeev et al. (2012) revealed that such felsic magmas may be dry and hot, with inferred H_2O_{melt} <1.5 wt%, temperatures approaching 1,000 °C, and storage pressure of 2–4 kbar. This is the sole experimentally documented instance of a dry and hot rhyolitic system; it is, therefore, not known whether it is representative of most hot spots. The dry and hot conditions may reflect melting of a (locally?) previously dehydrated crust. It is worth noting that the redox state of hot spot rhyolites lies close to the lower end of terrestrial values (i.e. fO_2 one log unit below FMQ, or FMQ–1), though it is not as reduced as for peralkaline rhyolites.

A number of phase equilibrium studies have been performed on the more mafic silicic magmas (dacites/andesites) dominantly erupted in subduction zones to constrain their pre-eruptive conditions and petrogenesis (e.g. Rutherford et al. 1985; Costa et al. 2004). For these silicic rocks, hornblende is generally the main hydrous phase, having an upper thermal stability of about 850–900 °C depending on composition (FIGS. 2E, 2F). When such magma is stored at pressures below 1.5 kbar, or when H_2O_{melt} is lower than ~4 wt%, hornblende is replaced by pyroxenes. However, in

the vast majority of studied cases, a storage pressure around 2 kbar seems to be the rule. At 2 kbar, pyroxenes and plagioclase are the liquidus silicate minerals (FIGS. 2E, 2F). Oxides, either magnetite or ilmenite or both, generally belong to this assemblage: as a rule of thumb, magnetite is present alone (as oxide) at fO_2 above NNO+1 whereas ilmenite is the single oxide at NNO–1 or below. The lack of amphibole in volcanic rocks, however, does not necessarily imply a dry magma or crystallization at shallow pressures. It may simply reflect that the temperature is too high to crystallize amphibole, possibly as a result of sustained mafic magma influx which buffers the reservoir temperature above the thermal stability of hornblende. Pre-eruptive T–H_2O conditions of intermediate (dacite to andesite) arc magmas retrieved from phase equilibria vary from 760 to 950 °C and from 4 to 7 wt% H_2O_{melt}, respectively. Corresponding redox states fall in the NNO–NNO+1.7 range.

It is worth stressing that the phase equilibria of metaluminous silicic magmas depend significantly not only on P, T and H_2O but also on redox state, though there are not enough detailed data to fully appreciate how fO_2 affects

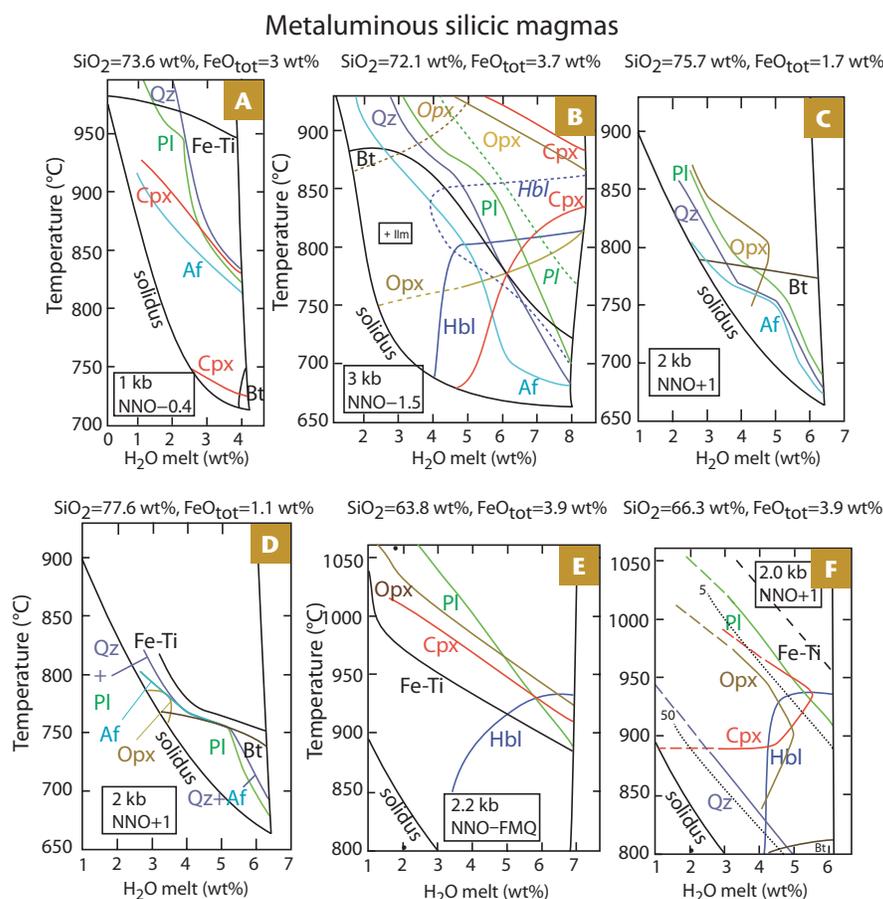## Metaluminous silicic magmas

FIGURE 2 Phase relationships of metaluminous silicic magmas (NNO and FMQ are reference solid fO_2 buffers: NNO+1 means an fO_2 one log unit above NNO; NNO–FMQ means an fO_2 between those two buffers). (A) Fe-rich granite from Australia (Clemens et al. 1986; composition 7 in TABLE 1). (B) Fe-rich granite from NE Brazil (Dall'Agnol et al. 1999; composition 6 in TABLE 1). (C) and (D) Fe-poor granites from Australia (Klimm et al. 2008; compositions 12 and 13 in TABLE 1, respectively). Dashed lines on Brazilian granite (B) show the effect of increasing fO_2 up to NNO+2 on mineral stabilities. (E) Andesite from Mt. St. Helens (Rutherford et al. 1985; composition 10 in TABLE 1). (F) Dacite from San Pedro volcano (Costa et al. 2003; composition 11 in TABLE 1). Dotted lines on the dacite phase diagram give the melt fraction in wt%. Phase abbreviations are as in FIGURE 1 plus Cpx (clinopyroxene), Fe–Ti (Fe–Ti oxides), Hbl (hornblende), Ilm (ilmenite).
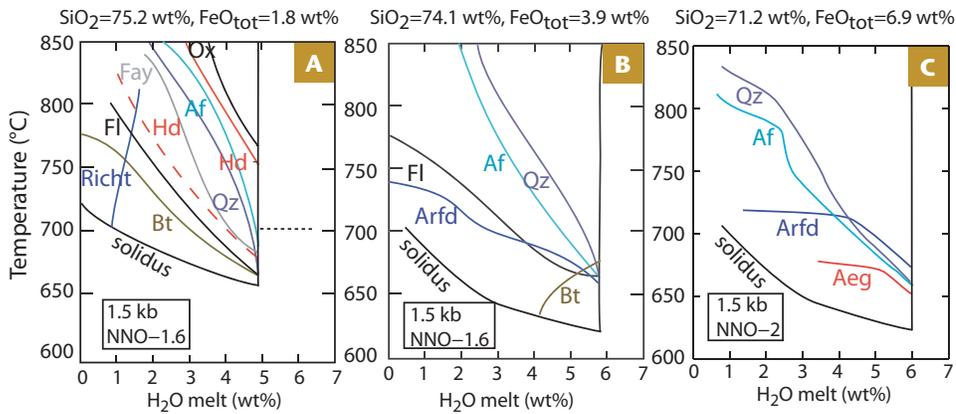
Peralkaline silicic magmas

SiO$_2$=75.2 wt%, FeO$_{tot}$=1.8 wt%   SiO$_2$=74.1 wt%, FeO$_{tot}$=3.9 wt%   SiO$_2$=71.2 wt%, FeO$_{tot}$=6.9 wt%

all silicic magma compositions. In iron-rich granites, low fO_2 (at or below FMQ) depresses the thermal stability of amphibole and expands that of orthopyroxene (FIG. 2B). Because fO_2 affects the stability fields of mafic minerals and the melt structure (Fe^{2+}/Fe^{3+} ratio), the stability fields of framework silicates, in particular that of plagioclase, also depend on fO_2, being somewhat depressed at low fO_2 (Dall'Agnol et al. 1999). This feature is also documented in basalt melting experiments (Sisson et al. 2005). Lastly, the effect of sulfur on phase equilibria has been explored in some detail (e.g. Costa et al. 2004). One of the most significant findings is that, under moderately oxidizing conditions (around NNO+1), biotite thermal stability is increased by elevated fS_2, whilst that of hornblende shows the opposite trend, possibly as a result of Ca–S complexation in the melt at high fO_2. As for fO_2, however, there are not sufficient data to establish quantitative and general trends related to changes of fS_2. Systematic investigation of the role of sulfur on phase equilibria, under controlled fO_2 and fS_2, clearly represents an important avenue for future research.

Peralkaline Silicic Magmas

Peralkaline magmas occur mostly in rift zones, back arc settings or hot spot environments and are typically associated with basalts of transitional affinity: ones that have alkali contents between those of mid-ocean ridge and alkali basalts. Together, peralkaline magmas and transitional basalts form strongly bimodal volcanic provinces.

The phase equilibria of peralkaline silicic melts were first investigated in synthetic systems. Petrologic evidence shows that most, if not all, peralkaline silicic magmas are quite reduced (NNO–1 or below; e.g. Scaillet and Macdonald 2001). The origin of the peralkaline character has long been a matter of debate and is still unresolved: No experimental study has produced a peralkaline silicic liquid by partial melting of a continental protolith. This in itself provides clear evidence that peralkaline silicic rocks result from processes involving differentiation from mantle magmas, consistent with field evidence and geochemical signatures.

Representative compositions of peralkaline silicic rocks that have been investigated experimentally are listed in TABLE 1, with the corresponding isobaric phase relationships shown in FIGURE 3. One of the key features of such magmas is their relatively low liquidus temperatures, despite having elevated bulk iron contents (compared to metaluminous systems) which vary between 2 wt% for incipiently peralkaline (A/CNK = 0.9, or A/NK = 0.95) up to more than 7 wt% for the most peralkaline (A/CNK = 0.49, or A/NK = 0.59) rhyolites. The phase assemblage is dominated by the crystallization

of alkali feldspar, the magma being too Ca-poor for plagioclase to be stable. In peralkaline rhyolites with higher Ca concentrations, which are the less peralkaline of a given series, the calcic silicate phase is Fe-rich clinopyroxene. In the less calcic and more peralkaline systems, amphibole of the sodic–calcic (riebeckite–arfvedsonite) end-members crystallizes. In contrast to calcic amphiboles from metaluminous systems (hornblende), the thermal stability of sodic amphibole increases with decreasing H$_2$O$_{melt}$ because of F–OH substitution. The F-rich character allows sodic amphiboles to be more stable at lower pressures (e.g. during ascent and surface outflow) than their calcic equivalent in metaluminous magmas. Amphibole occurrence as a near-liquidus mineral in peralkaline silicic rocks (i.e. crystal-poor volcanic rocks) indicates H$_2$O-rich conditions and temperatures below 750°C. Higher fO_2 promotes aegirine crystallization at the expense of amphibole. However, aegirine may also appear at low fO_2 but at lower temperature than amphibole (FIG. 3C).

Pre-eruptive conditions derived from experimental data indicate invariably water-rich conditions, with H$_2$O$_{melt}$ >4 wt%, temperatures below 800°C and even down to <700°C, and redox state at or below NNO–1. The pressure of magma storage or crystallization is inferred to be low, around 1 kbar, in agreement with geological/volcanological inferences. Clearly, there is no evidence that peralkaline rhyolitic magmas are drier than other silicic magmas. In contrast, their redox state, be it inferred from phase equilibria or mineral barometry in quenched volcanic rocks, lies at the low end of the redox range displayed by felsic terrestrial magmas.

CONCLUSIONS AND PERSPECTIVES

The constraints on magmatic water content from phase equilibria indicate that the vast majority of silicic melts contain several wt% H$_2$O in solution very early in their evolution (e.g. Whitney 1988). This is interpreted as occurring at their production site, with temperature and H$_2$O being roughly inversely correlated (Andújar and Scaillet 2012). Altogether, silicic magma compositions often reflect their source, including the source's redox state. Magmas originating from metasediments are peraluminous and reduced, with fO_2 possibly reflecting the graphite-saturated character of many sedimentary protoliths. Silicic magmas formed by partial melting of igneous sources are, on average, more oxidized, though some may be quite reduced. However, the common assumption that water-rich magmas are more oxidized than water-poor magmas is not supported by experiment. This is perhaps best illustrated by

the existence of reduced but H_2O-rich peralkaline rhyolites. There is, thus, a decoupling between magma redox state and degree of hydration.

In terms of phase equilibria, the fundamental distinction between S- and I-type silicic magmas appears to be still valid more than 40 years after its definition (Chappell and White 1974). The usefulness of the A-type category – defined to label granites that are not only rich in alkalis but also anhydrous and that outcrop in anorogenic settings – is less obvious (e.g. Clemens et al. 1986): for example, there is no clear distinction in their alkali/alumina ratio. Besides the fact that A-type magmas are not systematically drier than other types, experimentally produced metaluminous A-types are significantly different from A-types that lead to peralkaline melts, the latter producing some of the coldest magmas erupted on Earth (660 °C), while the former may yield some of the hottest silicic magmas (1,000 °C). Another difference between the metaluminous and peralkaline A-types is that metaluminous A-type systems often derive from the partial melting of older, continental crust igneous sources. In this respect metaluminous A-types differ little in terms of phase equilibria from I-types. In sharp contrast, peralkaline silicic magmas derive from the fractionation of basaltic parents either by protracted crystal fractionation or by small degrees of partial melting. These peralkaline magmas have little to no interaction with continental crust because any significant contribution of (Al-rich) crustal material will inevitably counteract the peralkalinity.

Although considerable progress has been made over the last two decades in constraining the P–T–X conditions of silicic magma production and evolution, the detailed investigation of the role of volatiles other than H_2O (i.e. S, F, Cl, CO_2 and others) still needs to be carried out so as to better model the conditions of silicic magma storage. Careful and systematic evaluation of the role of additional components to the haplogranite system, such as Ca and Fe, should also be pursued in order to provide accurate compositional datasets to go with thermodynamic modeling approaches.

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