



What controls chemical variation in granitic magmas?

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ARTICLE INFO

Article history:

Received 14 October 2011

Accepted 4 January 2012

Available online 12 January 2012

Keywords:

Granite

Chemical variation mechanisms

Peritectic assemblage entrainment

ABSTRACT

Consideration of the models that have been applied to explain the chemical variations within granitic rock suites shows that most are inadequate to account for the main variations. This stems from a variety of model deficiencies, ranging from physical or energetic inadequacies to incompatibility with the chemical data or internal inconsistency between models based on, for example, isotope or trace-element data and major-element data. We contend that any model that fails any of these tests of internal consistency cannot be considered further. Thus, although we can point to examples in which many of the traditionally accepted mechanisms have played secondary roles in producing variation, there presently remains but one viable choice for the primary mechanism by which most granitic magmas acquire compositions beyond the range defined by the compositions of crustal melts. That primary mechanism is peritectic assemblage entrainment (PAE).

We infer that once a partial melt has formed in a crustal protolith it may segregate from its complementary solid residue carrying small crystals of the peritectic phase assemblage formed in the melting reaction, and that the ratios of individual peritectic minerals in the entrained assemblage remains fixed in the ratio decreed by the stoichiometry of the melting reaction. For those elements with low solubilities in granitic melts, PAE (in varying degrees), accompanied by co-entrainment of accessory minerals, is responsible for most of the primary elemental variation in granitic magmas. In contrast, the concentrations of elements with high solubilities in silicic melts reflect the protolith compositions in a simple and direct way. The source is the primary control on granite magma chemistry; it dictates what is available to dissolve in the melt and what will be formed as the entrainable peritectic assemblage. The apparent complexity in granitic rock suites is largely a consequence of these processes in the source. All other mechanisms contribute only as a secondary overlay.

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1. Introduction

Magmas with broadly granitic chemistry can be generated by partial melting of a wide variety of protolith materials and also as the end-products of extreme fractionation of mafic magmas. However, the partial melting of basaltic or altered basaltic rocks produces sodic felsic magmas, allied to oceanic plagiogranites, the Archaean TTG suite and the modern adakites. Fractionation of basaltic magmas, likewise produces small volumes of mainly sodic and peralkaline granophyres and plagiogranites. From the outset, we wish to exclude such occurrences from further consideration. To be clear about the tectonic environments that we seek to cover, our analysis includes intracontinental settings and continental arcs. Our analysis thus applies to large-volume, silica-oversaturated, normal- to high-K, calcalkalic to alkali-calcic I- and S-type magmas generated in environments where continental crust is a likely major contributor to the magma volume. Such magmas have relatively high temperatures of formation and are markedly undersaturated in H₂O (Clemens, 1984; Scaillet et al., 1998). They have been demonstrated to have been produced mainly by fluid-absent partial

melting reactions, within Earth's crust (e.g. Clemens and Watkins, 2001; Stevens and Clemens, 1993). Though generated deep in the crust, such magmas are commonly emplaced at shallow crustal levels. These are the most important kinds of granitic magmas for the evolution of Earth's upper layers, as their formation and ascent have been linked with the processes of crustal growth, high-grade regional metamorphism and crustal differentiation (Clemens, 1990).

The kinds of granitic bodies and felsic volcanic sequences with which we are dealing vary in their major-element, trace-element and isotope chemistry (Fig. 1). These variations occur on a variety of scales, from the millimetric (subcrystalline) to the kilometric (pluton compositional zoning, sheeted or layered structures, concentric sequential intrusions, etc.). In some cases this heterogeneity is manifest in mineralogical variations that are obvious and commonly mappable. However, in some instances it remains cryptic (e.g. isotope heterogeneities or subtle whole-rock chemical differences without obvious mesoscopic mineralogical consequences). Field evidence shows that plutonic granitic magmas are generally delivered in pulses, from their source regions. Such pulsed magma delivery must play a significant part in the formation of heterogeneous intrusive masses (e.g. Coleman et al., 2004; de Saint Blanquat et al., 2011; Glazner et al., 2004). Although there are variations in magma volatile content, felsic volcanic magmas are fundamentally characterised only by a difference in

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emplacement mechanism. Thus, the volcanic magmas are probably also subject to pulsed magma delivery. Clemens et al. (2010) concluded that the bulk of the variation shown within granitic rock series is inherited from the magma sources (protoliths). This somewhat controversial finding implies that processes that might cause magma differentiation are not of primary importance but simply serve to locally complicate the primary, source-inherited heterogeneities.

Note that it is not our proposition that granitic rocks represent solidified granitic liquids. However, if we accept granitic rocks as magmatic, then they must have crystallised from magmas. That granitic magmas are commonly partially crystalline is axiomatic. The degree of crystallinity at the point of eruption or final intrusion of the magma, results from the fact that granitic magmas leave their source rocks as magma, from the partial crystallisation of the melt and possibly some crystal accumulation. Being partially crystalline is not the same thing as being differentiated, in the sense of the term that is usually understood – crystal-liquid separation, on the scale of the magma chamber, to produce a zoned structure with a range of magma compositions from an originally homogeneous parent magma. What previous work has shown is that granitic magmas do not seem to have differentiated on large scales at all. The arguments have most comprehensively been presented in Clemens et al. (2010). This is emphatically not to deny any sort of differentiation. In fact, locally, granitic magmas have evidently undergone extreme fractionation, for example to produce pegmatitic and aplitic residua. However, differentiation, by whatever mechanism, does not seem to be the main cause of heterogeneity in felsic magmatic bodies. Here we propose to explore this proposition further, asking the following questions:

- What are the major mechanisms that are responsible for variability in granitic magmas and rocks; do granitic magmas fractionate in magma chambers?
- Where and particularly how does this variability originate?
- How does this knowledge help us to interpret granitic and felsic volcanic sequences; what is the connexion between the magmas and the processes that led to their formation?

In the words of the fictional Sherlock Holmes (from *The Sign of Four* by Sir Arthur Conan Doyle, 1890) “When you have eliminated the impossible, whatever remains, however improbable, must be the truth.”

2. Models for the production of chemical variation in granitic magmas

Many different mechanisms have been suggested to be responsible for the production of heterogeneity in granitic magmas, most having been adapted from models that have been used, with varying success, to explain variations in intermediate to mafic volcanic rock suites. Such mechanisms can be divided into two essentially different sorts – those that involve changes in magma chemistry by mixing or hybridisation, and those that involve changes in magma chemistry by chemical or mechanical separation of suspended crystals (i.e. differentiation of a parental magma). In the latter category we can include separation of crystals and liquid at the magma source. Both categories of mechanism can operate either at depth (near the magma source) or at higher levels (in the magmatic plumbing system). In the following sections we review the characteristics of these mechanisms and attempt to come to a balanced judgement as to whether they have significance in the production of the variations presented by felsic igneous rock series.

3. A rogues' gallery of variation mechanisms

In this section we deal with a number of variation mechanisms that we judge to have little or no importance in the production of large-scale variations in granitic series. As such, a few relatively brief comments seem all that is necessary to demonstrate their unimportance. Among this group may be found one or two ‘sacred cows’, for which we make

no apology, but ask the reader to try to examine the evidence for a particular hypothesis without any affection for it.

3.1. Wall-rock bulk assimilation

The idea that magmas can assimilate significant volumes of wall rock, with which they come into contact, has been a prominent component of many models for the production of geochemical and isotopic variations in a wide variety of magmas. For example, it is explicit in the idea of assimilation and fractional crystallisation (e.g. DePaolo, 1981; Powell, 1984) and underpins the idea that granitic magmas can achieve their isotopic characteristics (commonly sitting between those of the mantle and those of the sedimentary crust) through assimilation of crust by mantle-derived mafic magmas (e.g. Beard et al., 2005). In theory, bulk assimilation may take place by either mechanical disaggregation of ingested xenoliths or by reactive dissolution and precipitation of crystals. These ideas have been effectively debunked by consideration of the energetic consequences of these processes (Glazner, 2007; Spera and Bohrsen, 2001). Essentially, the energy consumed in these processes results in considerable cooling, crystallisation and the formation of a hybrid magma so highly crystallised that it would be immobile and incapable of undergoing further magmatic evolution. Also, in many cases, assimilation models based on isotope or trace-element data, fail to pass the test of agreeing with the major-element chemistry of the modelled ‘hybrid’ rocks (e.g. Clemens et al., 2009, 2010).

In counterpoint, it should be understood that a more effective degree of hybridisation could be accomplished through mixing between partial melt from xenoliths and the host magma (e.g. Glazner and Mills, 2011). Nevertheless, similar strictures of energy consumption and the requirement that major-element abundances agree with isotope-based models also apply here. Additionally, if this mechanism were general in its applicability one would expect to find granites fairly littered with restitic xenoliths, and we have yet to see such a thing in nature. Our conclusion is that wall-rock assimilation can contribute, marginally, to a small amount of variation in some granitic bodies but it is most unlikely to be a major source of pluton-wide variation. It might be thought that the best evidence for this process could be generated where successive intrusions of more deeply derived granitic magma into the mid-crust advect sufficient heat into these zones that fertile country rocks begin to melt and contribute such melts to the pluton (e.g. Lackey et al., 2012). However, to do this would be to confute two distinct processes; this is not wall rock assimilation, but rather an advancing anatectic front.

3.2. Liquid immiscibility

In kimberlites and ultramafic to mafic lavas, evidence of small-scale immiscibility is sometimes observed as globules of carbonate or as two species of felsic glass coexisting in the interstices. High CO₂ contents in carbonated mafic to ultramafic magmas can lead to the formation of some types of carbonatite (e.g. Kjarsgaard and Hamilton, 1989) and the unmixing in the interstitial glasses of some basalts, particularly K-rich magmas (Philpotts, 1976, 1982). In granitic melts, experimental work has shown that immiscibility can occur when a granitic melt with very low Fe and Mg is doped with percent-level concentrations of fluorine (Kovalenko, 1978). However, this mechanism will only operate in highly felsic and fluorine-rich residual systems to produce tiny amounts of immiscible hyperaluminous, fluorine-rich melt (Manning et al., 1980). In granitic systems with high concentrations of Cl, tiny quantities of chloride-rich hydrosaline melt may coexist with hydrous silicate melt at the last stages of crystallisation (e.g. Frezzotti, 1992). However, there is no evidence that liquid immiscibility plays any volumetrically significant role in creating chemical variability in ordinary S- and I-type granitic magmas.

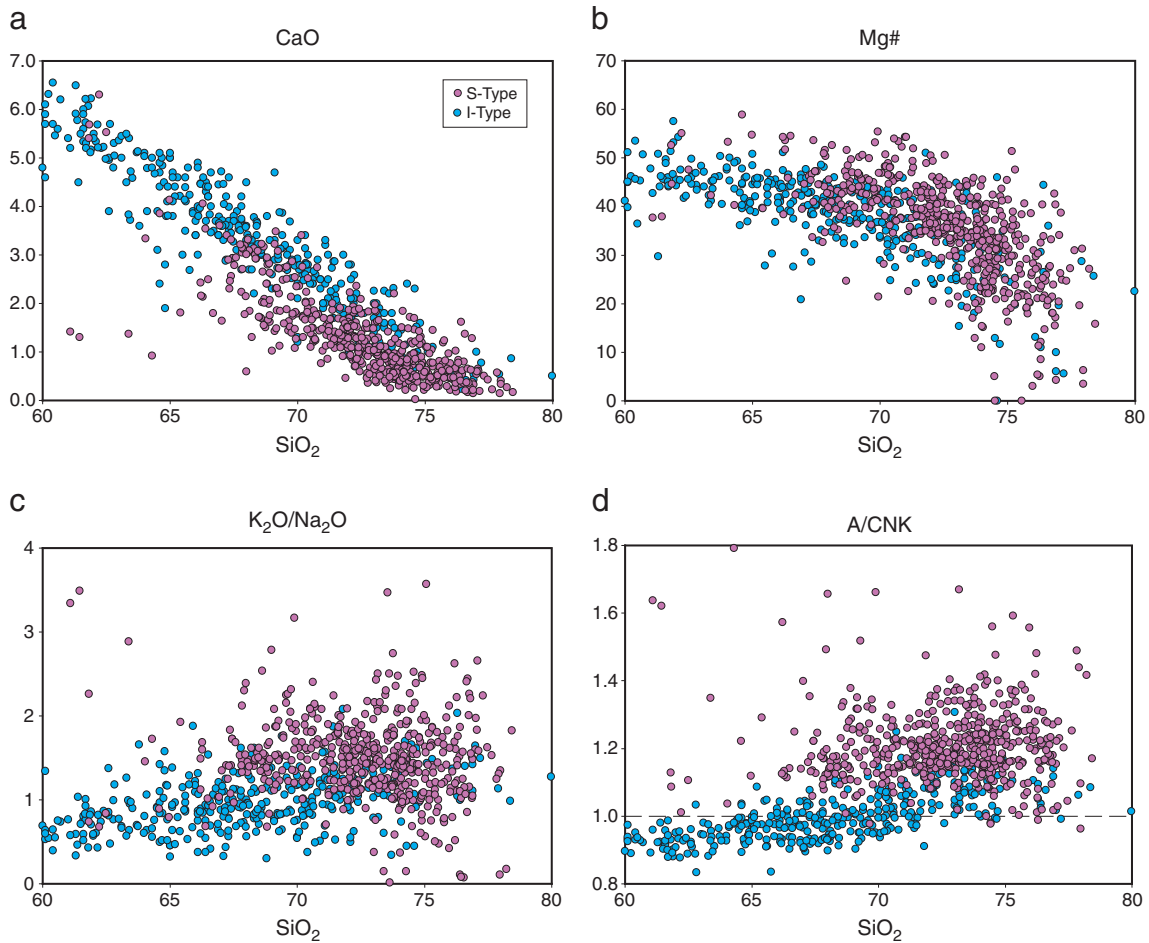


Fig. 1. An illustration of typical major- and trace-element chemical variations in S- and I-type granites on Harker plots. Stevens and Clemens (in press) and Stevens et al. (2007) showed that these major-element data arrays are also mirrored in the internal variations shown by numerous individual suites of rocks. Thus, where there is reasonable correlation between parameters (e.g. CaO and SiO₂) this exists because granitic rock suites generally exhibit higher degrees of correlation between the two parameters than that defined by the overall population. The greater degree of scatter in some other parameters is due to greater degrees of scatter within the individual suites. Note that any general model for the genesis of each of these granite types (I- and S-) must account for substantial compositional variation in all aspects of the chemistry of these rocks, whilst simultaneously accounting for the characteristic trends defined by the data points.

3.3. Vapour-phase alkali leaching

At conditions close to the solidus of a granitic magma a hydrous volatile-rich phase will normally separate from the residual melt. It is conceivable that, if this phase is not lost to the system rapidly (vented through fumaroles, for example), it may circulate through the magma or solid rock. In doing so, it will have the capacity to dissolve some alkalis and aluminium, and possibly some Fe, removing these elements from the residual melt. Since such fluids have subalkaline to peralkaline chemistry (Fyfe et al., 1978; Webster, 1997), they would commonly render the leached magma more aluminous. There are examples of this kind of process having produced hyperaluminous magma or rock (e.g. Currie and Pajari, 1981; Goad and Černý, 1981; Martin and Bowden, 1981). However, these are all unusual cases where there large reservoirs of fluid interacting with relatively small plutonic masses. Thus, although this mechanism can have potent effects, it is unlikely to be a major factor in producing the variation present in most large granitic plutonic complexes, and even less likely to play any significant role in volcanic situations.

3.4. Double-diffusive convection and Soret diffusion

These two proposed mechanisms are grouped together for two reasons. First, they are supposed to operate in purely liquid magmatic systems and second because they are united in the proposition that some large-volume silicic volcanic systems evolve by ‘convection-

driven thermogravitational diffusion’ (e.g. Hildreth, 1979). Double-diffusive convection (the interplay of thermal and compositional convection; e.g. Baker and McBirney, 1985; Clark et al., 1987) can result in the formation of complex layering and fingering in liquid systems, as long as the systems are not disturbed by chaotic magma flow or by significant crystallisation. Some horizontal layering features and fingering (vertical pipe-like features) in mafic intrusions have been ascribed to this sort of process operating in relatively low-viscosity magmas where convection is possible. In silicic magmas, with their elevated Rayleigh numbers, such processes are likely to be less prominent, though there is some field evidence that suggests that convection may have played a role in the formation of some metre-scale structures in granitic magmas (e.g. Barrière, 1981; Weinberg et al., 2001).

Soret diffusion occurs when a liquid is held within a temperature gradient. Some elements then diffuse toward the hot end and some to the cold. This is a very fragile chemical gradient because it is so easily disturbed by magma flow and convection and swamped by more robust processes in crystal-bearing systems. Moreover, experiments have shown that Soret diffusion results in chemical trends that run counter to those observed in felsic magmatic bodies (e.g. Baker and McBirney, 1985; Leshner and Walker, 1991; Leshner et al., 1982; Schott, 1983). Thus, if this process ever occurs, its effects would be most unlikely to be preserved and some other phenomena need to be called upon to explain compositional zonation in largely felsic liquid magma bodies.

Hildreth (1979) proposed that the Bishop Tuff magma had become chemically zoned by a combination of volatile-fluxed element migration and Soret diffusion, aided by convection. However, the objections cited above apply to this complex, composite model and the principle Occam's razor suggests that a simpler mechanism be sought. Indeed Hildreth and Wilson (2007) abandoned this idea in favour of multiple injections of fractionated liquid derived from a deeper source. We would agree that injection of multiple magma batches, prior to eruption, represents a far more credible solution to the problem of how compositionally zoned, crystal-poor ignimbrite magmas are formed. Convincing evidence for the operation of double-diffusive convection in silicic magma systems has yet to be presented.

3.5. Deep-seated magma hybridisation in MASH or 'hot' zones

Intermediate and granitic magmas in arc settings are typically out of compositional equilibrium with olivine-bearing mantle sources. Consequently, such magmas are proposed to form by two different processes, either by crystal fractionation from a primary, mantle-wedge-derived basaltic to magnesian andesitic magma (e.g. Grove et al., 2003; Rogers and Hawkesworth, 1989) or through partial melting of older crustal rocks (e.g. Izbekov et al., 2004; Petford and Atherton, 1996). Both these processes have been proposed to occur simultaneously, with heat and H₂O released from the crystallising primary magmas acting as the trigger for the crustal melting (Annen and Sparks, 2002). Assimilation of crustal rocks by the primary magmas is proposed to be important in shaping the compositions of the arc magmas (e.g. DePaolo et al., 1992). In combination, the magma modification processes described above are proposed to function within Melting, Assimilation, Storage and Homogenization (MASH) or deep crustal hot zones near the crust–mantle boundary (Annen et al., 2005; Hildreth and Moorbath, 1988) to produce large volumes of intermediate to granitic magmas. For intermediate to felsic rocks in the Southern Volcanic Zone of the Andes in Chile, Hildreth and Moorbath (1988) invoked MASH zones to explain along-arc changes in isotope and element ratios that suggest a northward increase in the continental crustal component. However, this geochemical trend has also been interpreted to reflect the presence of a northward increase in the proportion of subducted crustal component in the mantle wedge (e.g. Stern, 1991; Stern and Skewes, 2005). The net result of MASH processes and re-melting of newly crystallised magmatic additions to

the lower crust by fresh influxes of basaltic magma would produce very similar results. The efficacy of MASH depends on the efficient co-functioning of fractional crystallisation, assimilation and magma mixing. Previous authors examined these processes independently, and it is probably best to keep to such a strategy, since the complex and simultaneous interplay of these processes would be extremely difficult to model. However, it should be noted that the efficiency of these processes might differ significantly in the base of the arc crust and in the middle to upper crustal sites of intrusion. Do we need MASH to explain the origin of arc granites? Probably not, since partial melting of juvenile dioritic material in the lower crust and generation of the more mafic granites through PAE would achieve the same geochemical results without the rather awkward requirement for homogenisation of mixed magmas. The efficacy of mixing is further addressed in the following section.

3.6. Shallow magma mixing and mingling

All granite petrologists are aware of the spectacular examples of field evidence for the coexistence of mafic and felsic magmas. Mafic bodies in felsic host rocks occur as synplutonic dykes, pillows and enclaves, sometimes with evident hybridisation at their rims. Magma mixing constitutes a convenient and simple explanation for the fact that the isotope characteristics of most I-type granites lie between those characteristic of the mantle and those characteristic of sedimentary rocks. The idea is essentially that highly felsic melts of the continental crust mingle and mix with more mafic, mantle-derived magmas to produce monzogranitic to tonalitic hybrids with the appropriate isotope ratios. In terms of major- and trace-element variation, magma mixing would produce linear correlations between elements and oxides in Harker plots. As pointed out by Clemens et al. (2010) numerous studies have shown that granitic rock bodies can contain isotopic and elemental heterogeneities that exist despite the complete absence of any evidence that they were produced by magma mixing (magmatic enclaves, pillows, crystal resorption textures and reactive overgrowths, etc.). Additionally, in some situations where there is field evidence that was proposed to represent magma mixing, isotopic evidence and major- and trace-element compositions commonly do not couple in coherent magma-mixing arrays (e.g. Barbarin, 1988). Within rock suites produced by magma mixing, it might be expected that maficity (mol. Fe + Mg) should scale in proportion to isotope ratios, with the most mafic

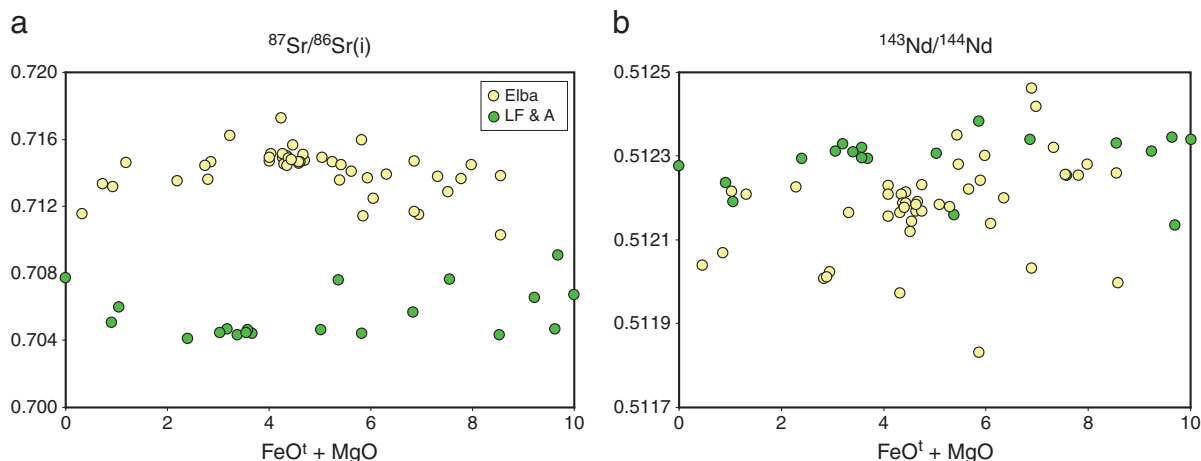


Fig. 2. Isotopic variations with maficity for two I-type granitic suites. The data from Elba (Italy) are taken from Dini et al. (2002), Farina (2008), Farina et al. (2010), and Gagnevin et al. (2004). Those from the Scottish Loch Fyne and Arrochar suite (LF & A) are from Clemens et al. (2009). The Elba rocks are characterised by spectacular swarms of mafic enclaves in places. Thus, these rocks could be advanced as field evidence that “proves” magma mixing. If the major-element compositional range in these rocks reflected mixing between a felsic crustal magma and a mafic magma, it would be reasonable to expect Sr and Nd isotope ratios to scale proportionally with maficity. They do not scale in this way, which reveals a significant disparity in the amounts of mantle melt that would be required to be mixed, as calculated from isotope ratios, and the amounts required by major-element constraints. The Loch Fyne and Arrochar data illustrate similar trends in a suite of I-type granites with co-magmatic mafic rocks where a magma mixing hypothesis would seem to be potentially reasonable based on major-element variations.

magmas being characterised by the most mantle-like isotope ratios. However, this is commonly not the case (Fig. 2). Nevertheless magma mixing is commonly proffered as an explanation for the chemical variations in groups of I-type granitic rocks. We would rather suggest that protolith heterogeneity is the source of the isotopic variations, and that the chemical variations are also related to the melting reactions in the protoliths. For a detailed treatment of these arguments, see the section below on peritectic assemblage entrainment, Clemens et al. (2010) and Clemens et al. (2011).

Farina and Stevens (2011) demonstrated that radiogenic isotope variability in granitic magmas is the inevitable consequence of mineral and larger scale isotopic disequilibrium in typical heterogeneous crustal protoliths and the withdrawal of magma batches in a progressive melting process. Thus, it is not necessary to invoke magma mixing to explain such heterogeneities. Also, partial melting of meta-igneous crustal rocks, themselves not long previously extracted from the mantle and not having had a prolonged crustal recycling history, would also serve to explain the

radiogenic isotope characteristics (e.g. initial $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd_T) of I-type granites (only a little more evolved than the mantle). Thus, andesitic sequences, with some volcanoclastic component in arc terranes would be ideal candidate protoliths. Such rocks have been shown, experimentally, to produce granitic to granodioritic melts. Nevertheless, many I-type granites do contain intermediate to mafic magmatic enclaves and other evidence for the coexistence of magmas with different origins. The question here is whether these phenomena point to a major geochemical process, or rather to the fact that such mafic, mantle-derived magmas commonly constitute the heat source that powers crustal melting. One important fact to remember here is that, in any mixing system, one end-member is usually considerably in volumetric excess over the other. In the vast majority of the plutons under consideration it is the granitic fraction that dominates. Thus, by simple mass balance, if the observed volumetric ratio is representative, it will be the enclave magmas that become significantly hybridised, leaving the volumetrically superior host granitic magmas relatively unaffected.

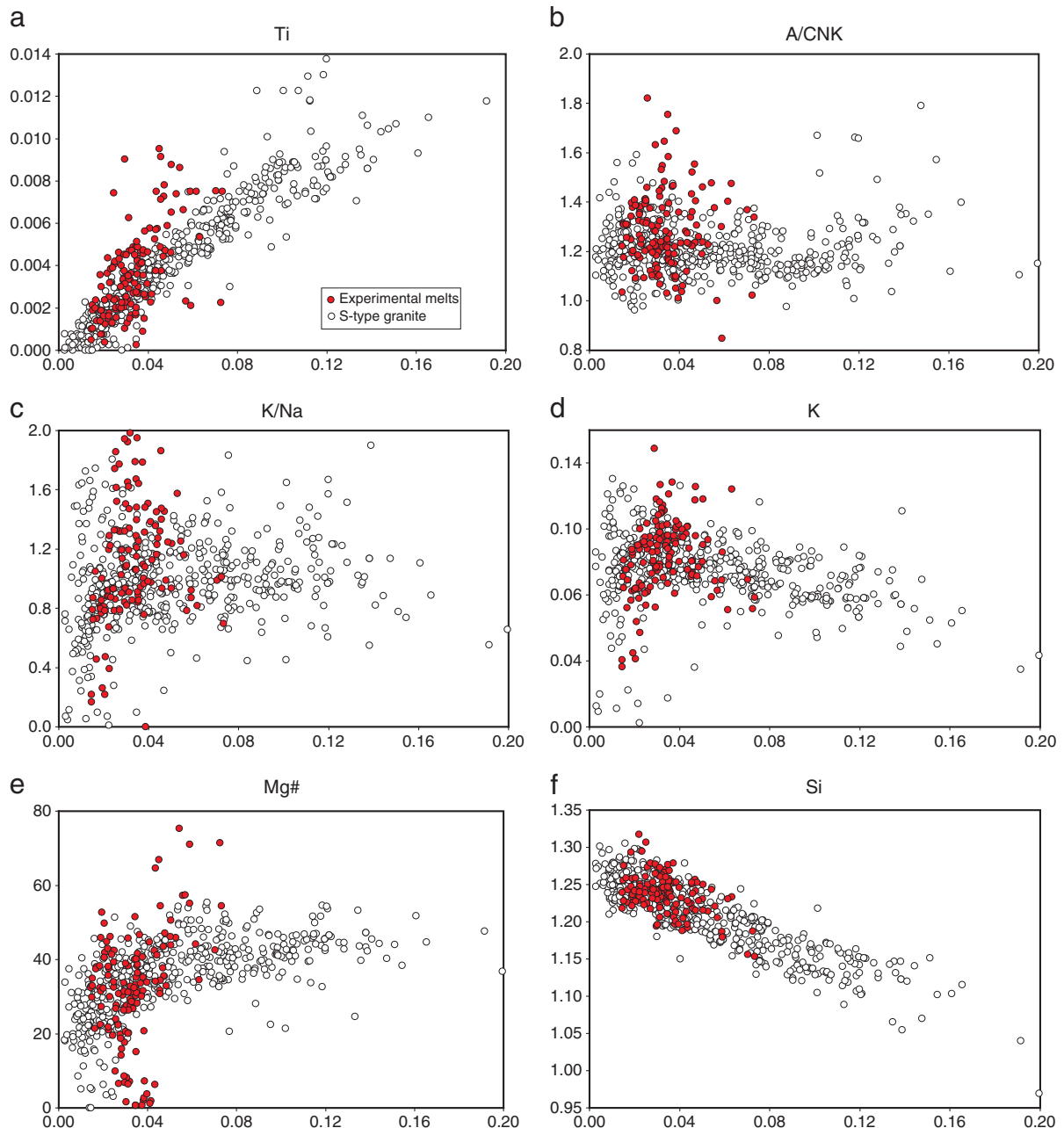


Fig. 3. Element or atomic ratio vs. maficity plots for S-type granites and relevant experimentally produced melts.

It is also worth recalling that many I-type suites do not contain significant populations of mafic to intermediate enclaves. Indeed, even where they are present, these are clearly the products of emplacement-level mingling textures and do not necessarily indicate extensive magma mixing. True mixing by chemical diffusion has commonly been shown to be minor, even when these spectacular magma mingling textures are present or it is the minor mafic component of the mafic–felsic systems that shows discernible mixing, rather than the host felsic magma (e.g. [el Desouky et al., 1996](#); [Frost and Mahood, 1987](#); [Sparks and Marshall, 1986](#)). True mixing by mechanical stirring is either complete (since evidence for it does not seem to be common) or it does not occur. Experiments and theoretical calculations indicate that mixing is rather inefficient in granitic magmas that typically have low Reynolds numbers (e.g. [Bergantz, 2000](#); [Sparks and Marshall,](#)

[1986](#)) and that it is normally the enclaves that become hybridised, leaving the voluminous host magmas little affected. In some cases, it can even be shown that the enclaves do not form part of the chemical or isotopic lineage of the host rocks (e.g. [Clemens et al., 2009](#)). In those cases they appear to be low-volume magmas that accompanied the felsic magma to its emplacement site. These were derived from the enriched mantle and became heavily hybridised through immersion in the host granitic magma. In other cases, elaborate mixing models do not stand up to quite simple geochemical tests (see e.g. the analysis of [Cristofides et al., 2007](#) by [Clemens et al., 2010](#)).

The arguments presented above are unlikely to sway those who have worked on suites of rocks in which physical evidence suggests co-existence of contrasting magmas and isotope evidence suggests that mixing could have operated. Thus, we present the following analysis,

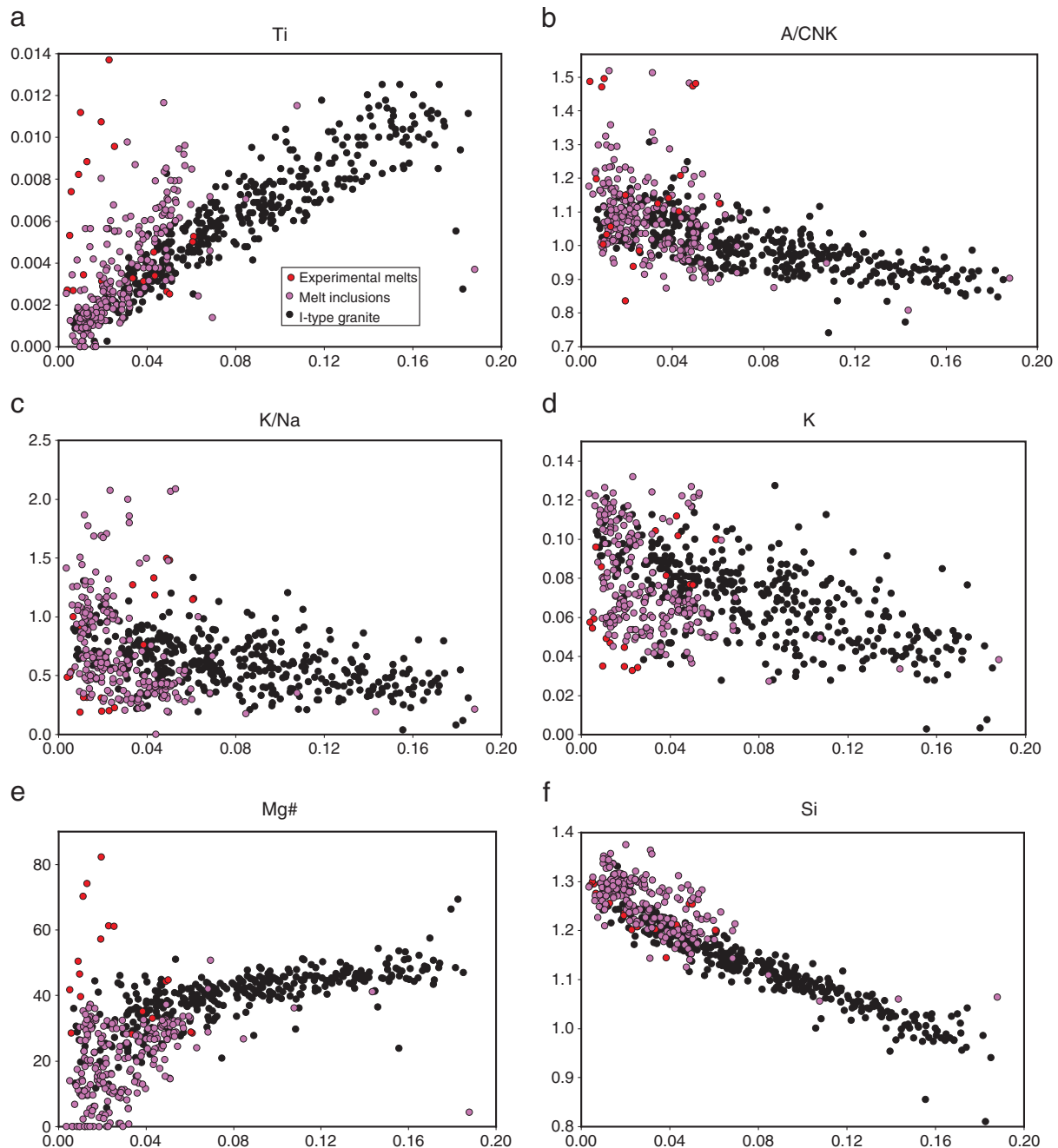


Fig. 4. Element or atomic ratio vs. maficity plots for I-type granites, relevant experimentally produced melts and melt inclusions. Note that, in this case, the number of relevant experiments is low because of the requirement that the melts should be granitic in character. The products of experiments on the melting of broadly basaltic (and amphibolitic) sources have been excluded because these produce sodic melts that are trondhjemitic to tonalitic.

based on the major- and minor-element chemistry of I-type granitic series. The dataset used here contains rocks from many different terranes of many different ages and includes numerous plutons for which the existing explanation for the chemical variations is magma mixing.

3.7. Progressive partial melting

As shown by Clemens and Watkins (2001) partial melting of Earth's crust, to produce voluminous, mobile, granitic magmas occurs by fluid-absent reactions that involve the breakdown of micas and amphiboles (mainly muscovite, biotite and hornblende), either alone or in combinations. It is entirely reasonable to suppose that the variation exhibited among granitic suites might, at least in part, reflect the advance of isotherms through the protolith. In other words, that the earlier magmas withdrawn from a particular source terrane might represent lower-temperature melts while magmas developed later might represent higher-temperature melts. We know that some crustal rocks should undergo partial melting in pulses, due to the occurrence of successively higher-temperature melting reactions. Thus, for example, a metapelite may yield melt first by muscovite breakdown and later by biotite breakdown reactions, and these melts will be different in composition. Even in a protolith in which there is just a single melting reaction, progressively higher temperatures should lead to the production of successively more mafic and calcic partial melts. Clemens (2006) summarised the experimental data on fluid-absent partial melting of crustal rocks, illustrating the common melting pulses and documenting, in broad terms, the types of melts that can be produced from different protolith types.

What is required here is a more detailed analysis of the compositions of experimentally produced partial melts from the kinds of protolith materials likely to be involved in the genesis of granitic magmas (other than the Archaean TTG series). Stevens et al. (2007), Clemens et al. (2011) and Stevens and Clemens (in press) have collated databases of the compositions of fluid-absent partial melts of metamorphosed pelites, greywackes, biotite–quartz–plagioclase rocks, dacites and andesites, together with data from natural holohyaline materials of granitic composition (obsidians, pitchstones and some granitic melt inclusions in various rocks). These data allow us to see exactly what the geochemical trends are among partial melts formed at temperatures up to 1000 °C. Figs. 3 and 4 show the data cloud for the melts in comparison to those for I- and S-type granitic rocks. The compositional database for the crystalline rocks is taken from a variety of sources, as detailed in Stevens and Clemens (in press), and the graph is plotted in terms of moles of the elements per 100 g of rock of glass. As was introduced by Stevens et al. (2007), the x axis in the plot is maficity (mol. (Fe + Mg)/100 g).

The striking feature of the data in Fig. 3 is the general lack of coincidence between the trend shown by the glasses (melts) and those shown by the crystalline granitic rocks. For example, as temperatures increase in the experimental dataset, the Ti contents of the glasses increase far more steeply with maficity than do the crystalline rocks. The glass and rock compositions do overlap at the low maficity (low-*T*) end, but the divergence between the two is already apparent in the “granite” compositional field; monzogranites and granodiorites show a trend completely distinct from that shown by the higher-*T* melts. At the low-maficity end of the variation, melting temperature (along with protolith bulk composition) must play a role in shaping the compositions of the granitic partial melts. However, since the experimental melt compositions plotted in Figs. 3 and 4 include those generated at temperatures likely to exceed the maximum commonly attainable within the crust (1000 °C), the inescapable conclusion is that the bulk of the variation shown by granitic rocks cannot be attributed to variation in melting temperatures. Furthermore, it follows that the more mafic granitic rocks (monzogranites and granodiorites) cannot be the products of crystallisation of pure crustal melts withdrawn from their partially molten protoliths. We have already

concluded that the array of granitic magma compositions cannot be primarily due to mixing between crustal melts and mafic magmas derived from the mantle. In a fluid-absent rock system undergoing partial melting, the only phases that can contribute to the composition of a magma are the melt and the residual crystals. Taken together these conclusions mean that natural monzogranitic to granodioritic magmas must contain components derived from the crystalline residue (restitic, peritectic and accessory), as well as those derived from the melt phase, and that it is the presence of these components that is responsible for the main geochemical trends in the more mafic granitic rocks. We will return to this point in Sections 3.9 where we discuss the viabilities of various crystal mixing and unmixing models.

3.8. Crystal fractionation and phenocryst unmixing

In using the term crystal fractionation we are essentially hypothesising that the variations in granitic series might be due to disequilibrium crystallisation in which earlier-formed crystals are either mechanically separated or kinetically isolated from their coexisting residual liquids, such that they fail to re-equilibrate as crystallisation proceeds. The rock compositions would then be described either as a series of fractionated liquids, as the accumulated solids, or as mixtures between these cumulates and fractionated liquids. In the absence of constraints on the exact extent of such disequilibrium, we assume that the Rayleigh fractionation equation applies. In theory, this kind of fractionation should result in curved liquid evolutionary trends on Harker plots. In contrast, we choose the term ‘phenocryst unmixing’ to apply to the possible process in which a degree of crystallisation (equilibrium or fractional) occurs in a cooling magma, followed by progressive separation of that compositionally fixed ‘phenocryst’ assemblage from the residual melt, before final crystallisation. This process would result in linear trends on Harker diagrams.

Examples in which variations in granitic series are ascribed to crystal fractionation are legion. One of us has published on supposed examples and perhaps misguidedly opined that “Crystal fractionation probably plays the major role in the differentiation of very many granitic magmas, including most S-types, especially those emplaced at high crustal levels or in the volcanic environment.” (Clemens, 2003, p. 1). However, there are few cases where the variations are described as being due to phenocryst unmixing (but see Phillips et al., 1981) even though this mechanism would readily explain linear trends on Harker plots. As detailed in Stevens et al. (2007), the high degree of correlation between Ti and maficity, inherent in all suites of granitic rocks, combined with the antithetic relationship between K and maficity, pose seemingly insurmountable challenges to any idea that the range in maficity within such suites arises through the accumulation of biotite or hornblende. Accumulation of appropriately Ti-rich biotite in S-type magmas and biotite, with or without hornblende, in I-type magmas can be modelled to produce the highly correlated Ti-maficity arrays shown by granitic suites. However, this scheme also results in sympathetic variation between K and maficity, a feature not present in the data for the compositions of granitic rocks (Fig. 5).

The concept of a large and largely liquid granitic magma chamber has effectively disappeared from the psyche of most granite petrologists. As already mentioned in Section 1, this has happened because the evidence now points to the assembly of granitic plutons through multiple, relatively small injections of magma, with partial solidification of each magma batch before subsequent injections and very limited mixing between magma batches. Thus, along with rejection of the concept of a large initially homogeneous magma chamber, we are forced to the conclusion that, if crystal fractionation occurs, it will operate mainly within relatively small regions of a pluton and independently in different sectors of that pluton. Although fractionation may be extreme, as is required, for example, in the formation of aplites and light-element-enriched leucogranites, these must be relatively small-scale and local phenomena in batholiths. The same

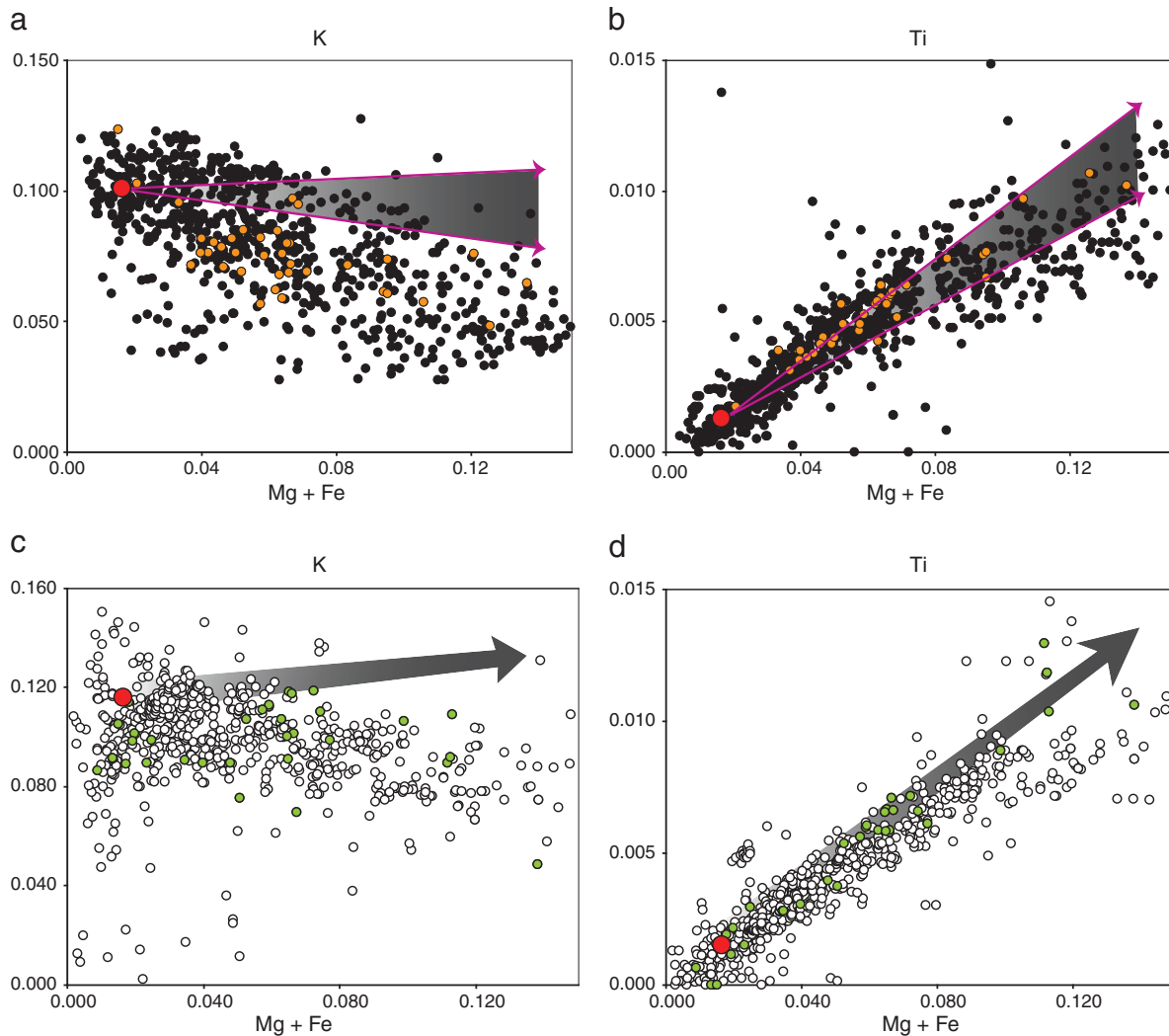


Fig. 5. K and Ti vs maficity plots for I-type (a. and b.) and S-type (c. and d.) granites comparing the trends in the granite populations with the model trends for magmas produced by biotite accumulation, with or without hornblende, in I-type magmas (a. and b.) and by biotite accumulation in S-type magmas (c. and d.). The red dots indicate the melt composition. The upper purple arrow in the I-type plots indicates the compositional trend resulting from biotite accumulation; the lower arrow represents the trend for hornblende. Compositions produced by the simultaneous accumulation of these minerals would plot in the shaded area between the arrows. The tight Ti-maficity correlations in granitic rocks are commonly held to be the product of fractionation of Ti-bearing minerals (biotite and/or hornblende), or other Ti-free ferromagnesian silicates co-fractionating with Fe-Ti oxides. The modelled arrays indicated by the arrows on the Ti-maficity diagrams fit with this hypothesis. However, mineral textural and macroscopic evidence for fractional crystallisation is normally lacking in granites, despite the fact that the most mafic rocks would need to consist of approximately 30 wt% of accumulated biotite and/or hornblende (the end points of the arrows). The K-maficity plot is particularly useful in discrediting this proposition while simultaneously explaining the general lack of evidence for fractional crystallisation. Accumulation of these minerals would produce a trend of K increasing with maficity, a prediction that is at variance with the data in the overall granite population as well as the data for within individual rock suites.

arguments apply to the concept of phenocryst unmixing. If it occurs, it must be a local phenomenon. Also, since it is only an unmixing phenomenon, phenocryst unmixing could never lead to the sorts of extreme fractionation that evidently took place in some plutons. Elements such as Li, Be, B and F will concentrate in the final, interstitial liquid fractions in any crystallising granitic system. However, in some granitic plutons there are relatively large bodies of rock rich in minerals such as tourmaline and beryl. Such high concentrations of highly incompatible elements suggest considerable degrees of fractionation, since much larger volumes of the parent magma would need to have been scavenged for these elements. This indeed suggests extreme fractionation, but the process involves fluid and melt migration, late in the crystallisation history of the pluton and does not imply any large degree of physical crystal fractionation affecting the earlier magmatic mafic minerals, feldspars and quartz.

We argue that neither of the two processes dealt with in this section can represent the primary cause of pluton-wide heterogeneities. In agreement with Clemens et al. (2010) we conclude that the

isotopic and elemental heterogeneities that occur on various scales (from millimetric to kilometric) in granites are essentially inherited from heterogeneities acquired at or near the magma sources. In considering the applicability of crystal fractionation it may be worth noting that, in cases where this mechanism does seem to have been responsible for pluton-wide differentiation, the parent magma seems to have been intermediate to mafic in composition, rather than granitic. Wyborn et al. (2001) assign these kinds of plutons in southeastern Australia to the 'Boggy Plain Supersuite' and state (p. 531, Wyborn et al., 2001) that "These rocks range in composition from 45 to 78% SiO₂, with a marked paucity of examples in the range 65–70% SiO₂, the composition dominant in most other granites of the Lachlan Fold Belt." The Boggy Plain pluton is the type example and interpreted as having solidified from the margin inward, expelling fractionated granitic liquids toward the top of the body. Our overall conclusion regarding crystal fractionation is that it can and does occur on relatively small spatial scales in granitic magma bodies and that it can be an important mechanism responsible for differentiation

in some more mafic and less viscous magmas. Phenocryst unmixing may also occur, but it is difficult to judge how common it is. We also conclude that neither of these mechanisms represents the primary cause of the heterogeneities present in many granitic plutons. In the following section, the real culprit is revealed.

3.9. Crystal entrainment and unmixing

In Section 3.7 we concluded that the geochemical data for natural and synthetic granitic melts show that monzogranitic to granodioritic magmas must contain components derived from the residual crystalline solids that coexisted with the melts in the partially molten protoliths. There are essentially three classes of crystalline material that could potentially be involved. First there are the major silicate minerals that were present in the protolith prior to the onset of partial melting and which were either in excess or did not participate in the melting reactions. These are classically known as restites and, following partial melting, they will form the crystalline backbone of the rock, deformation of which can cause the segregation of a magma. Second, there are the typically very small crystals of accessory minerals such as Fe–Ti oxides, titanite, zircon, monazite, apatite, etc. At subsolidus conditions, and for reasons of heterogeneous nucleation, these are commonly concentrated as inclusions in the hydrous mafic minerals (commonly biotite and hornblende) that break down in the partial melting reactions. Thus, these small crystals will be liberated during the melting reactions and will remain, if they are either stable or metastable within the surrounding melt. Third, in the incongruent breakdown of hydrous mafic silicates in the melting reactions, those components in the crystalline hydrates that have low solubilities in the melt phase will form new anhydrous minerals, co-formed with the hydrous melt. These newly created crystalline products of the melting reactions are termed peritectic phases and they are commonly represented by such minerals as pyroxenes, garnets, Fe–Ti oxides and relatively calcic plagioclase. The rest of this section deals with the possibility that granitic magmas represent mixtures of the melts with one or more of these three classes of crystalline residual phases.

3.9.1. Restite unmixing

The model known as restite unmixing stems from papers from the research group of Bruce Chappell and the late Alan White, in Australia. The model first surfaced in the 1970s, but is most clearly articulated in Chappell et al. (1987). As acknowledged in that paper, this model has never met with general acceptance and indeed has been the subject to comprehensive refutations (e.g. Clemens, 1989, 2003; Wall et al., 1987). Before briefly listing the chief objections to this model, we should be clear on exactly what it entails.

The restite unmixing model states that most granites represent mixtures between a low-*T* melt and a proportion of the total solid mineral assemblage remaining after the melting reaction. Thus, all three classes of residual solids (identified above in Section 3.9) are considered as 'restite'. The unmixing part of the model arises from the requirement that the whole, partially molten source be mobilised and ascend, and that all the granite compositions be then derived by progressive separation between the melt and the entrained solids. That is, this model involves initial quantitative entrainment of the 'restite'. One implication is that granites image their sources in a very simple way, with the most mafic granite in a suite representing the composition of the source material (melt plus residual solids in the same proportions as in the protolith). Such a mobilisation of the entire partially molten source effectively requires a diapiric upwelling mechanism of magma transport. The following objections to the validity of the restite unmixing model are summarised from Wall et al. (1987) and Clemens (1989).

A major shortcoming of the restite unmixing model is the lack of textural and mineralogical evidence for the presence of significant

quantities of restite in the rocks. Certainly, there is abundant evidence for the presence of inherited zircon and monazite in granites. However, the kinds of textures and mineralogical characteristics that would be expected to characterise restitic minerals seem to be very scarce in most granites. Additionally, the presence of inherited zircons cannot be taken as evidence that the rock containing them also contains an appreciable quantity of restitic quartz, feldspar, pyroxene or garnet, for example (c.f. Wyborn et al., 1981). When foliated metamorphic rock inclusions are present in granitic rocks, they generally have mineralogical characteristics inconsistent with those expected of high-*T* restitic rocks. For example, they contain hydrous minerals (usually biotite) forming what appear to be prograde foliations. The pyroxenes and garnets in these granites have textural characteristics of magmatically precipitated crystals (e.g. euhedral shapes and oscillatory zoning patterns).

Given the dubious role played (or rather not played) by diapirism in granitic magma ascent and emplacement (Clemens and Mawer, 1992; Petford and Clemens, 2000), the required diapiric transport of restite crystal-rich (up to 50 vol.%) magmas does not seem reasonable. The only possible examples of this sort of source mobilisation occur in diatexitic migmatites. These arise by low-*T*, mainly fluid-present partial melting and are, at best, feebly mobile. The products are mineralogically and texturally dissimilar to plutonic granites, especially the huge batholiths emplaced in the shallow crust. However, among this peculiar kind of diatexitic granite, there may be examples in which a degree of restite unmixing has operated to produce variation (e.g. Williamson et al., 1997). Nevertheless, given the compositions of most granitic bodies, the idea that the most mafic granite in a series represents the source composition is also a thesis that cannot be supported by the geochemical data. If it were valid, we should see batholiths and very large plutons with the compositions of andesites (i.e. diorites) and pelites, for example. We do not see such things.

The quasi-linear chemical trends shown for granitic series when plotted on Harker diagrams (various elements or oxides plotted against SiO₂) have been cited as a critically important piece of evidence for the operation of a mixing (or unmixing) mechanism. We would essentially support this view, but point out that the identification of the mechanism as restite unmixing is unreliable. Such linear trends can be brought about by a wide variety of mechanisms. Indeed, as pointed out by Wall et al. (1987), even crystal fractionation can produce near-linear trends, as long as the bulk distribution coefficient for the fractionating assemblage lies between about 0.3 and 3, as it usually does. In judging the linearity of a variation trend, we must also pay attention to how the data are plotted. Expansion of the SiO₂ axis can effectively linearise a curvilinear data distribution. We conclude that although there is good evidence for the presence of some restitic and accessory crystalline material entrained into granitic magmas, its volume is very small and the mechanism of restite unmixing cannot be responsible for the major chemical variation in granitic series. The generality of this mechanism is supported by neither the data nor the physics of magma behaviour.

3.9.2. Peritectic assemblage entrainment

As discussed above, in the section considering progressive melting, there is a substantial mismatch between the major-element compositions of monzogranites and granodiorites and those of experimental melts generated by the fluid-absent reactions that are responsible for the generation of mobile granitic magmas. Stevens et al. (2007) noted that the compositions of S-type granites, of all ages and from all continents, are characterised by very strong correlations between Ti and Mg + Fe, while showing substantial scatter in other parameters, such as ASI or K/Na. They also noted that the Ti/(Mg + Fe) ratio in S-type granites mimics that in biotite crystals from granulite-facies anatexitic rocks, and that both Ti and the mafic components within biotite have low solubilities in the granitic melts produced by incongruent biotite breakdown. Thus, this insoluble fraction of biotite must express itself

as an assemblage of peritectic minerals produced by the incongruent melting reactions. Stevens et al. therefore proposed that the compositions of strongly peraluminous granitic magmas are produced, in the source, by entrainment of the peritectic assemblage into the magma. They further suggested that magmas leaving the source would exhibit the maficity range and $Ti/(Mg + Fe)$ characteristics outlined above, as a consequence of the entrainment of the peritectic assemblage in proportions that vary from 0 to approximately 30 mol% (Fig. 6). Villaros et al. (2009a) described the strong, positive inter-correlations between Zr, Ti and maficity within S-type granites. In such rocks, a substantial fraction of the Zr budget is contained within inherited zircons. Thus, it cannot be argued that such correlations depend, in any strong way, on the melting temperature or compositional controls on Zr solubility in the melts. Villaros et al. therefore concluded that the accessory suite is co-entrained to the magma with the peritectic assemblage, as a result

of the common occurrence of accessory minerals as inclusions in biotite and hornblende. The melts, the tiny crystals of accessory minerals, and the small, neo-formed peritectic grains are all present in the same physical locations in the partially melting rock. This facilitates extraction of the accessory and peritectic crystals, along with the melts.

I-type granites are characterised by $Ti/(Mg + Fe)$ correlations similar to those described for S-type granites. Among the I-types, leucocratic granites also have compositions very similar to relevant experimentally produced melts. Similarly the more mafic granites depart strongly from the compositions of experimental melts generated at crustal P – T conditions. In contrast with the S-type granites, I-types become metaluminous with increasing maficity, despite the fact that melts and leucocratic granites in this system are mildly peraluminous. This, coupled with the $Ti/(Mg + Fe)$ behaviour (which is not a characteristic of basaltic magmas) allowed Clemens et al. (2011) and

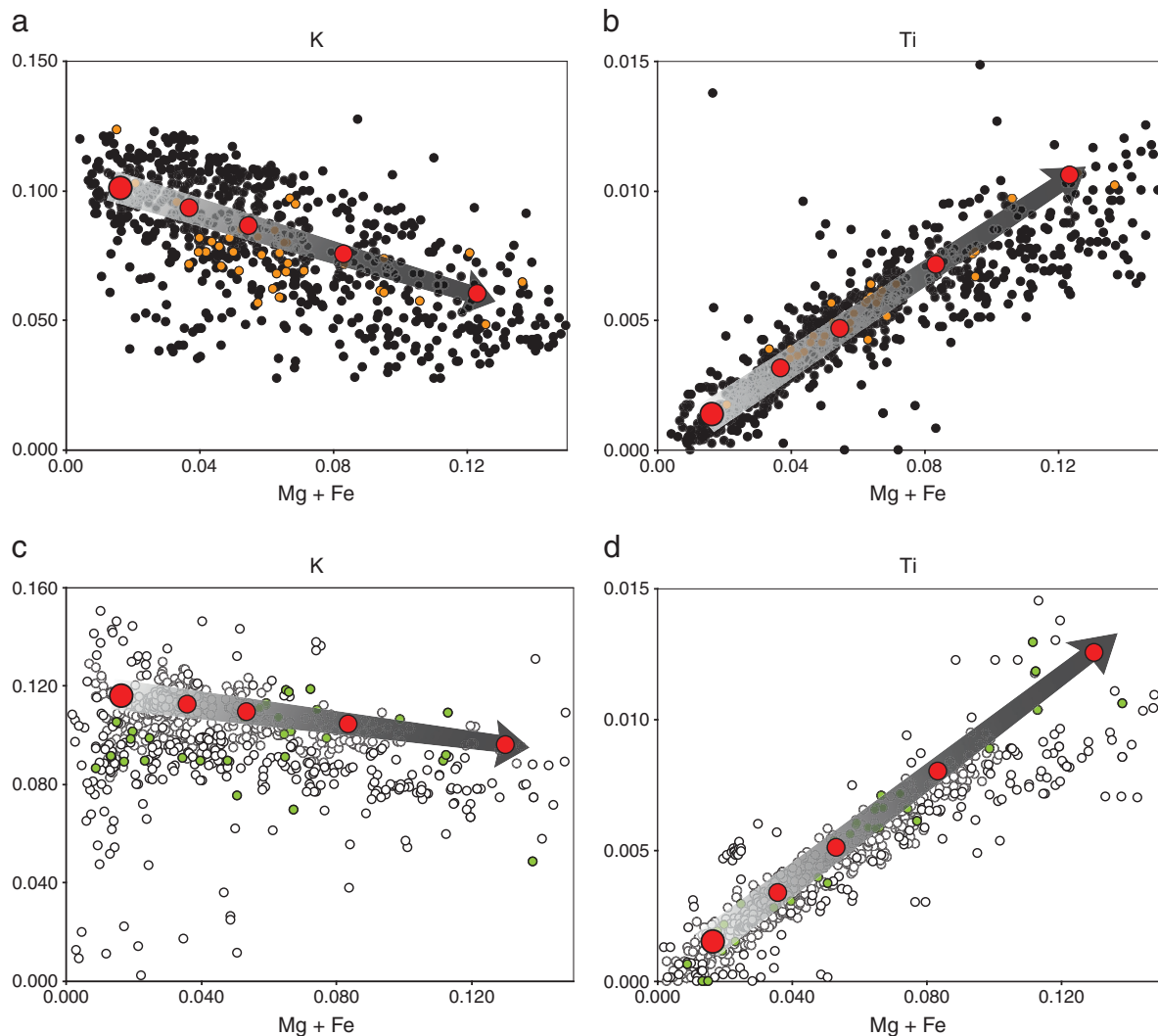
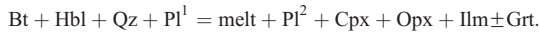


Fig. 6. K and Ti vs maficity plots for S-type (a. and b.) and I-type (c. and d.) granitic rocks, comparing the trends in the rock populations with the model trends for magma compositions produced by peritectic assemblage entrainment in broadly K-rich andesitic systems in which both biotite and hornblende partially melt (a. and b.) and for biotite melting in a metapelitic protolith (c. and d.). The approach followed in constructing these diagrams is explained in Stevens and Clemens (in press). The large red dots represent the arbitrary melt compositions (simply chosen to lie within the field occupied by melt compositions, as shown in Fig. 4). The smaller dots along the arrows represent the magma compositions produced by entrainment of 5, 10, 20 and 40 mol% of the peritectic assemblage produced in the melting reaction. The orange dots (in a. and b.) and green dots (in c. and d.) represent, respectively, the compositions of rocks of the Glen Fyne and Arrochar Suite and the Violet Town Volcanics (Clemens, 1981; Clemens and Wall, 1984), for reference. In the case of the I-type source, the melting reaction consumes biotite and hornblende and produces a peritectic ferromagnesian assemblage dominated by clinopyroxene. This is essential to producing the characteristic that I-type rocks have decreasing A/CNK with increasing maficity, extending into the metaluminous range (Clemens et al., 2011). The equivalent peritectic assemblage in the S-type source is dominated by orthopyroxene or garnet, depending on the composition of the metasedimentary protolith. This trend produces magmas that either become slightly more peraluminous with increasing maficity, or display flat A/CNK-maficity arrays. In both cases, K decreases with maficity, in a manner that reasonably replicates the natural rock behaviour. The production of ilmenite in the peritectic assemblages ensures that entrainment of this assemblage produces magmas with compositional arrays that mimic the slope of the Ti-maficity array controlled, of the compositions and proportions of the reactant biotite and hornblende (Clemens et al., 2011; Stevens et al., 2007).

Stevens and Clemens (in press) to conclude that the compositions of these magmas are also conditioned by the process of peritectic assemblage entrainment (Fig. 6). However, in the case of the partial melting reactions responsible for production of I-types, hornblende is an important co-reactant, along with biotite. Reactions are inferred to be of the form (Clemens et al., 2011):



This results in clinopyroxene being an important component of the peritectic assemblage. Entrainment of this clinopyroxene produces the trend toward more strongly metaluminous compositions as maficity increases.

The findings described above suggest that the chemical variability typically exhibited in granitic suites and individual plutons is inherited directly from the protoliths by three different mechanisms: (i) *Source control of the melt composition*. This defines the granitic character of the magmas and introduces variations in the concentrations of incompatible elements (e.g. K, Rb, Sr, Ba and Na), reflecting the compositions and proportions of the tectosilicate reactant minerals in the source, as well as the buffering residual assemblage. These elements commonly show substantial compositional variations at any given bulk-rock $\text{MgO} + \text{FeO}$ or maficity value, reflecting compositional variations in the protolith; (ii) *Peritectic assemblage entrainment control on magma composition*. This process accounts for the strong, positive $\text{Ti}:\text{Mg} + \text{Fe}$ correlation that all granitic associations have in common. Importantly, this correlation, while being a fundamental characteristic of granitic rocks is absent among basalts of all types. Thus, this characteristic, interpreted to have been induced by peritectic assemblage entrainment, is a characteristic of the physical behaviour of melts and crystals during partial melting in the crust (Stevens and Clemens, in press). This attribute of granitic magmas poses a substantial challenge to the notion that their chemistry is significantly moulded by mixing with mafic to intermediate mantle-derived magmas; (iii) *Co-entrainment of the accessory mineral suite*. Co-entrainment of the accessory suite controls the concentrations of elements that are hosted within zircon, monazite, xenotime and allanite. This accounts for the fact that elements concentrated in these minerals (e.g. Hf, Zr and REE) correlate positively with compatible major elements that do not reflect their solubilities in the melt, but rather the operation of peritectic assemblage entrainment.

At this point we must state that we do not expect to be able to petrographically identify peritectic mineral grains within granitic rocks. The small grain sizes of these peritectic crystals, entrained as they are before they can grow and texturally mature, will mean that they are readily reequilibrated with the magma during ascent and emplacement. This will occur through a number of processes. Peritectic feldspar will have a high propensity to dissolve as the magma ascends and water solubility in the melt decreases. Ferromagnesian peritectic minerals will commonly react with melt, as temperature decreases and water activity rises, to form biotite and/or hornblende. In cases where the peritectic mineral remains part of the magmatic assemblage, a coupled dissolution–precipitation process results in efficient reequilibration of even slow-diffusing minerals (such as garnet) to the pressure–temperature conditions of the magma during ascent (Villars et al., 2009b). Taylor and Stevens (2010) have demonstrated that, even in migmatites, garnet crystals only faithfully reflect their peritectic character within structures that lost melt efficiently and rapidly. Within domains of melt accumulation in the anatexic source, dissolution–precipitation acted to re-equilibrate entrained peritectic garnet with the new magma composition. Consequently, it should not be expected that peritectic minerals exist within granites, despite clear chemical evidence for the involvement of the peritectic assemblage in the genesis of the magma. The chemical components of this former peritectic assemblage are predestined to be expressed as what will appear to be crystals of purely igneous origin.

4. Conclusions

The common view that the compositions and compositional ranges displayed by granitic rocks reflect a range of complex processes that might occur in magma chambers is incorrect. Such views are a consequence of inadequate understanding of the processes that control the compositions of granitic magmas as they form and leave their partially melted source rocks. For elements that have low solubilities in granitic melts, PAE (in varying degrees), accompanied by co-entrainment of accessory minerals, is responsible for most of the primary elemental variation in granitic magmas. For example, this accounts for the tight inter-element correlations between Ti, Fe + Mg, Zr and Ca in most granitic rock suites. In contrast, the concentrations of elements with high solubilities in the melts are controlled by the compositions of the particular protoliths, through the solubilities and proportions of the major quartzofeldspathic minerals that are present. This accounts for the poor degree of correlation of elements such as K and Na with maficity. Thus, the protolith (or magma source rock) exerts the primary and most important control on the chemistry of a granitic magma. It does this by determining what remains unreacted as restite, what is available to dissolve into the melt and what will be formed as the peritectic mineral assemblage, a proportion of which will be entrained. All other mechanisms contribute only in a secondary way to produce the variations that are displayed within granitic bodies.

5. Unsolved questions

The physical chemistry of crustal melting is reasonably well known. However, there is almost no information available on the relationships between rock texture, mineral nucleation kinetics, crystal size distributions, the physics of magma segregation and peritectic mineral entrainment. As a consequence, we are presently unable to say why batches of granitic magma appear to have left their protoliths with differing proportions of entrained minerals. Additional unsolved questions surround the preservation of magma heterogeneities derived from the protoliths. We know that such things exist and we also know that these heterogeneities seem to have been preserved on scales ranging down to centimetres in granitic rocks. However, how these heterogeneous magma batches have migrated away from their protoliths, how they have been preserved (or partially eradicated) during magma ascent and what happens (physically and chemically) to these batches during magma emplacement and solidification are all questions yet to be adequately addressed. The recognition that granitic magma composition is primarily controlled by PAE thus opens doors to a host of other metaphorical rooms for exploration by petrologists, geochemists and magma physicists.

Acknowledgements

GS acknowledges NRF (South Africa) funding through the SARChI programme. Part of the manuscript was written while JC was at the University of Salzburg, as part of the academic exchange programme with the University of Stellenbosch. Financial support from both institutions is gratefully acknowledged. We are grateful for the critical and useful reviews provided by Bernard Bonin and Chris Harris, as well as the editorial guidance offered by Nelson Eby.

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