# Magmatic Processes: Review of Some Concepts and Models

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**Abstract** Magmas are commonly high-temperature, high-entropy silicate solutions of wide compositional range, and may crystallize to form a variety of igneous rocks viz. ultramafic, mafic, felsic to intermediate igneous rock types. Most igneous rocks in space and time may or may not be part of a co-magmatic suite but may have evolved by a number of major and subsidiary magmatic processes operating from source to sink regions. Two essentially important major processes reviewed and discussed herein, fractional differentiation and mixing of magmas, which may operate either separately or concurrently and are commonly responsible for the textural and chemical evolution of most igneous rocks. The methods and validity of qualitative and quantitative geochemical models of these processes are also described and evaluated in the light of field and textural observations.

# 1 Introduction

Natural magmas are polycomponent silicate melts from which mineral phases separate during crystallization according to their solubilities, primarily governed by chemical potentials of components as function of temperature, pressure and composition (e.g. Dickson 2000). The diversity in mineralogical and chemical compositions of igneous rocks suggests their origin and evolution from primary magmas by the process of *magmatic differentiation*. Commonly, homogeneous and heterogeneous modes of differentiation may be recognized by which magma may undergo compositional changes. In *homogeneous* differentiation, only magma as primary melt is itself involved whereas *heterogeneous* differentiation causes separation of either melts or crystals from magma (Muller and Saxena 1977).

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S. Kumar and R. N. Singh (eds.), *Modelling of Magmatic and Allied Processes*, Society of Earth Scientists Series, DOI: 10.1007/978-3-319-06471-0\_1, © Springer International Publishing Switzerland 2014

Most geochemical models of magmatic differentiation assume formation of crystals homogeneously throughout the cooling magma chamber. However, crystallization may proceed along the walls and roof of a magma chamber causing boundary layer fractionation, and the products of such processes would be different from those formed by homogeneous crystallization that can be modeled numerically (Nielsen and DeLong 1992).

It is very difficult to recognize the nature of primary magmas because of uncertainty in the composition of the source region and the later processes acted upon them modifying their compositions significantly. Magmas may contain some residues derived from source regions and/or early fractionated crystals before they erupt on surface or emplaced in magma chamber at crustal depth. A number of theories and models on the accumulation and style of magma ascent and emplacement has been proposed (e.g. Clemens and Mawer 1992; Petfort et al. 2000; Dietl and Kovi 2011; Ferré et al. 2012), which are not discussed herein. Magmas as mixtures of melt plus crystals ascend to higher levels along fractures or as diapirs, and because of heat loss or buoyancy the outermost magma begins to crystallize and cease its upward movement (Paterson and Vernon 1995 and references therein). Several models have been proposed to explain the mechanism of magmatic differentiation which may occur at any scale (mm-kms) in a variety of tectono-magmatic environments. Differentiation of magmas may be accompanied by a number of subsidiary but significant processes, such as liquid immiscibility, thermo-gravitational diffusion, melt-melt interaction, crystal-liquid fractionation, crystal-charged magma mixing, and partial assimilation of wall rocks (Wyllie 1971; Wilson 1993). Such processes of magmatic differentiation, operating either separately or in combination, have commonly contributed in the evolution of magmas (Fig. 1). It is, therefore, almost impossible to postulate a unique genetic model of magma evolution due to the intricacies and complexities of the involved processes. Nonetheless, viable models of magma production and evolution can be proposed based on textural, mineralogical and chemical criteria. In most cases, two essentially important processes, fractional crystallization (separation of crystals from parental melts) and mixing (hybridization) of magmas, separately or concurrently, have been suggested responsible for the textural and chemical evolution of magma.

### 2 Liquid State Differentiation

An initially homogeneous magma may separate into two or more compositionally distinct magmas by the processes of *liquid immiscibility*. For example, many tholeiitic basalts contain two co-existing glass phases. There is credible laboratory evidence of liquid immiscibility between alkaline silicate liquid and carbonate-rich fluids, which forms a strong genetic link to understand the evolution of the carbonatite-ijolite–nephelinite rock association. Such unmixing or exsolution or magma splitting is restricted to magmas of evolved composition and is not a



Fig. 1 Summary of major and subsidiary processes responsible of magma generation, emplacement and differentiation that occur in liquid or crystal-liquid or liquid-vapour conditions (based on Wyllie 1971; Muller and Saxena 1977; McBirney et al. 1985; Clemens and Mawar 1992; Wilson 1993; Kumar 2010)

significant process during differentiation of more primitive magmas (Wilson 1993). Compositional gradients in magmas may cause diffusion and redistribution of elements that are result of *Soret effect*. It may also occur in homogeneous, non-convecting magmas that are subjected to thermal gradients. Unlike the normal trend in fractional crystallization, the hotter parts of a magma chamber may be silica-rich whereas the colder regions may be of iron-rich mafic compositions. Thus, care must be taken when dealing with chilled-margin materials because gradational compositions of an igneous body might have been produced by the Soret effect. The diffusion of chemical species in silicate melts governs the kinetics

of most magmatic processes including partial melting, fractional crystallization, magma mixing and crystal growth. Different components of a silicate melt might diffuse in different directions, depending upon diffusion coefficients, in the same temperature gradient. Perugini et al. (2006) observed that even at a micrometric length-scale, small volumes of magma can be strongly influenced by the coupled action of chemical diffusion and chaotic flow fields because of *diffusion fractionation*. Some regions of the co-existing magmas with contrasting temperature and compositions may partially to completely equilibrate chemically by the process of chemical diffusion depending upon resident time of liquid condition and diffusion coefficient of chemical species (e.g. Kumar and Rino 2006 and references therein).

It has been experimentally shown that, upon crystallization or melting at the walls of the shallow chamber, the liquid fraction may segregate to form compositionally distinct magmas that are still largely in liquid state (McBirney et al. 1985). This explains the occurrence of common types of volcanism and differentiation patterns observed in many shallow-level plutons.

### **3** Crystal-Liquid Separation and Associated Processes

Crystal fractionation is considered as the dominant process of magmatic differentiation, where an effective physical separation of phases, normally one liquid and the others crystalline, takes place. Conceptually crystallization of magma in a chamber forms a mixture of solids (phases) and residual liquids. Magma differentiation is dominantly driven by residual melt extraction from a partially crystalline magma chamber. Initially gravity settling of crystals was considered the most plausible mechanism of crystal accumulation on floor or wall of the magma chamber but on closer examination it is clear that other mechanisms such as in situ crystallization, flowage differentiation, diffusive exchange, compaction (filterpress) and convective fractionation in a crystallizing boundary layer may also be equally or partly effective to explain the process of crystal-melt separation at varying degrees. This is because many crystallizing magmas behave as Bhingham liquids, and thus even the dense ferromagnesian minerals may not be able to sink if they are unable to overcome the field strength of the magma. Flowage differentiation calls upon shear stresses in magma to help moving the crystals. Convecting magma can transport crystals in suspension to proximal or distal depositional sites forming typical cumulates such as schliers, mineral aggregates, clots or layers.

Fractional differentiation of magma may form a framework of touching crystals, commonly termed as cumulate, and need not essentially imply a process of crystal settling as discussed earlier. Cumulate terminology was indeed developed for describing the textural relations of the Skaergaard layered intrusion, which was formed by fractional crystallization of a single batch of tholeiitic parent (e.g. Wager et al. 1960; Wager and Brown 1968; Jackson 1967; Irvine 1982, 1987; Wadsworth 1985). *Primocryst* refers to unzoned, early-formed crystals in contact with each other in a magma which may be referred to as *cumulus crystal*. The most interior calcic part of cumulus plagioclase can also be termed the primocrystic part of the crystal according to definition given by Maaløe (1985). Cumulate nomenclature can even be used for all fractionated minerals which do not touch each other because of the presence of postcumulus or intercumulus materials (Fig. 2a, b). Postcumulus refers to events occurring after the development of initial cumulus fabric whereas intercumulus refers to the products of such postcumulus processes. After the formation of cumulus crystals, the intercumulus liquid may solidify in situ to produce postcumulus crystals, which are defined by the analogous primary porosity (e.g. Irvine 1982), residual porosity (e.g. Morse 1979) representing the amount of trapped liquid at complete solidification.

Mineral layering (rhythmic or cryptic) may be developed in cumulate rocks, primarily controlled by differentiation mechanisms such as crystal nucleation, resorption and coarsening phenomena, crystal sorting, in situ crystallization and current transport (Irvine 1982; McBirney 1995), other than density current, size of crystals and gravitational segregations. Layering may result from the differences in the rates of chemical and thermal diffusion, and one simplest process is double-diffusion which resembles the mechanism proposed for oscillatory crystallization and zoning of plagioclase (McBirney 1984).

Cumulates are more common in mafic magmas than the felsic magmas because of the viscosity contrast of residual liquids. In high viscosity felsic magma, convection in the magma chamber may inhibit cumulate-forming process (e.g. Ewart et al. 1975) or may result in a texture that is not a typically cumulative (e.g. Bachmann et al. 2007). However, crystal fractionation in felsic magma may result in the accumulation of crystalline materials at the margin of the magma chamber by the process of centripetal accretion similar to as observed in Tuolumne Intrusive Series (Fourcade and Allégre 1981) and Modra Massif (Cambel and Vilinovič 1987).

In *filter pressing*, a mat of crystals compacts under its own weight and expels less (or more) dense interstitial or residual melt. Another mechanism is gas-driven filter press in which gas-saturated residual melts from nearly solidified magma having a large amount of crystal-mush are driven out in a propagating fracture to form dykes or veins. Melt can also flow through a dense mat of groundmass crystals and can be driven by the differential pressures between small, recentlynucleated vesicles (higher pressure) and larger, early-formed vesicles (lower pressure). The small vesicles are formed because of crystallization of anhydrous groundmass minerals, resulting in the exsolution of gases, a process termed as second boiling (Sisson and Bacon 1999). Latent heat of crystallization may induce the effect of second boiling. Eichelberger et al. (2006) have demonstrated a mechanism of aplite dyke formation in a mostly crystallized felsic magma chamber which has gained sufficient strength to support the external anisotropic stress field. Melt pressure exceeds least principal stress ( $P_m > \sigma_3$ ) when the strength of the crystal framework is also exceeded, resulting in propagation of a fracture as a melt dyke in plane perpendicular to the least principal stress (Fig. 3). Deering and Bachmann (2010) have recently suggested an upper limit of



Fig. 2 a Plagioclase cumulus suspended in high proportion of intercumulus clinopyroxene forming gabbro cumulate. *Crossed Polars*. Base of photo equals 4 mm. b Olivine and plagioclace cumulus phases with minor amount of intercumulus clinopyroxene forming cumulate. *Crossed Polars*. Base of photo equals 4 mm. Locality: Phenai Mata Igneous Complex, near River Heran, Chalamali village, Baroda, India

extraction at 50 % melt because removing more than 50 % of melt will exceed 75 % crystals in the residue, and consequently permeability will drop which will hinder melt extraction severely.

In situ crystallization is commonly evident in mineral assemblages that include zoned crystals as an extended sequence of crystallization, particularly true in the case of a small and relatively rapidly cooled igneous body like Skaergaard intrusion. In *fractional crystallization* (Rayleigh distillation law) equilibrium is assumed only between the surface of the crystallizing phases and the melt, and crystallized minerals are assumed to become isolated from the residual melt and accumulate on the floor or walls of the magma chamber. The liquid path (LLD: liquid line of descent) for fractional crystallization is almost identical to that for equilibrium crystallization but the crystal compositional path is quite different (e.g. Ragland 1989). Magma generated in diverse tectonic settings, such as dry-reduced magmas in hot-spot divergent margins or in wetter and more oxidizing in arc environments will evolve along different LLD, thus leading to different trace element evolution (Deering and Bachmann 2010). Geochemical modelling of cumulus and associated processes is discussed in "Geochemical Modelling of Melting and Cumulus Processes: A Theoretical Approach".

# 3.1 Assimilation of Solid Rocks

Assimilation of crustal rocks (deeper lithology and/or country-rocks) could be an important process in determining the compositional diversification of magmas during its ascent and emplacement, particularly for deep-crustal magma reservoirs.



Assimilation coupled with fractional crystallization (AFC) can be an important process in the evolution of much continental magmas. Assimilation of low-density crust and synchronous fractionation increases buoyancy required for ascent, and passages for ascent are created by removal or stopping of overlying crustal rocks into the magma chamber. Bulk assimilation of magma thus represents summation of interaction with components from all levels of crust traversed by magma (e.g. Beard et al. 2005). Conventional FC models assume that crystals are removed instantaneously from the magma as soon as they are produced. However, recent studies suggested that the crystals are suspended within the magma body for a certain period, affecting the whole-rock composition in response to intra-grain isotopic zoning, which enabled to develop a mass-balance model for *assimilation and imperfect fractional crystallization* (AIFC) responsible for magma evolution (Nishimura 2012).

# 3.2 Replenishment of Magma Chamber

Most magma chambers are episodically replenished by new pulses of magma, periodically tapped and continuously fractionated (Wilson 1993). In a magmatic system undergoing paired recharge and fractionation, the LLD for the major elements is similar to that produced by fractional crystallization. For example, in a simple ternary system crystallizing ol + cpx + pl (Fig. 4), adding a pulse of more primitive magma will push it back into the olivine phase field from where it will evolve back towards the ol + cpx cotectic. In such a delayed long-term situation the amount of ol + cpx fractionated from the system will be higher than those in a closed system.



### 4 Magma Mingling and Mixing

Magma mingling and mixing have been recognized as major magmatic processes both in plutonic and volcanic environments. Interaction between coeval mafic and felsic magmas has been viewed as a prime cause of thermal rejuvenation as a result of mafic magma underplating and volatile supply to crustal-derived felsic melts. Water content, crystal size, degree of initial crystallinity, mass fraction, composition and temperature are important parameters determining the rheology of interacting mafic and felsic magmas (Frost and Mahood 1987). Low viscosity, minimal rheological differences, and thermal equilibrium between coeval mafic and felsic magma will produce convective overturn forming a hybrid magma zone (Huppert et al. 1984). After thermal equilibrium the interacting magma system is open for chemical and mechanical (already crystallized mineral) exchanges. Crystals may reveal a complex record of open system processes during magma ascent from deeper to shallower levels in the conduit, in response to decompression crystallization and H<sub>2</sub>O degassing (Humphreys et al. 2006).

Enclaves represent all kind of *lithic materials* enclosed within granitoids (Didier 1973; Vernon 1983). Enclaves can be broadly classified into several types depending upon their relationships with the enclosing granitoids. (1) *Xenoliths* are partly digested or undigested fragments of country rock or of an enroute deeperderived lithology. Country rock xenoliths should be confined to the margin of the pluton; (2) *Cognate* (autolith) enclaves must have cogenetic affiliation with felsic host, as early-crystallized phases forming cumulates *or* segregation of mafic phases *or* early-formed mafic border facies of felsic magma itself; (3) *Restite* represents the refractory residue left after partial melting; (4) Mafic or mafic–felsic hybridized magma globules, commonly referred to as *microgranular enclaves*, undercooled and mingled into relatively cooler, partly crystalline felsic melt;

(5) Synplutonic mafic dyke may intrude and disrupt at waning stage of felsic magma evolution, and take the form of the angular to subangular enclaves.

Enclaves must bear some relevant field, petrographic, mineralogical, geochemical and isotopic signatures relevant to operative magmatic processes. One of the most common indicators of magma mixing and mingling is the occurrence of microgranular enclaves (ME) of contrasting compositions with respect to felsic host, mostly forming the calc-alkaline igneous complexes. Therefore, the ME in granitoids serve as a potential tool to understand the processes of coeval mafic and felsic magma interaction in the plutonic environment. Likely processes of mingling and hybridization resulting from mafic magma injection into a felsic magma at various stages of its crystallization are shown in Fig. 5. The ME generally form rounded to elongated shapes on two-dimensional surfaces when mafic magma interacts with felsic magma at its initial or intermediate (partly crystalline) stages of evolution. Synplutonic mafic dykes may inject into most crystallized felsic magma and may disrupt to form angular to subangular (brecciated) enclaves. Thus the mafic-felsic magma interacting system may truly represent a MASLI (composite mafic-silicic intrusive) system (Wiebe 1994). The ME may be aligned in the direction of magma mingling and flow and the degree of elongation correlates with the intensity of flow foliation in the host granitoids, suggesting that both ME (semi-solidified) and granitoids were deformed during semi-crystalline magmatic flow conditions (Vernon et al. 1988).

It is important to distinguish between magma mingling (or co-mingling) and magma mixing processes. Magma mixing causes homogenization of interacting melt phases and the conversion of early crystals to partly dissolved (corroded) forms in a new hybrid magma, whereas mingling or co-mingling involves partial mixing or interpenetration of felsic-mafic magmas without pervasive changes (Kumar et al. 2004). The occurrence of mafic enclaves inside the ME (i.e. composite enclaves, Kumar 2010), abundance of features like magmatic flowage, mafic/felsic xenocrysts, acicular apatites, and pillow-like shapes of the ME etc. indicate co-existence and mixing of magmas with contrasting compositions and temperatures. Other features supporting magma mixing are (1) a more-or-less rounded shape of ME with occasional crenulated chilled margin (2) an intermediate composition between the composition of the felsic host and mafic endmembers (3) rounded crystals through partial dissolution and coated by another mineral in equilibrium with host granitoids giving rise to rapakivi-like texture, and (4) presence of quartz ocelli (Fig. 6a). Quenched enclaves may represent the composition of pristine mafic magma or hybrid (intermediate) magma. In some large undercooled ME (d > 12 cm) residual (rhyolitic) melt may have been driven out of enclaves into the partly crystalline host magma (Kumar et al. 2004).

The ME range in size from 1 cm to several meters across and their contacts are commonly sharp with the host granitoids but diffused contacts are also noted because of quenching of mafic (enclave) magma against cooler and semi-crystalline granitoid melt (Fig. 6b), which implies that felsic and mafic magmas coexisted. The ME with serrate or cuspate margins, with lobes convex towards the host granitoids, may also be observed (e.g. Vernon 1983). Near the contact of host granitoids the ME generally show mineral alignment along the contact outline.



Fig. 5 Schematic presentation of various types of magma interactions resulting from injection of mafic or hybrid magma into felsic magma at different stages of its crystallization (slightly modified after Barbarin 1989, Barbarin and Didier 1992). Field features shown against various stages (1–4) of mafic–felsic interacting magma system can be observed in the central and eastern parts of the Ladakh batholith (Kumar 2010). See text for explanation

Felsic and mafic grains from the granitoids may penetrate partly into the ME particularly where semi-solidified ME interacts with partly crystalline felsic host magma, suggesting crystal-charged magma interactions. On the contrary, country rock xenoliths may show a reaction signature with the host granitoids suggesting solid-liquid interaction.

At any stage of mafic-felsic magma mingling and mixing, the magma system may be frozen (solidified). Magma interaction is indeed a chaotic process during which a portion of mafic magma can survive mixing process (Perugini et al. 2003). In the same system, mixing process may be characterized by chaotic regions in which intense hybridized regions represent *active mixing region* (AMR) whereas less efficient mixing dynamic regions are called *isolated mixing regions* (IMR), which may contain blobs of magmatic enclaves. More recently, Perugini and Poli (2012) reviewed the intricacies of magma interaction processes both in plutonic and volcanic environments and suggested that time spent by the magmatic system in the molten or partial molten state is a crucial factor for the preservation of magma mixing fingerprints. They further argued that the new conceptual models of *chaotic mixing* and *diffusion fractionation* may pose serious problems for the



**Fig. 6 a** Ocellar quartz in quartz diorite, which formed in a magma mixing environment. *Crossed Polars.* Base of photo equals 4 mm. **b** Enclave and granitoid contact showing distinct chilled margins imprinted on lower crystal faces of amphibole which suggests quenching of enclave magma against relatively cooler and partly crystalline granitoid melt. *Crossed Polars.* Base of photo equals 4 mm. Locality: Hodruša Štiavnica Intrusive Complex, Central Slovakia (after Kumar 1995)

interpretation of compositional variability of igneous rocks if rely only on pre-existing conventional models of magma mixing. Magmas affected by coupled action of chemical diffusion and chaotic field flow, and trapped as melt inclusions will provide misleading information about melt composition (Perugini et al. 2006).

# **5** Qualitative Assessment of Magmatic Processes

# 5.1 Geochemical Variations

Magmas are in a viscous state due to entrained restite commonly derived from the source region and the presence of early-formed crystals (McBirney 1993). Crystalcharged magmatic processes are therefore considered most important in the evolution of igneous bodies whereas processes occurring in the liquid state are not so significant in the bulk evolution of igneous magmas. In the classical work of Harker (1909) it was realized that the great diversity and compositional variations within many igneous rock bodies can be attributed to differentiation processes. Advancement in theories and ideas of magmatic differentiation postulated that the geochemical variations of any igneous rock suite alone cannot point to the operative processes. For example, near-linear variations on Harker plots (Fig. 7) can be caused by several possible processes such as fractional crystallization (or crystal fractionation), mixing of magma end-members and melt-restite separation during progressive partial melting (Wall et al. 1987; Clemens 1989). It has been further



**Fig. 7** Linear geochemical variation of igneous rocks can be viewed in three major ways. I: Crystal fractionation of a primary magma (*A*), forming cumulates (*B*) and subsequently evolved residual or differentiated magma (*C*). Element 'X' (mostly SiO<sub>2</sub>) or any other parameter can be chosen as "*index of differentiation*". II: The same geochemical variation can be generated by the mixing of two magma end-members 'A' and 'B' in various proportions, forming members of a hybridized (mixed) igneous rock suite. III: The same geochemical variation can be formed by the processes of melt-restite unmixing or separation during progressive melting of a source region (protolith 'A'), which will form a small melt fraction initially at 'B' and then gradually follows the compositional path of B-B'-B'' with increasing degree of melting

argued that typical *Rayleigh fractionation* (i.e. disequilibrium crystallization) will result in a curved linear trend on Harker plots whereas *phenocryst unmixing* (term used to the explain the process in which degree of fractional or equilibrium crystallization occurs in a cooling magma followed by separation of compositionally fixed *phenocryst* assemblage from residual melt before final crystallization) would generate a linear trend on Harker plots (Clemens and Stevens 2012). It has also been pointed out that how the data are plotted, e.g. expansion of the SiO<sub>2</sub> axis on Harker plots, can significantly linearise a curvilinear data-set.

Many igneous rocks preserve physical, textural and chemical characteristics that also point to differentiation processes involved in their formation and evolution. Chemical features of crustally-derived granitic rocks, in particular, are highly influenced by the presence of restitic materials (melted or unmelted parts of protoliths), accessory minerals (Fe-Ti oxides, titanite, zircon, monazite, apatite etc. as poikilitic inclusions in early crystallized phases) and peritectic phases (newlyformed crystalline products of the melting reaction). The elements with low solubilities in granitic melts with varying proportions of *peritectic assemblage entrainment* (PAE) accompanied by co-entrainment of accessory phases, are considered mainly responsible for the chemical variations of granitic rocks whereas concentration of elements with high solubilities in felsic melts may simply reflect protolith compositions (Clemens and Stevens 2012). For the identification of magmatic processes, chemical variations of igneous rocks should therefore be combined with field, textural, mineral and other physical observations.

Conventionally, chemical elements in magma are present in an ionic state or have polymer structures that form silicate chains during crystallization (Masson 1965). Recently, Vigneresse et al. (2011) introduced a new and advanced concept of hard-soft acid-base (HSAB) interaction to characterize a magma that consists either of solid, melt or an exsolved gaseous phase. This concept of HSAB has offered a new insight into the way magma differentiates. For example, felsic magma commonly follows a trend towards higher hardness driven by increasing silica content whereas almost constant hardness of mafic/ultramafic magmas are driven by ferro-magnesian minerals with nearly equal hardness values, and hence these evolve towards minimum electrophilicity. This bimodal chemical evolution of magmas satisfactorily explains the natural occurrence of most common igneous differentiation trends; one tholeiitic trend effectively determined by iron enrichment and another evolving towards silica enrichment with little or no iron enrichment, as commonly observed in calc-alkaline series, corresponding to Fenners' and Bowens' trends respectively (Keelmen 1990 and references therein).

### 5.2 Pearce Element Ratios

Pearce element ratios (PER) are eminently suited to test the internal petrological hypothesis concerning the mechanism of magmatic differentiation for basaltic magmas (Pearce 1968, 1970, 1990; Russell and Nicholls 1990). A conserved (or excluded) element during magmatic differentiation can be defined as one element that is neither added to the system by assimilation nor removed by fractionation (bulk distribution coefficient, D = 0). The *conserved* element is common to both axes (orthogonal axes) as denominator. Commonly a single conserved element is used as denominator but functions of more than one conserved element can also be used. Molar mineral components taking part in melting or crystallization can be calculated for any set of composition (Russell and Nicholls 1988; Stanley and Russell 1989; Pearce 1990). The use of PER diagrams in petrology has received strong criticism due to difficulties disentangling any geological effect from the spurious correlation effect (e.g. Rollinson and Roberts 1986). Pearce (1987) convincingly explained that (i) the divisor must be constant and the trend of variation should not pass through the origin, and (ii) the slope and intercept of an observed or simulated trend are much more important than the correlation between the ratios. Nicholls (1988) further argued that PER diagrams provide an unambiguous test of petrologic hypothesis because they are based on the stoichiometry of rock-forming minerals. The PER have been successfully applied to identifying magmatic processes of volcano-plutonic mafic igneous complexes (e.g. Trupia and Nicholls 1996; Kumar 2003).

### 5.3 Synchronous Mixing-Fractionation Trends

Mixing of two coeval liquids may define a straight line on variation diagrams as long as the liquids are not concurrently fractionating. However concurrent mixing-fractionation processes of coexisting magmas may provide complex chemical evolutionary trends. Mafic to hybrid enclaves in granitoids may represent various stages of interactions between mafic and felsic magmas (e.g. Barbarin and Didier 1992; Janoušek et al. 2004; Barbarin 2005; Słaby and Martin 2008; Bora et al. 2013). The ME in granitoids causes physical and chemical complexities in magma chambers and as a whole will largely affect the evolutionary history of the granitic pluton. Chemical variations of compatible elements against silica play significant role in recognizing the operative processes involved in the temporal and chemical evolution of mafic, hybridized and granitoid rocks as schematically presented in Fig. 8. Magma with the lowest silica content and enriched in compatible elements may represent a mafic end-member, which can evolve along a trend of decreasing compatible elements and concurrently mixed with fractionating felsic melt forming a series of hybrid rocks. These combined processes are regarded as mixing-fractionation of coeval mafic and felsic magmas during syn-crystallization with increasing polymerization and crystal loads (e.g. Barbarin 2005; Słaby and Martin 2008; Bora et al. 2013). However, non-colinearity or high data-scatter of elements would have been caused by non-linear (chaotic) mixing and diffusive fractionation processes (e.g. Perugini et al. 2008; Słaby et al. 2011).

# 6 Semi-Quantitative Assessment of Crystal-Fractionation

Geochemical variation diagrams are not considered to have much potential for examining the petrological hypothesis precisely, unless combined with other geological and petrographical evidence. Compositional variations in many igneous rock sequences may show good coherence, suggesting fractional crystallization has played a dominant role but this must be tested against petrographic or field criteria. Often a hypothesis emerges first from a consideration of field and petrographic observations, and is then tested against chemical dataset. In the formulation of a crystal fractionation hypothesis, the constructed chemical variations should be capable of showing both the liquid and fractionating minerals, which is possible in a two-element variation diagram, commonly referred to as a mixing calculation (Cox et al. 1979), similar to as Harker plot with additional consideration of solid compositions. Diagrams constructed based on the principles of mixing calculation are capable of explaining addition or subtraction (or 'extract') of phases but do not imply a specific mechanism. A basic principle of mixing calculation lies in the lever rule as commonly used in the phase diagrams. Two chemical parameters X and Y may represent percentages of oxides or parts per million of trace elements or any other weight expression of analytical data (Fig. 9). Addition of 'B' composition to 'A', the resulted mixture M will evolve in a straight line A-B, depending upon the relative proportions of 'A' and 'B' in the mixture 'M' (Fig. 9a). Similarly extraction of 'A' from a parent 'M' will evolve residual liquid towards 'B', where A-M-B is a lever with point 'M' at the fulcrum. At any specific point of mixture such as 'M' the proportion of two end-members 'A' and 'B' can be calculated. Bulk extract E formed by crystallization of two phases A and B from parent P will evolve the residual liquid towards D (Fig. 9b).

Given a known liquid path (LLD from parent P to daughter D liquid represented by whole rock compositions) caused by fractionation of multiple phases, it may be



possible to construct an extract polygon (triangle A-B-C) geometrically using compositions of each fractionating mineral. No unique solution for bulk extract E can be determined alone from this diagram (Fig. 9c) because of the fact that the intersection of a line and a triangle in the same plane is a line. However, with the help of several pairs of such two-element extract diagrams, the proportion of extract phases can be determined by transformation of values obtained by intersection of non-equilateral chemical polygons with LLD vectors onto a equilateral triangle formed by fractionating three-phases, which will provide proportions of fractionating phases from a parental magma, and subsequently the bulk cumulate composition. The presence of inter-cumulus trapped liquid may, however, cause a mismatch of a typical cumulate composition.

All LLD may not essentially be a single straight line. There may be a break or point of inflection in the slope of the LLD because of increasing number of phases in the crystallizing assemblages somewhat analogous to crystallization of magma in primary phase field A, at cotectic A-B, and at eutectic A-B-C in a ternary phase diagram (e.g. Ragland 1989; Wilson 1989,1993).

### 7 Quantitative Assessment of Crystal Fractionation

As the member of phases participating in the fractionation increases, graphical methods of fractionation become more difficult to apply. Petrographic mixing of solids (crystallization of phases forming a mixture of solids i.e. cumulate  $\pm$  trapped melt) and residual liquids have therefore provided a conceptual basis to envisage the mathematical method for modelling the multiple phase fractionation of magma (e.g. Bryan et al. 1969; Wright and Doherty 1974; Albarède 1995). In this method a



**Fig. 9**  $\mathbf{a}$ - $\mathbf{c}$  X-Y element variations (**a**) showing the evolution of mixture 'M' in a straight line as a result of addition of 'A' to 'B' (**b**) Bulk extraction 'E' of two phases A-B from parent 'P' evolving daughter 'D' (**c**) Bulk extraction 'E' (*thick grey line*) of three phases A-B-C from a parent 'P' evolving daughter 'D' (after Cox et al. 1979; Ragland 1989; Wilson 1989). See text for explanation

mixture of given minerals fractionates from a parental magma to produce daughter (residual) liquid in a best-fit to the regression line of compositions. This method has the advantage of using more phase assemblages but has certain inherent limitations when it applies more complex phase assemblages. In "Mass Balance Modelling of Magmatic Processes in GCDkit" method and application of R-language based software Geochemical Data Toolkit (GCDkit 3.0) are described. The programme can compute the proportion of the fractionating minerals and calculated daughter magma composition from a parental melt using minerals and whole rock data-set based on the basic principle of chemical mass-balance. From the obtained solution, the bulk composition of cumulate can also be calculated using the composition of the fractionating minerals and their fractions constituting the bulk cumulate. The obtained sum of the residual squares of the model may be slightly more than the mathematically acceptable value ( $\Sigma r^2 \ll 1.00$ ) but can be considered reasonably valid provided the model is petrographically and geologically consistent (e.g. Naslund 1989; Kumar and Kmet 1995; Kumar 2002). Hunter and Sparks (1987) carried out an exhaustive mass-balance calculation for the evolution of Skaegaard parental magma producing a substantial amount of silica-rich residual melt that received criticism (e. g. McBirney and Naslund 1990) on the firm ground that one can achieve the desired solution in a pure mathematical sense by adjusting and manipulating some compositions and weighing factors of elements without field and petrological constraints.

Fractional crystallization (Rayleigh fractionation) is widely used to constrain trace element evolution of crystallizing melt as described by the equation (Gast 1968; Neumann et al. 1954):

$$\mathbf{C}_{\mathbf{I}}^{i} = \mathbf{Co}^{\mathbf{i}} \mathbf{F}^{(\mathbf{Di}-1)}$$

where,  $C_L^i$  = concentration of element i in the residual melt,  $C_O^i$  = concentration of element i in the initial melt, F = fraction of melt left, and D<sup>i</sup> = bulk partition coefficient of the crystallizing mineral assemblage for element i. The distribution

coefficients (Kd<sup>s</sup>) for various phases in magma are experimentally determined from the glass and phenocrysts.

There may be a large difference between calculated and observed residual magmas for certain incompatible elements by a factor of two to three, which can be explained by assimilation of crustal melt with the residual magma during the fractional crystallization process (AFC) or concomitant fractionation-mixing of coeval magmas. Alternatively, use of inappropriate Kd<sup>s</sup> for some chemically very sensitive phases to their respective melts may result in erroneous values. Quantitative modelling of fractional differentiation thus requires precise Kd<sup>s</sup>, which are generally functions of temperature, pressure, oxygen fugacity and bulk composition of magma.

In quantitative modelling of fractional crystallization the damping effect of Mg/Fe during the progress of fractionation may lead to erroneous results that can be minimized by the use of multiphase Rayleigh fractionation (Morse 2006). The modified Rayleigh equation for multiphase fractionation is:

$$\mathbf{C} = \mathbf{CoF}_{\mathbf{L}}^{\mathbf{f}\alpha(\mathbf{Di}-1)}$$

where C and Co are compositional terms stated in terms of  $X_1^L$ , and refer to the mole fractions of end-members within the binary solution as projected from other components or phases,  $F_L$  = fraction of liquid remaining,  $f_{\alpha}$  = fraction of the active crystal phase relative to total crystals, and D = partition coefficient  $X_1^S / X_1^L$ . By active crystal phase (here  $\alpha$ ) is meant that causes C to evolve, with all other phases being passive.

More recently, the concept of *concurrent fractional and equilibrium crystallization* (CFEC) in a multi-phase magmatic system in the light of experimental results on diffusivities of elements and other species between minerals and melts has been proposed, and applied successfully to demonstrate coherent and scattering of elemental trends of melts of Bishop Tuff by the CFEC (Sha 2012). Langmuir (1989) proposed a model of in situ crystallization at the cooling interface of magma chamber, which was further developed by McBirney (1995). O'Hara and Fry (1996) provided an explicit numerical solution for observed lateral variations in the mass fraction crystallized with position in the magma chamber by the integration of residual liquids from crystallization in addition to other factors such as imperfect fractional crystallization, refilling of magma chambers during fractionation, and in situ crystallization.

### 8 Mixing Test of Two-Magma End-Members

A magma system may form by mixing (hybridization) of two magma end-members. This hypothesis can be tested using elemental concentrations of participating magma end-members and a mixing equation (Fourcade and Allègre 1981), which will estimate the proportion of mafic to felsic components needed to produce a hybridized magma system. If the concentration of an element (i) in hybrid or **Fig. 10**  $C_A^i - C_B^i$  versus  $C_M^i C_B^{i^-}$  mixing-test variation diagram, where  $C_A^i = \text{content}$ of 'i' element in felsic magma A;  $C_B^i$  = content of 'i' element in mafic magma B;  $C_M^i$  = content of 'i' element in hybrid magma M; and m = fraction of felsic magma in the mixture (hypothetical regression line) represented by slope. Grey region represents domain of invalid mixing between A and B magma end-members (after Fourcade and Allègre 1981)



mixture  $(C_m^i)$  is formed by two-component i.e. felsic  $(C_A^i)$  and mafic magma  $(C_B^i)$  end-members in various weight proportions (x), then the mixing equation can be written as:

$$\begin{split} C_{m}^{i} &= x \ C_{A}^{i} + \ (1-x) \ C_{B}^{i} \\ C_{m}^{i} &= x \ C_{A}^{i} + \ C_{B}^{i} - \ x C_{B}^{i} \\ C_{m}^{i} - \ C_{B}^{i} &= \ x (C_{A}^{i} - C_{B}^{i}) \end{split} \tag{1}$$

Equation (1) can be used to calculate the proportion (x) of felsic to mafic magma in the mixture for each element (i). If we plot  $(C_m^i - C_B^i)$  versus  $(C_A^i - C_B^i)$  for a chemical database, a straight line would result whose slope will provide the mass proportion (x) of felsic magma in the mixture (Fig. 10). In this plot, mixing domain will be delineated by the slopes between *zero* and *one* because the sum of proportions of felsic and mafic magmas that formed the hybrid magma will never exceed one.

Simple two-component linear mixing can be used to geochemically model the hybridized magma system but for non-linear and complex chaotic mixing system fractal (scale-invarient) geometry can be more useful and demonstrative (e.g. Perugini and Poli 2012, and references therein).

**Acknowledgments** I extend sincere thanks to R. N. Singh, Senior INSA Scientist, CSIR-NGRI, Hyderabad, who helped me to understand the numerical basis of magmatic processes. Fruitful discussion with Igor Petrík, Vojtech Vilinovič, Igor Broska, H. R. Naslund, Ewa Słaby has enhanced knowledge of modelling the magma chamber processes. Sita Bora and Hansa Joshi are thanked for assisting me while finalizing this chapter. Science and Engineering Research Board (SERB), New Delhi is highly acknowledged for financial support. David R. Nelson is especially thanked for fruitful and generous comments that highly improved the earlier version. Permissions from Elsevier and Veda Publishing House for using some materials in this chapter are gratefully acknowledged.

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