Chemical emplacement of magma

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Chemical emplacement of magma

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Abstract

Reaction cells are proposed by which magma bodies move by cycling excess energies along gradients of temperature, pressure and composition in open systems and gravitational fields of the earth. Crystallization energy released by exothermic crystallization at cell bases migrates upward by convective overturn in liquid zones and is absorbed by endothermic dissolution of roof rocks. Rock–liquid interfaces, liquid zones, and accumulations of crystals rise. Dissolved country rocks mix with magma. Granitic minerals form under disequilibrium conditions. Reaction cells consume or add excess energy during transit. Cells that reach the surface supply volcanic fields; those that consolidate below form intrusive terrains. Granitic rocks replace country rocks by passive processes that generate silicate liquids. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

This paper describes chemical mechanisms by which, cells of magma move upward by cycling excess energy of liquefaction (Dickson, 1995), in dissolution–crystallization reactions along temperature–pressure-concentration (TPX) gradients in the earth's gravitational field.

1.1. Granite controversy

The granite debate refuses to die (Atherton and Gribble, 1983; Atherton and Tarney, 1979; Bowen, 1928, 1948; Brown et al., 1996; Buddington, 1959; Gilluly, 1948; Pitcher, 1983; Read, 1948, 1957).

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Difficulties stem from regarding magmas as igneous melts. Plutons are held to: move forcefully as diapirs and quench in cooler host rocks; lose energy mostly to country rocks by cooling; be at freezing conditions and lack superheat; have limited interactions with surroundings; and crystallize at near-equilibrium in response to drops in T and P. Thoughts are directed toward closed systems and equilibrium processes.

However, strong evidences support granite-forming systems to have had energy sufficient to passively replace country rocks. Dynamic, near-equilibrium processes do not provide sources of energy and components or mechanisms of mass exchange.

Transformists likewise cannot account for sources of energy and mass, or explain liquids that accompany entry.

Important questions and issues remain (Hales, 1992; Misch, 1949; Pitcher, 1993; Read, 1957; Roddick, 1982; Roubalt et al., 1975; Taylor, 1980). In addition to room and energy problems, they include: departure from equilibrium in granitic rocks revealed by textures and compositional inhomogeneities; bimodal distribution of igneous rocks; restriction of granitic rocks to continents; presence of crustal matter in granitic systems; regional gradations of granite gneisses to granites; and trends of gneissic and migmatitic compositions toward experimental "minimum-melt" compositions.

Petrologists acknowledge difficulties in igneous melt theory. Paterson and Fowler (1993) concluded that diapiric actions were not adequate entry mechanisms, that material transfers were necessary. Saleeby (1990) held that much of the crust below the Sierra Nevada had been reconstituted to granitic material.

1.2. Underlying concepts of reaction cells

Concepts on which reaction cells are based are:

1. disequilibria prevail in nature, equilibria are rare;
2. reactions with finite rates require energy in excess of equilibrium levels;
3. excess energy drives processes along TPX gradients;
4. earth systems are open;
5. cyclic reactions are generated in gravitational fields; and
6. silicate liquids crystallize by rules of solution chemistry.

2. Melts and solutions

2.1. Melts and liquid silicates

Melts differ from silicate solutions. True melts are liquids in univariant equilibrium with solids of the same compositions (Dickson and Hsu, 1998, Dickson and Hsu, 1999, Dickson and Hsu, 2000; Levin et al., 1956; Rastogi and Misra, 1983). Melting temperatures are sharp, reproducible and functions of P only. Silicate liquids in nature are polycomponent solutions

from which phases separate according to solubilities, governed by chemical potentials of components as functions of *TPX*. Magmas crystallize over ranges of *TPX* conditions.

2.2. Excess energy of liquefaction

Converting solid rocks to liquids requires excess energy introduced as heat or other forms of energy. Excess energy of liquefaction in liquid silicate bodies, magmas, causes them to be out of equilibrium with surroundings. Energy as defined in equilibrium thermodynamics differs from excess energy of this paper that drives disequilibrium reactions along gradients in *TPX* (Prigogine, 1997).

2.3. Zone melting

Among mechanisms proposed for intrusive processes are analogues to industrial zone melting (Pfann, 1958), in which metals and other solids are purified by passing fused zones along rods and partitioning impurities to liquids. "Zone-refining" by Harris (1957), and "zone-melting" by Dickson (1958) and Vinogradov (1958, 1968), consider that liquid zones migrate upward along *TP* gradients, melt cover rocks, absorb fugitive constituents, and freeze at bases. Dickson in 1958 regarded chemical effects as essential and at the time did not appreciate differences between melts and solutions. Mechanisms of this paper depend on solubilities of phases in silicate solutions, not rising thermal zones or melting.

2.4. Cycling crustal materials and granite formation

Geochemical cycling has generated lower densities and higher silica contents of continental rocks compared to average crustal rocks. Barth (1961) concluded that continental matter has been extensively reworked. His calculations of the total volumes of rocks eroded through time are orders of magnitude larger than volumes of existing sediments. He pointed out that steady-state compositions of seawater through geologic time necessitated cycling of sediments.

Hales (1992) summarized evidences on cycling of sedimentary rocks into plutonic systems; granites of the Lachlan fold belt, Australia, contain zircons with older cores and sedimentary-derived isotopes. He recognized that liquefying conditions were reached by sedimentary rocks in descending slabs, but that to form granites required additional sources of energy and mechanisms to sort components into silica-rich upward and basic downward. To form magmas, Hales appealed to Elliston's hydro silicate mechanisms (Elliston, 1984, 1985) that release water and excess energy by breakdown of metastable sediments to more stable minerals. Elliston's applications of hydro silicate mechanisms to origin of rapakivi textures and orbicules have not been widely accepted. Elliston compiled textures of plutonic rocks documenting disequilibria and called attention to importance of metastable reactions in the crust.

3. Disequilibrium processes in the earth

3.1. Movement of excess energy

Earth is in disequilibrium. Excess energy, as heat, steadily migrates outward. Gradients in *TPX* exist. Movement of excess energy is accelerated in hydrothermal fluids and magmas.

3.2. Gradients and disequilibrium reactions

Disequilibria prevails in the earth. Equilibrium in liquid columns with gravitational pressure gradients, at constant *T*, are thermodynamically possible (Gibbs, 1874-1878); gradients in concentration are needed to offset pressure effects on chemical potentials. Reactions that proceed at finite rates require energy in excess of equilibrium requirements. Excess energy (Dickson, 1995; Dickson and Hsu, 1996, 2000) drives reactions along gradients in *TPX* in the gravitational fields. With increasing departure from the equilibrium, reactions become unpredictable, turbulent, and chaotic.

Disequilibria in granitic rocks is displayed by zoned, broken crystals, distorted inclusions, and multi-generations of minerals (Augustithis, 1973; Elliston, 1984, 1985; Flinders and Clemens, 1996).

Disequilibria and irreversible thermodynamics are treated by deGroot and Mazur (1962), Kreuzer (1981), Nicolis and Prigogine (1989), Prigogine (1961, 1997), and Prigogine and Stengers (1984). Equilibrium is difficult to attain, or to maintain, once gained. Reactions in inorganic and organic systems can depart greatly from equilibrium; complex reactions (Prigogine and Stengers, 1984; Prigogine, 1997) produce patterns of nature. Kinetics of reactions displaced from equilibrium are functions of *TPX* (Lasaga and Kirkpatrick, 1981) and factors such as grain size, stress, and flow rates.

3.3. Peter Ortoleva

Peter Ortoleva's applications of irreversible thermodynamics to geology were important to concepts of this paper. The reaction cells are called "ortolevan reaction cells" to acknowledge his work (Dickson, 1995; Dickson and Hsu, 1996). Peter Ortoleva is a distinguished Professor of Chemistry and Geological Sciences and Director of Laboratory of Computational Geodynamics, Indiana University, Bloomington, Indiana. His group applies principles of irreversible processes to chemical and geological problems (Ortoleva, 1992, 1994a, 1994b, in press; Dewers and Ortoleva, 1989, 1990). Ortoleva (1994a) treats geological processes driven by excess energy in cells with defined boundaries, at regional to microscopic scales, for sedimentary basins, metamorphic and igneous rocks, and ore deposits. He developed concepts of geochemical self-organization by internally controlled, coupled disequilibrium reactions (Ortoleva, 1994a). Use of Ortoleva's concepts gave insights to replacement in the Papoose Flat pluton, Inyo Mountains, California (Dickson, 1996).

3.4. Petrologic implications of Papoose Flat pluton

At Papoose Flat, Dickson (1996) concluded that minerals of a quartz monzonite pluton rearranged in response to excess energy of stress (Bienfait and Kern, 1968; Dewers and Ortoleva, 1990). Megacrystals of barium-zoned orthoclase and bipyramidal quartz replaced host minerals in newly solidified quartz monzonite pluton and adjacent aureole rocks (Brigham, 1984; Nelson, 1987). Megacrystals grew in groundmass containing medium-sized grains of subhedral non-zoned orthoclase and anhedral quartz. Destabilized granitic minerals dissolved and released components to thin coatings of intergranular fluids. New minerals nucleated and grew; excess energy of stress cycled at interfaces of dissolving and in-growing phases, by endothermic dissolution coupled with exothermic crystallization. Minerals dissolved regardless of identity. That minerals grew during stress is evidenced by parallelism of oriented internal features (mineral inclusions and oscillatorily-zoned concentric layers) from crystal centers to margins, to external shapes of orthoclase, whether euhedral or rounded. Quartz monzonite at Papoose Flat rearranged to 50% or more of igneous-appearing porphyroblasts by cycling excess energy of stress.

Magmas have excess energy of liquefaction. They are out of equilibrium with surroundings. Mechanisms of this paper stem from considering whether excess energy in plutons likewise cycles by dissolution–precipitation reactions, along *TPX* gradients in gravitational fields.

4. Chemical activity in and around plutons

4.1. Freezing of albite-melt body, system NaAlSi$_3$O$_8$

A melt body of pure NaAlSi$_3$O$_8$ in the crust is unlikely, but discussing behavior of one contrasts melts and solutions. Fig. 1 shows the TP curve for univariant equilibrium of albite with melt (NaAl$_3$O$_8$), which is 1130°C at 1 bar, and 1360°C at 25 kb (Boyd, 1964). Along the curve, chemical potentials of component NaAlSi$_3$O$_8$ (molar free energies) in albite and melt are equal. By the phase rule, $f = c + 2 - p$; in this case, number of components, c, are 1, number of phases, p, are 2, and degree of freedom, f, is 1. One independent variable, T or P, sets the state and properties of the system.

Consider a liquid body 100 m high, at 1200°C, in albite terrain at 1000°C and 1000 bar mean pressure. Albite melting temperature at 1000 bar is about 1150°C. Pressure difference in country rocks along side, is about 75 bar; melting temperature of albite is about 0.8°C, lower at the top than at base. Melting albite from country rocks absorbs excess energy; T of liquid drops until freezing starts at the highest pressure at the base, where excess energy of freezing is released. Excess energy transported to tops would melt cap rocks and be absorbed; gradients would be established that promote vertical movements. However, effective delivery of excess energy across a temperature difference of 0.8°C in viscous liquids is unlikely; excess energy would be consumed by turbulence and heat losses to wall rocks.

4.2. System NAlSi₃O₈–H₂O

Adding H_2O creates solutions. Effects of H_2O on "melting" of albite were measured by Davis (1972), Goranson (1936, 1937), and Hamilton and Oxtoby (1986). The reaction is: albite $(NaSi_3O_8)$ + H_2O = solution $(NaAlSi_3O_8–H_2O)$. H_2O concentrations are maximum when partial pressures of H_2O equal total pressures. H_2O activities are functions of T, P and concentrations of H_2O, and in principle can be measured by semi-permeable membranes. Systems of two components and two phases have 2 degrees of freedom. Two variables among T, P, $X(H_2O)$ [or $X(NaAlSi_3O_8]$ must be chosen to set state; at constant P or T, concentrations of X must be specified. Albite and liquid are stable at various combinations of T, P and H_2O activities.

According to Gibbs (1874-1878), equilibrium is possible in liquid columns along gravitational P gradients, at constant T. Goranson (1937) discussed migration of H_2O along pressure gradients, at 1000°C, in $NaAlSi_3O_8–H_2O$ liquids, as an osmotic pressure effect. Kennedy (1955) plotted concentrations of H_2O for constant "partial pressures"; each curve has an upper limit where water pressures equal total pressure (Fig. 2). Along equipotential curves, chemical potentials of H_2O are the same except for small departures equal to that caused by weights of H_2O in vapor columns over the same heights.

Fig. 3 depicts a body 100 m high, of $NaAlSi_3O_8–H_2O$ solution with 1% H_2O, initially at 1000°C and 1000 bar that is out of equilibrium with albite host rocks at 1000°C and mean P
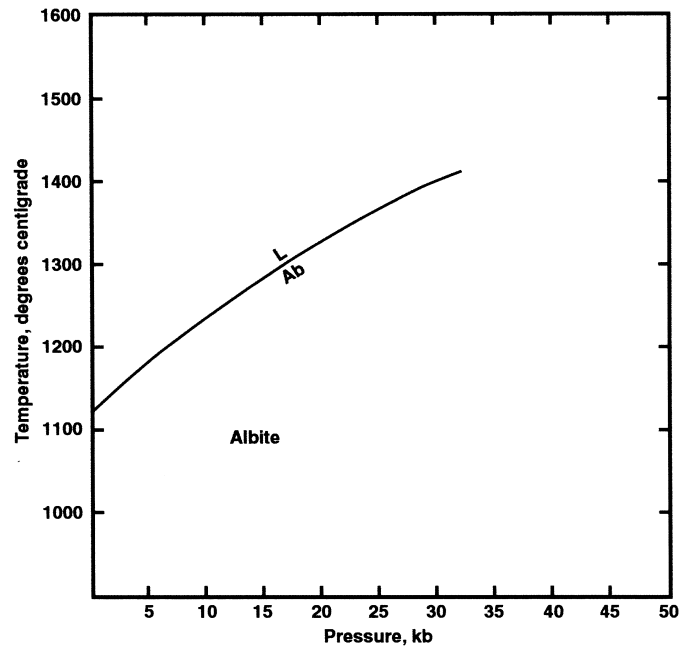

Fig. 1. Albite-melt univarient equilibria as a function of temperature and pressure (Boyd, 1964).

of 1000 bar. Host rocks differ about 75 bar over 100 m. Conditions in the body shift with reactions. Components in solution adjust. Diffusion along pressure gradients is toward near-equality of chemical potentials of H_2O. Chemical potentials of $NaAlSi_3O_8$ in solution at a given T–P level are inversely proportional to concentrations of H_2O. Saturation with albite is attained at the highest P and lowest H_2O content at cell-bases. At tops, dissolved albite in $NaAlSi_3O_8$–H_2O solutions drops H_2O concentrations and absorbs excess energy; gradients in concentration and T are established. Separation of albite at bases releases H_2O and excess energy that migrate toward dissolution zones by convective overturn. Gradients are maintained. Albite–liquid interfaces and zones of crystallized albite rise. Solutions of granitic composition can be made by adding components of granitic rocks to $NaAlSi3O_8$–H_2O solutions, adjusting T and P to maintain presence of liquids.

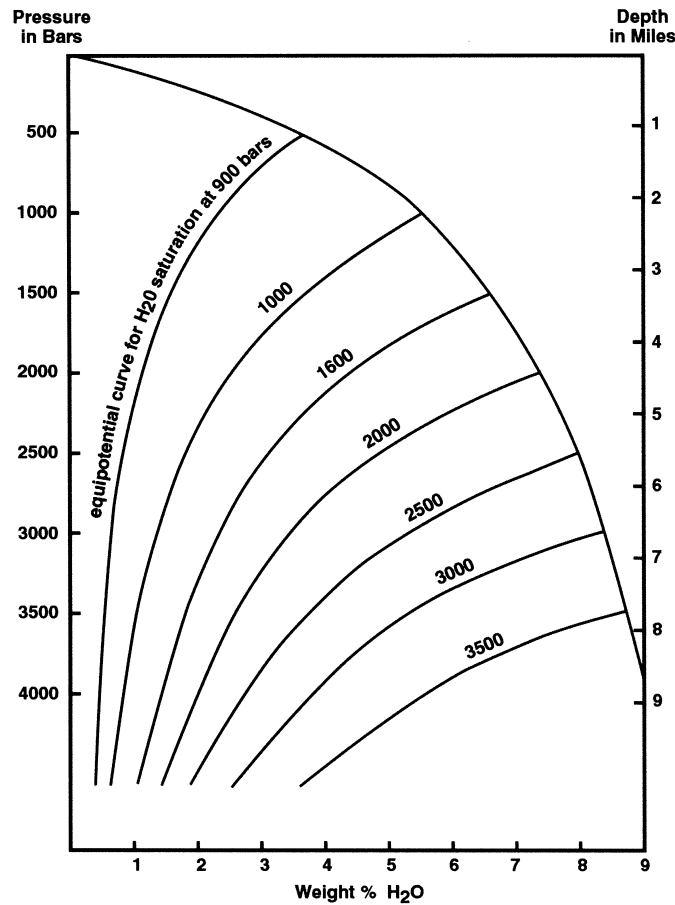Fig. 2. Kennedy (1955) plot of H_2O concentrations in $NaAlSi_3O_8$–H_2O solutions versus depth in miles, subject to gravitational pressure gradients, at constant H_2O fugacities ("partial pressures" of H_2O), 1000°C and 1000 bar.

5. Ortolevan reaction cells

5.1. Ortolevan reaction cells concept

Proposed ortolevan reaction cells (Fig. 4) move by cycling excess energies of liquefaction between endothermic dissolution reactions at roofs and exothermic precipitation reactions at bases, connected by liquid zones of mixing and transport of excess energy. Dimensions depend on local conditions. Field evidences support diameters ranging from hundreds of meters to tens of kilometers. Heights need be great enough to establish significant T and P gradients, probably hundreds of meters. Cells emplace granitic plutons within 10 km of the earth's surface. Distances between tops and bases lessen as excess energy dwindles. Columns of crystalline materials grade downward to denser, more mafic rocks. Size and shape of cells depend on amounts of excess energy stored, before breaking away as plutons and excess energy gained or lost along paths. Excess energy and mass flow more effectively upward along TP gradients than transversely, resulting in cylindrical cross sections, steep contacts with host rocks, and narrow zones of thermally affected rocks.

Internal conditions in reaction cells differ in time and space. At tops, roof rocks destabilize regardless of type and dissolve, causing retreat of solid–liquid interfaces; country rock and fugitive components are absorbed, and excess energy consumed by dissolution. Dynamic upper
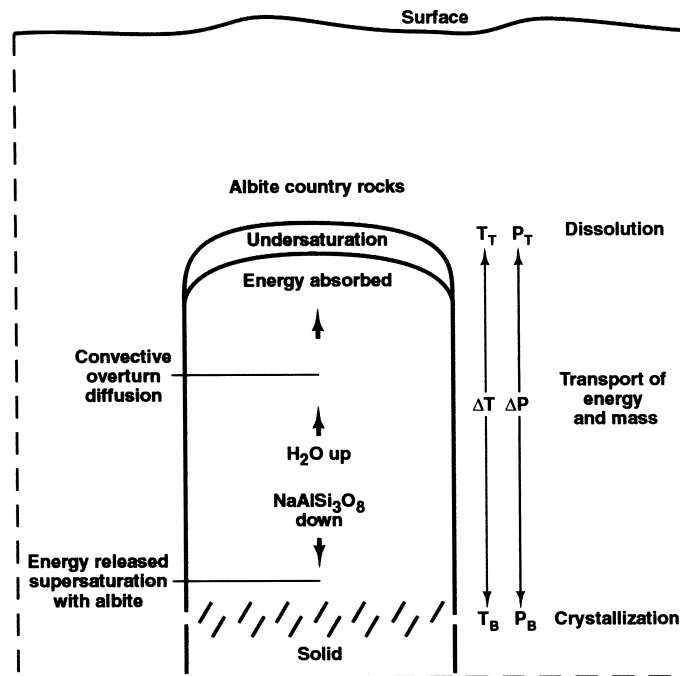

Fig. 3. Cross section of reaction cell of 1% H_2O $NaAlSi_3O_8$–H_2O solution initially 1000°C and 1000 bar, in albitic terrain at 1000°C, subjected to diffusion along gravitational pressure gradient; albite crystallizes at highest P at base and dissolves at lower P of top, energy and H_2O flow upward, dissolution front rises.

zones are most distant from equilibrium, and may be chaotic. Central zones are paths for upward migration of energy and mass by convective overturn. At bases, processes are closest to equilibrium; minerals that separate at basal *TPX* conditions precipitate exothermically, releasing excess energy that maintain upward gradients. Basal solutions become depleted in components of minerals that separate.

Compositions of liquids move toward experimental "minimum melt" compositions. Mafic minerals tend to have lower solubilities at higher *TP* conditions and to precipitate in greater proportions at lower levels. Silicate liquids evolve toward higher silica and K contents. Cell tops enrich in fugitive components absorbed from country rocks.

Ortolevan reaction cells supply surface volcanic fields and underlying intrusive systems. Those halting below the surface emplace intrusives.

5.2. Energy balance along paths

Excess energy represents net energy available to drive processes. During travel, ortolevan reaction cells gain or lose excess energy depending on: heat added or lost; work done by or on bodies; endothermic reactions at tops versus exothermic reactions at bases; exchange of volatiles with surroundings; and entropy production. Absorption of rocks such as shale, which contain metastable minerals and aqueous fluids, increases excess energy compared to basalt or
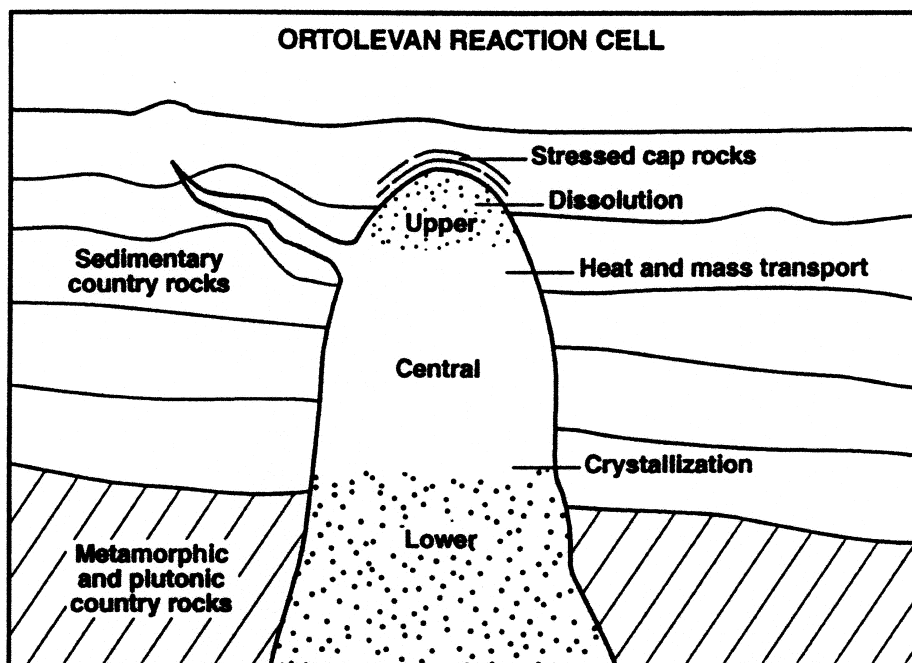

Fig. 4. Cross section view of ortolevan reaction cell, showing three zones: endothermic dissolution reactions at top, movement of energy and mass in central liquids, and exothermic crystallization at base. Column of granitic minerals below. Scale not included, size depends on amount of excess energy.

limestone. With rise and diminution of excess energy, amounts of liquids decrease; ortolevan reaction cells that halt contain excess energy of newly emplaced plutons, which is dispersed by upper crustal processes, such as, heating wall rocks and interactions with ground waters. Excess energy is consumed by irreversible spontaneous processes. Where *TP* conditions of cells are close to environmental, energetic factors tend to be small or off-setting, and consumption of excess energy is mostly for irreversible processes.

5.3. Generating ortolevan reaction cells

Generating liquids in the crust require inputs of energy that are partially understood. Energy is released by decay of radioactive elements. *TPX* conditions suitable for liquefaction are encountered along leading edges of descending slabs. Great volumes of plutonic intrusives and volcanic matter require inputs of excess energy and accreting mechanisms that are difficult to evaluate by igneous melt concepts. Where excess energy concentrates in the earth, ortolevan reaction cells can form, as has been suggested to happen at nodes on the core–mantle boundary (Dickson, 1998).

5.4. Processes in ortolevan reaction cells

Processes in reaction cells range from chaotic to near-equilibrium. Mineral assemblages at bases of cells form close enough to equilibrium to be interpreted from experimental equilibria. Rates of internal processes are important, but difficult to assess. Rates in aqueous fluids heated step-wise from below in Benard cells over small gravitational gradients increase orders of magnitude with the onset of convection (Prigogine and Stengers, 1984).

5.5. Late stages

As excess energy is expended, amounts of liquid lessen. Blocks of undissolved country rocks persist as inclusions in granites when excess energy has dwindled and solutions are less aggressive.

Stress plays roles. Ortolevan reaction cells that rise to cooler terrains exert buoyant stress on roof rocks. Dikes and sills in stress-induced fractures that connect with granitic intrusives document presence of liquids during entry (Dickson and Hsu, 1997). Energy of stress tends to destabilize minerals at surfaces.

6. Discussion

Diverse features of petrology result from disequilibrium processes in open systems. Problems difficult to solve by igneous melt theory can be approached by concepts of irreversibility. Ortolevan reaction cells combine with other processes. Diapirs rising along favorable structures may halt, and chemical processes take over. Chemical ascent may switch to diapiric when low liquid densities develop or tectonic paths appear. Unraveling physical and chemical processes in intrusive complexes is the challenge to petrologists.

Acknowledgements

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