Crystallisation history of granitic magma: evidence from trace element zoning

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The evolution of the major and trace element chemistry of a magma is dependent on a number of factors, especially the order of crystallisation and the degree to which early formed crystals re-equilibrate with the magma as it cools. The chemical zoning which is observed in many minerals, even for coarse-grained rocks formed by slow cooling, demonstrates that equilibrium between minerals and melt is rarely maintained (Paterson and Stephens 1992). The zoning can be used to understand the progressive evolution of the magma during crystallisation. Indeed since the early formed crystals are effectively removed from equilibrium, the progressive changes within minerals should give a strong indication of how the magma might evolve during fractional crystallisation.

The petrography and mineral chemistry of two granodiorites from a single plutonic complex have been studied in detail. Analyses have been made of the chemical zonation of both major and accessory minerals by ion and electron microprobes. The two granodiorites differ in major element chemistry with BPSRT1 (T1) being lower silica (SiO_2 = 60%) than BPSRG1 (G1) (SiO_2 = 73%); both are dominated by the major mineral phases plagioclase, quartz and K-feldspar and contain the accessories apatite and zircon. While biotite is present in both rocks, it is subordinate to hornblende in T1. Importantly the two rocks differ in the dominant *REE*-bearing accessory mineral, G1 containing monazite and T1 titanite. Although the Ba, Sr, Nb and the Rare-Earth-Elements (*REE*) contents are higher by over a factor of 2 in T1, compared to G1, the overall chondrite normalised *REE* pattern for both is similar: the *REE* concentrations fall rapidly through the light *REE* (*LREE*) but with an essentially flat pattern through the heavy *REE* (*HREE*).

Despite the similarities in *REE* patterns between the two rocks, the trace chemistry and zoning show significant differences:

Feldspar. In T1, both the plagioclase and K-feldspar are zoned with respect to the *LREE*, with the rims having a lower concentration of *LREE* and a greater decrease in the chondrite normalised concentrations with increasing atomic number (ionic radius). Eu could only be measured in the plagioclase; the positive Eu anomaly also increased from core to rim. In contrast both plagioclase and K-feldspar in G1 are essentially unzoned with respect to the *LREE* and have flatter chondrite normalised *REE* patterns. If only the cores of the crystals are considered, the partitioning of the *LREE* between plagioclase and K-Feldspar is similar for both rocks, the *LREE* (Plag/K-Feld) ratios increasing from about 8 for La to 42 for Pr. The values for La are similar to those observed in coexisting feldspars from volcanic rocks and support the co-crystallisation of plagioclase and K-Feldspar in both rocks.

Apatite. The chemistry of the apatites in the two rocks shows marked contrasts. In both cases their *REE* chemistry would suggest that they crystallised relatively late, despite the euhedral nature of some of the grains. T1 apatites have a uniformly very steep, *LREE* enriched, pattern and no (or even a slight positive) Eu anomaly. In contrast G1 apatites are strongly zoned. The cores have relatively flat *LREE* patterns and are depleted in the *HREE*, whereas the rims are depleted in the La but relatively enriched in the heavy *REE*. All G1 apatites have similar Sm contents and a negative Eu anomaly which remains constant with time.

Monazite. The *LREE* are an essential constituent of monazite and the average *LREE* pattern is very close to that of the whole rock. In contrast, the *HREE* decrease rapidly from Gd to Lu. The partitioning of Eu^{2+} into monazite can be inferred to be very low from the low Sr content of this phase (Sr Min/WR = 0.3). The negative Eu anomaly (Eu = 0.1) probably reflects the Eu^{2+}/Eu^{3+} ratio of the magma at the start of crystallisation. The *REE* pattern changes little with time, La decreasing slightly relative to Ce with the increased substitution of Th. U strongly correlates with Th; the Th/U ratio (30) does not change significantly from core to rim.

Titanite. The titanites in T1 initially show a marked preference for the middle range *REE* and a negative Eu anomaly (Eu* = 0.6). In euhedral grains, the *REE* decrease outwards, the *REE* pattern becomes steeper and the negative Eu anomaly decreases. The later overgrowths and grains intergrown with apatite and hornblende have a very steep *REE* pattern and positive Eu anomaly. Th is initially concentrated into the titanite, but decreases by a factor of 36 from core to last overgrowth, compared to a decrease of only 3.6 for U. Nb similarly decreases rapidly from core to rim.

Hornblende. The hornblende in T1 is similar to titanite with the *REE* decreasing, the pattern steeper and the negative Eu anomaly becoming positive, from core to rim of the crystal.

The major differences between the chemistry of the minerals in the 2 rocks can be explained by the crystallisation order coupled with the low degree of re-equilibration. In T1, the titanite crystallised early and its preference for the middle range *REE* resulted in a relative enrichment of the melt in La and Ce and to a lesser extent, Yb and Lu. Continued crystallisation of titanite increasingly removed the mid range *REE*, increased the melt La/Ce ratio and thus imposed progressively steeper *REE* patterns on the later crystallising feldspar and hornblende. Apatite formed late and is strongly enriched in the *LREE* relative to the bulk magma. In G1, by contrast, the monazite had only a very weak preference for the individual *LREE* but effectively rejected the *HREE*. Crystallisation of monazite effectively removed over 90% of the La but only 50% of the Gd and 3% of the Lu. The feldspars probably crystallised at an early stage and may have maintained equilibrium with monazite. In contrast, the G1 apatite crystallised very late from a melt with essentially a flat *REE* pattern.

The two rocks also differ significantly in the change in the Eu anomaly with time. Although the whole rocks have no Eu anomaly, the presence of both Eu^{2+} and Eu^{3+} in magmas, under normal oxygen fugacities, leads to fractionation of this element from other *REE*. In the granodiorites analysed here only feldspar strongly favours Eu^{2+}

relative to Eu^{3+}. It should be noted that Sr is a very good analogue for Eu^{2+} and this element is not strongly zoned in any of the minerals analysed. It may therefore be inferred that Eu^{2+} partitioning did not change substantially as crystallisation proceeded. G1 monazite and apatite probably grew in equilibrium with feldspar permitting the Eu anomaly to remain constant. By contrast, the decrease in the negative Eu anomaly in all T1 phases can be ascribed to the poor extraction of Eu^{2+} by titanite and the relatively late crystallisation of feldspar. The change in the Eu anomaly could be ascribed to changes in oxygen fugacity of the magma as crystallisation proceeded. However, even if the magma became more oxidising as crystallisation proceeded, a positive Eu anomaly may only be created in a phase which excludes Eu^{2+} if the total Eu has already been enriched relative to the other *REE*. It is possible that further electron probe analyses of the hornblendes will establish whether the oxygen fugacity changed with time.

Calculation of the distribution of the elements between phases highlights the domination of monazite on the *LREE* content of G1 (90% of the *LREE*). Plagioclase holds nearly all the Eu (70%) and Sr (78%) in G1. Nearly all the Th (98%) is in the monazite. However, only 25% of the U can be accounted for in the minerals analysed to date. In T1 the *REE* are more equally distributed between the various phases. While titanite dominates the mid-range *REE* budget it also contains 55% of the Eu. The feldspars account for 99% of the Sr but only 27% of the Eu, again this may be due to their late formation.

Melts evolving by fractional crystallisation from the two rock types would obviously differ significantly. That crystallising monazite would have a flat *REE* pattern and Th enrichment. This is similar to late stage aplites. Melts crystallising titanite would be depleted in Th and have a steep *REE* pattern.

Paterson, B.A. and Stephens, W.E. (1992) *Contrib. Mineral. Petrol.*, **109**, 373–85.