

Part III Modelling Trace Elements

Equilibrium (the underlying assumption to most petrological and geochemical modelling) is attained when the activities of all components in the geological system become equal (Spear 1994). In magma, such equilibrium should govern the partitioning of an element between the crystal and surrounding liquid. However, the relationships between activities and concentrations are not straightforward, as it is difficult, if not impossible, to express them in a rigorous form for all elements and minerals present in the system. Hence, geochemical modelling relies on several simplifying assumptions.

For major elements, the mineral chemistry is generally nearly constant during melting or crystallization. Thus the easiest approach is to ignore the activities altogether, and measure, or assume, the mineral chemistries. Note, however, that even in this case activities and equilibria can be calculated (Holland and Powell 1998).

Trace elements¹ pose a different challenge. With a few exceptions (Kelsey and Powell 2011), no activity–composition models are available. Also, the trace-element contents in minerals are highly variable, and usually poorly constrained. It is, therefore, generally not possible to use the same mass-balance approach as for major elements.

In the case of trace elements that occur in small amounts in the crystal lattice (so are sufficiently ‘dilute’), the activity should be proportional to their concentration (Henry 1803). The coefficient of proportionality depends on the nature of the mineral but *not* on the concentration of the element. Consequently, activities can be again ignored and replaced by the simpler concept of element partitioning between different phases (in igneous petrology, a liquid and crystal(s)). Whereas the major-element modelling relies on the *absolute concentrations* in the solid phase, the key parameter for the trace elements is the *ratio* of their concentrations in the solid phases and the liquid (Chap. 10).

¹ In this text the term “trace element” implies low whole-rock content. However, such an element can still be the main component of an accessory mineral, as is the case for Zr in zircon (ZrSiO₄).

This approach, however, fails when dealing with trace-element-rich phases. Some elements, termed essential structural constituents (ESC) (Hanson and Langmuir 1978), form a substantial part of the crystal lattice of certain accessory minerals. These are e.g., Zr in zircon, P in apatite or P, Th and LREE in monazite. Henry's Law is not applicable anymore and the strategy based on partition coefficients is inappropriate. Furthermore, activity–composition relationships are not perfectly, or not at all, established. The best approach is therefore largely empirical, based on experiments and on the notion of the mineral solubility in a silicate melt (Chap. 13).

References

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