

V. M. Goldschmidt Medalist Lecture

The principles controlling trace element partitioning in igneous processes.

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Understanding and predicting the behaviour of the chemical elements in the earth's crust, mantle and hydrosphere is a fundamental task in geochemistry. Qualitative predictions date from the work of Goldschmidt (1937) who used a small number of measurements of element concentrations in minerals as a means of systematizing element behaviour during crystallization from liquids or gases. This led to the 3 'rules' of element partitioning, which may be summarized as follows: 1) Any two ions of the same charge and very similar ionic radius have essentially the same crystal-liquid partition coefficient ($D = [I]_{\text{xtl}}/[I]_{\text{liq}}$ where $[I]$ is the concentration of element i). 2) If there is a small difference of ionic radius the smaller ion enters the crystal preferentially. 3) For ions of similar radius but different charges, the ion with the higher charge enters the crystal preferentially. These principles were taught to generations of students and, as I will show retain, under certain circumstances, a degree of validity. They are not, however, universally correct nor do they have any quantitative applicability.

Real advances in the quantification of the principles established by Goldschmidt date from the paper of Nagasawa (1966) who calculated from elastic strain theory the energetics of replacing a small (major) ion by a large trace ion in a crystal of known elastic properties. This demonstrated that Goldschmidt's rule (2) is correct, provided that the trace ion is larger than the major ion.

With the development of precise methods for measuring trace element partitioning between solids and melts (electron microprobe, SIMS, LA-ICPMS) a plethora of experimental data have, in the last 25 years, been collected under controlled conditions of pressure temperature and composition. Computer simulation methods have become powerful enough to enable the energetics of ion exchange processes to be investigated in detail. Together the experimental data and simulations provide the means to expand and quantify Goldschmidt's

rules. Research carried out in Bristol demonstrates that equilibrium partitioning depends primarily on 2 energies of substitution into the crystal (a) the energy of elastic strain generated by inserting an ion which is either too large or too small for the site. (b) the electrostatic work done in inserting an ion which is either more or less highly charged than the major ion normally occupying the site.

Good approximations to trace element substitution energies are arrived at by treating the crystal as elastically isotropic and the area around the substituent as a dielectric continuum. Thus, following Brice (1975), we can calculate the crystal-liquid partition coefficient D_i of an ion of radius r_i as a function of its radius, the Young's modulus of the site and D_0^{Z+} the partition coefficient for the ion which has the same charge as i , and which does not strain the lattice.

The link between D_0 values for ions of different charge is established by calculating the electrostatic work done in replacing an ion of charge Z_0 (which exactly matches the charge on the site) by a trace ion of charge Z_c . This gives us D_0^{Z+} as a function of charge Z , the effective dielectric constant of the medium ϵ and the radius of the ion r .

The theory requires modifications to Goldschmidt's rules (2) and (3). Rule (2) should now be: The site has a preferred radius of ion (r_0) which enters most easily. For ions of the same charge, those which are closest in radius to r_0 enter most easily. Ions which are smaller or larger are discriminated against.

Rule (3): The site has a preferred charge Z_0 . For ions of similar size, but different charge the one whose charge is closest to Z_0 enters most easily.

These quantitative extensions to Goldschmidt's rules enable us to predict the geochemical behaviour of most ions quantitatively. A number of examples and applications to geological processes will be presented