Insights into trace-element mineral melt partitioning from atomistic simulation and *ab initio* theory

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We discuss recent advances in computational approaches to trace-element incorporation in minerals and melts and the implications of these results for analysing and understanding modern partitioning experiments. Thanks to advances in ab initio theory it is now possible in many cases to compare results calculated with classical forcefields with those from periodic density functional theory (quantum mechanical) calculations – in most cases agreement is very good.

It is crucial to take explicit account of the local structural environment of each ion in the solid and the change in this environment as the surrounding atoms move following the introduction of a foreign atom or atoms. Several different energy terms contribute to the overall energetics of the partitioning process and the 'lattice strain energy' used in most current predictive mineral-melt partitioning models is only one of these. When considering heterovalent substitution the energetics of incorporation of the charge-compensating defect must also be included.

Applications include incorporation of trace elements in garnet end members and solid solutions and the trace-partitioning behaviour of the noble gases, uranium and thorium. We also discuss the importance of allowing explicitly for segregation of trace elements to grain boundaries and other interfaces, particularly when there is a large charge or size mismatch between the trace element and the ions in the host solid.

δ^{15}N-δ^{13}C covariations in organic matter through eons: Tracing the evolution of metabolic pathways

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Nitrogen in Paleoarchean kerogens is characterized by lower than present δ^{15}N values from -7 to +3‰ (where $\delta^{15}N = (R/R_{air}-1) \times 1000$; $R = {}^{15}N/{}^{14}N$). Relatively light C ($\delta^{13}C_{PDB}$ from -38 to -30‰) accompanies the light N. Approaching the Archean-Proterozoic boundary kerogens show isotopically heavier N (δ^{15}N from +10 up to +30‰ for BIF samples) and C (δ^{13}C from -30 to -20‰). This isotopic shift has been interpreted as a redox change in the atmosphere-ocean. Early Archean reduced conditions enhanced *N-fixation* of inorganic N by chemolithoautotrophs, possibly living in hydrothermal environments [1]. Low δ^{13}C values are compatible with inorganic C assimilation by methanogens flourishing in hydrothermal environments [2]. When oxygen rose as a by-product of photosynthesis, limited nitrate sources could have been cycled by photoautotroph and heterotroph organisms. In an Early Proterozoic ocean, containing limited amounts of nitrates, the *nitrification–denitrification–assimilation* process could have easily produced a higher isotopic shift than that observed in the modern ocean, because of the earlier scarceness of nitrates as a reactant. With the formation of a quantitative global nitrate pool in response to the oxygenation of the ocean, the emergence of microbial processes that led to the enrichment in δ^{15}N in the nitrate pool and to a continuous supply of nitrates, the isotopic shift would have decrease to the modern average value of +5‰ [1].

Supported by new unpublished and literature data, here we show that several δ^{15}N-δ^{13}C trends exist for set of samples of different ages and locations. Co-variations between δ^{15}N and δ^{13}C perhaps indicate different metabolic pathways available at respective ages and locations, reflecting possibly changes in the environmental conditions, such as the redox. These relationships also exclude the possibility of mixing between inorganic (i.e. mantle) and organic sources of C and N to explain their isotopic variations during eons [3].

[1] Shen *et al.* (2006) *AGU Geophys. Monogr.* **164**, 305-320. [2] Ueno *et al.* (2006) *Nature* **440**, 516-519. [3] Kerrich *et al.* (2006) *GSA Memoir* **198**, 81-104.