

## The partitioning of trace elements between clinopyroxene and trachybasaltic melt during rapid cooling

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### Variation of trace element partition coefficients

We present the variation of trace element partition coefficients measured at the interface between rapidly cooled clinopyroxene crystals and co-existing melts. Results indicate that, Ds for REE, HFSE and TE increase with increasing cooling rate, in response to clinopyroxene compositional variations. The entry of REE into the M2 site is facilitated by a coupled substitution where either Na substitutes for Ca on M2 site or Al<sup>iv</sup> substitutes for Si in the tetrahedral site. Due to the lower concentration of Ca in rapidly cooled clinopyroxenes, LILE on M2 decrease at the expense of monovalent cations. Conversely, higher concentrations of HFSE and TE on the M1 site are facilitated as the average charge on this site increases with the replacement of divalent-charged cations by Al<sup>vi</sup>. At both equilibrium and cooling rate conditions, Ds for isovalent cations define parabola-like curves when plotted against ionic radius, consistent with the lattice strain model.

### Implications

Although crystallization kinetics alter clinopyroxene composition, deviations from equilibrium partitioning are insufficient to change the tendency of a trace element to be compatible or incompatible. Consequently, there are regular relationships between ionic radius, valence of the trace element and D. Under both equilibrium and cooling rate conditions, the partitioning of trace elements is driven by charge-balance mechanisms; cation substitution reactions can be treated in terms of the energetics of the various charge-imbanced configurations.

## A Pilot Br Isotopic Study of Arid Playa Lakes and Ordinary Chondrites

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**Introduction:** Bromine possesses a chemistry broadly comparable to that of Cl and F, however its heavier mass and lower abundance results in slightly different behaviours in geochemical cycling. For example it is disproportionately enriched in sea water with respect to Cl. Br can be considered to be a “hydrophile” element, and hence its behaviour is in governed by that of water. It possesses two isotopes <sup>79</sup>Br (50.686%) and <sup>81</sup>Br (49.314%).

This study has developed new chemical extraction, and most significantly, new mass spectrometric protocols for Br isotopes on silicates, evaporites and waters using N-TIMS methodologies. Existing CF-IRMS methodologies offer internal precision of ~0.3‰ (1SD, [1]), whereas N-TIMS measurements of laboratory HBr and seawater standards produce external reproducibility of <0.07‰ (1SD) over an 18 month period with internal precision typically <0.06‰ (1SD) on single analyses.

This study presents the first high precision, N-TIMS isotopic data on playa lake evaporites and ordinary chondrites, recording a >5‰ variation in solar system <sup>81</sup>Br/<sup>79</sup>Br.

[1] Shouaker-Stash *et al.*, *Anal. Chem.*, **77**; p4027-4033, 2005.