Computation of Li equilibrium isotope fractionation between minerals and aqueous solution

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We present an efficient *ab initio* based computational method for prediction of the equilibrium isotope fractionation factors in the high pressure and temperature materials, including fluids. The method originates in the Bigeleisen and Mayer [1] approximation and requires only the knowledge of the force constants acting on the fractionating element. An important aspect of the proposed method is the explicit modelling of materials as continuous media. This allows for investigation of the expansion and compression effects, which influence the fractionation process in high -T and -P materials. We have tested our method by computing the Li isotope fractionation factors between complex Li-bearing crystalline solids (staurolite, spodumene and micas) and aqueous solution, and by comparison of the results with the existing experimental data [2]. We show that we are able to reproduce correctly the experimental isotope fractionation sequence: staurolite-fluid-mica-spodumene and reproduce the measured values within 1 ‰.

We also have investigated the predictive power of the widely used cluster approach, in which a fluid or solid is represented by a cluster of atoms and treated as a large molecule for derivation of the vibrational spectrum - the input for the computation of the equilibrium isotope fractionation factors. We show that representation of the aqueous solution by Li $(H_2O)_n$ cluster results in the correct estimation of the isotope fractionation at low pressure ($P<1GPa$) but dramatically fails even on the qualitative level for higher pressures. This is because when computing materials under extreme conditions one has to account for the volume effects, such as compression or expansion, and structural changes in the fluid. These effects cannot be modelled unambiguously using the cluster approach. The proposed method accounts for these effects and predicts increase of isotope fractionation with pressure, which is more realistic and in agreement with the recent high pressure ($P=8GPa$) measurements for spodumene [3].

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In situ δ^{18}O and Mg/Ca analyses of diagenetic and foraminiferal calcite: Implications for paleoceanographic proxy records

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The vast majority of planktic foraminiferal shells in deep-sea sediments are affected by various degrees of diagenesis; the effect on oxygen isotope ratios and minor/trace element abundances may be profound, but is debated. Previously, numerical models were applied to describe the oxygen isotope exchange during burial and recrystallization of deep-sea carbonate [1]. Furthermore, the partition coefficients for minor and trace element incorporation in diagenetic calcite are not clearly defined; in particular, the conversion of Mg/Ca ratios from diagenetically altered foraminiferal shells to water temperature is not straightforward.

We used an ion microprobe to analyze δ^{18}O and Mg/Ca in 200-500 μm sized diagenetic calcite crystallites cementing small aggregates of foraminiferal shells from the Early Paleogene section of ODP Site 865, Central Pacific. The δ^{18}O values of these diagenetic crystallites range from 0.1‰ to 2.2‰ [PDB] with an average of 1.2‰, and are in agreement with values predicted by numerical models [1]. The δ^{18}O of these diagenetic calcites are ~6‰ higher than that previously reported from *in situ* measurements of unaltered domains (basal areas of muricae) within planktic foraminiferal shells from the same core samples [2]. Thus, both the endmember biogenic and diagenetic δ^{18}O values are determined.

Mg/Ca of the diagenetic calcites range from ~25 to 100 mmol/mol with sharp gradients (variations of ~70 mmol/mol over 100 μm), implying complex, small-scale processes of dissolution and recrystallisation that are not reflected in the δ^{18}O. The average Mg/Ca ratio of 60 mmol/mol confirms previous results from inorganic precipitation experiments [3] and is >10 times higher than the Mg/Ca of biogenic foraminiferal calcite. In contrast Mg/Ca ratios of diagenetically altered foraminiferal shells from the same core samples are not significantly elevated. Low Mg/Ca does not prove preservation of biogenetic values because the processes governing foraminiferal diagenesis differ from those that mediate the precipitation of interstitial cements.

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