

From small-scale chemical processes to long-term (radioactive) contaminant migration predictions

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Migration rates of (radioactive) contaminants in porous materials, such as soil rock and concrete, are dominated by distribution of ions over pore solution and solid phase. Precipitation and adsorption are small-scale chemical processes that determine the distribution and in this way control migration rates at larger scales. The often multicomponent nature of such interactions results in a strong dependence of single element behaviour on chemical conditions, which complicates the translation of experimental results to field conditions. Credible contaminant migration predictions require a model that contains the major soil reactive phases / surfaces, e.g. the different oxide and organic matter surfaces, dissolved organic carbon, including their mutual chemical interactions in a thermodynamic consistent way[1]. The combined CD-MUSIC model for oxides, the NICA-DONNAN model for organic matter, and the LCD model go a long way achieving this. To accommodate these combined models an advanced numerical framework is required[2]. It is, however, important to realize that whatever the assumed sophistication of the conceptual- or numerical model, careful evaluation of model accuracy is essential for its usefulness in practice. Such an evaluation can only be done by testing the model on truly independent data [3].

[1] Schröder et al. (2005), *Environmental Science & Technology* 39, 7176-7184. [2] Meeussen, (2003), *Environmental Science & Technology* 37, 1175-1182. [3] Dijkstra, et al. (2009) *Environmental Science & Technology* 43, 6196-6201.

The structural determinants of silicon fractionation properties of silicate minerals: a First-Principles Density Functional Study

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Silicon is among the new isotopic systems that are emerging due to recent analytical progress in mass spectrometry. Thorough understanding of the parameters influencing natural Si-isotope variation is therefore of great importance to assess potential geochemical applications.

Ab initio methods based on density functional theory have proven successful in predicting equilibrium fractionation factors as a function of temperature (e.g., 1). We use the PBE functional, combined with norm-conserving pseudopotentials and plane wave basis sets. We focused on phyllosilicate minerals: kaolinite, lizardite, talc and pyrophyllite, which appear to span a wide range in fractionation properties despite having the same basic silicate polymerization. In this family of silicates, calculated Si isotope fractionation appears to be correlated with chemical composition:

$$\Delta^{30}\text{Si}(\text{min, quartz}, T) = \sum a_X(T) \frac{X^{\text{eq}}}{\text{Si}^{\text{eq}}} \quad (1)$$

with X^{eq} representing the cation equivalents of $X=\text{Al, Mg, Si}$, i.e. the number of $\frac{1}{2}(\text{SiO}_2)$, $\frac{1}{3}(\text{Al}_2\text{O}_3)$, (MgO) units in the mineral, and $a_X(T)$ is a parameter depending on temperature. Further analysis leads us to interpret this relationship as an electron donation effect, such that $a_X(T)$ should increase with decreasing electronegativity of X. To assess the generality of this relationship, we computed fractionations for a more diverse suite of minerals. Within the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system, relation (1) continues to hold for quartz, pyrope and enstatite ($R^2 = 0.99$, $n=7$), but forsterite is strongly anomalous. To assess the effects of Ca^{2+} , Na^+ , K^+ and tetrahedral Al^{3+} on Si fractionation, we computed the properties of albite, anorthite, microcline, diopside, wollastonite, jadeite, grossular, and the three Al_2SiO_5 polymorphs. Preliminary results suggest almost all of these minerals follow relation (1) reasonably well (excepting wollastonite), if tetrahedral Al^{3+} is assumed to have no effect on Si fractionation ($\Delta^{30}\text{Si}(\text{Al}^{3+})=0$).

These results suggest that particular attention should be given to chemical compositions in Si isotope studies.

[1] Meheut et al. (2009) *Chem. Geol.* **258**, 28