

Assessing the role of incongruent weathering

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Quantifying the variations in continental erosion throughout the Earth's history remains crucial for reconstructing the link between global temperatures and the drawdown of atmospheric carbon dioxide from chemical weathering. However, the use of changes in marine radiogenic isotope compositions, like the $^{87}\text{Sr}/^{86}\text{Sr}$, to act as proxies for changes in the rate of continental erosion may need to be revised. Recent work has suggested that marine isotopic variations may not simply reflect the degree of erosion, but rather shifts between incongruent weathering of refractory mineral phases and the congruent weathering of the whole rock.

Records of the radiogenic isotope composition of seawater (Nd, Pb and Hf) in the North Atlantic suggest that over Northern Hemisphere Glaciation (NHG) there has been an increase in their input via Labrador Sea Water (LSW). Recent modelling suggests that the isotope composition in the North Atlantic for these elements are likely to be relatively insensitive to rates of LSW formation. Thus, the signal relates to a change in the degree and nature of weathering and erosional transport accompanying glaciation. The mis-match between the timing and degree of change in the radiogenic isotope time series indicate that changes cannot be caused by a simple increase in the bulk continental erosion around the Labrador Sea. Several workers have recently suggested that a change between congruent and incongruent weathering of mineral phases are the direct source of the radiogenic isotope variations, without a change in the provenance of material. This can be tested. Any change in the source of material being eroded is likely to result in a change in the age of material being delivered to the Labrador Sea and Baffin Bay.

We have used Ar-Ar dating on individual amphibole mineral separates to constrain the age distribution of detrital grains in the Labrador Sea. Preliminary results have been obtained for ODP site 647 and these indicate variations up to 1.5 Ga in the age of the source material. The data appear to show that the source material has changed significantly over the course of NHG. Prior to ~1.5 Ma there is a larger fraction of mineral grains from terrains older than 2 Ga, whilst the age distributions over the last 1.5 Ma contain a larger fraction of material from the Early Proterozoic terrains of the Churchill Province.

Although there are variations in the provenance of material eroding into the Labrador Sea over NHG, the variations in the radiogenic composition from the different provenances are counter to those changes expected from the deepwater records. Thus, there must be an increase in the amount of incongruent weathering to explain the difference between the detrital ages and dissolved record of radiogenic isotopes in the Labrador Sea.

Coordination Chemistry of Metals in Crustal Fluids: Theory and Experiment

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Ligands such as Cl^- , HS^- and H_2O form complexes with metals in aqueous solutions. Such complexes enhance mineral solubilities and allow metals to be transported through the Earth's crust. In spite of its fundamental geochemical importance, however, we still have a very incomplete knowledge of metal complexation in aqueous solutions.

The solvation properties of water and the nature of metal complexes appear to change dramatically over the pressure-temperature range of the crust. Indeed, the changes in coordination chemistry in aqueous solutions just within the Earth's crust may be greater than those found in solid minerals from the crust to the core-mantle boundary! Pressure and temperature-induced changes in metal complex stabilities have been modelled in terms of the Born theory of solvation and the pressure-temperature changes in the dielectric constant of water. This continuum approach is the basis of the currently used thermodynamic data base of mineral solubilities in high PT aqueous solutions.

Spectroscopic methods can give us a direct probe of metal complexation in aqueous solution. With the development of bright synchrotron radiation sources, we can begin to explore the coordination chemistry of metals under realistic geochemical conditions using EXAFS and XANES spectroscopy. However, the results of these experiments spectra can be difficult to interpret and, with existing technology, it is difficult to study dilute solutions at supercritical conditions.

Developments in computational technology, however, allow us to investigate hydrothermal fluids using atomistic calculations. Such calculations can be based on first-principles (using the density functional formalism of quantum mechanics) or on classical mechanics using interatomic potentials. The effect of temperature and pressure can be determined using molecular dynamics or Monte Carlo methods. In this talk, I will show how atomistic simulations (classical and ab initio molecular dynamics) shed insight on the hydrothermal chemistry of metal cations (Sn, Zn, Cu and Ba) in NaCl brines under experimentally accessible conditions and beyond.