

## Does low temperature and/or life demand disequilibrium? An Fe isotope perspective

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It is commonly stated that disequilibrium is the rule, rather than the exception, for systems at low temperatures or where life is involved. Chemical and isotopic equilibrium are not equivalent, the later determined by the kinetics of isotopic exchange. For example, Fe isotope exchange between Fe (II)<sub>aq</sub> and Fe (III)<sub>aq</sub> is rapid enough to maintain isotopic equilibrium even in systems not in chemical equilibrium, such as at neutral pH in an O<sub>2</sub> atmosphere, where Fe (II) is rapidly oxidized. Isotopic equilibrium at low temperatures between mineral and solution is strongly controlled by mineral surface energies, sorption, solubility, and other driving forces such as electron exchange; these factors are well illustrated in iron oxides. Iron isotope exchange between Fe (III)<sub>aq</sub> and nano ferrihydrite is very slow and limited to surface Fe sites. Isotopic exchange between Fe (III)<sub>aq</sub> and hematite can be increased at high-energy surfaces, where dissolution/re-precipitation occurs, but is still relatively slow. Very fast exchange may occur between Fe (II)<sub>aq</sub> and well-crystalline Fe (III) oxides such as goethite, driven by surface energies, sorption of Fe (II), and electron exchange, allowing isotopic equilibrium to be reached relatively quickly.

Dynamic processes such a microbial dissimilatory iron reduction, where electrons are pumped to the iron oxide surface, and new surface layers are continually exposed by reduction, can maintain Fe isotope equilibrium between surface Fe atoms and Fe (II)<sub>aq</sub>, although the bulk oxide may remain out of isotopic equilibrium with the solution. In contrast, other processes, such as abiologic or biologic oxidation of Fe (II)<sub>aq</sub> to ferric oxide/hydroxide precipitates at neutral pH generally do not occur in isotopic equilibrium, reflecting both kinetic effects upon precipitation and the relative insolubility of ferric iron precipitates at neutral pH. An exception is biologic oxidation that occurs in the periplasm, where redox cycling between Fe (II) and Fe (III) occurs, which apparently produces equilibrium Fe isotope fractionations between Fe (II) and ferric hydroxide precipitates. We conclude that low-temperature and/or life does not universally demand disequilibrium, and, in fact, life may involve processes that increase the likelihood of producing isotopic equilibrium at a variety of physical scales, rather than inhibit equilibrium.

## Accounting of injected CO<sub>2</sub> during geologic storage using chemical and isotopic approaches

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Carbon capture and geological storage is a potential technology to reduce CO<sub>2</sub> emissions into the atmosphere from fossil fuel intensive industries [1]. Monitoring of CO<sub>2</sub> storage sites is required by many of the emerging regulations [2, 3, 4]. Of particular interest to the regulatory bodies is accounting of injected CO<sub>2</sub> [4] but there is no general consensus on how accurately this can be done for various target reservoirs. We have used chemical data and carbon and oxygen isotope ratios of produced fluids and gases sampled repeatedly from various observation wells to: a) trace the movement of injected CO<sub>2</sub>, b) assess pore space saturation with CO<sub>2</sub> and c) develop an approximate carbon budget for the Pembina Cardium CO<sub>2</sub> Monitoring Project in central Alberta, Canada. The distinct carbon isotope ratios of injected CO<sub>2</sub> in association with gas compositional and flux data were used to determine the percentage of injected CO<sub>2</sub> produced at several observation wells using two endmember mixing calculations. Changes of δ<sup>18</sup>O values of produced fluids by up to 4 ‰ due to injection of isotopically distinct CO<sub>2</sub> enabled a quantitative assessment of CO<sub>2</sub> dissolved in the fluids and of free phase CO<sub>2</sub> in the pore space. Lastly, CO<sub>2</sub> solubility calculations for the oil phase were performed. This resulted in a partitioning of injected CO<sub>2</sub> in oil, water, free-phase and produced at individual well locations followed by upscaling to a reservoir model using geostatistical tools that take into account reservoir geology to ascertain a field-wide carbon budget. Results indicate that the majority of the CO<sub>2</sub> remained in a free phase within the reservoir with lesser amounts of injected CO<sub>2</sub> in dissolved phases and produced at wells two years after commencement of CO<sub>2</sub> injection.

- [1] Schrag (2007) *Science*. **315**(5813), 812. [2] U.S. EPA, 2008. *Federal Register*, Vol. **73**(144), pp 43534–43541. [3] European Commission, 2009. Directive 2009/31/EC [4] Ministerial Council on Mineral & Petroleum Resources, 2005. CCS Australian regulatory guiding principles. Available at, <http://www.epa.gov/fedrgstr/EPA-WATER/2008/July/Day-25/w16626.pdf>, Available at, [http://www.ret.gov.au/resources/Documents/ccs/CCS\\_Aust\\_Regulatory\\_Guiding\\_Principles.pdf](http://www.ret.gov.au/resources/Documents/ccs/CCS_Aust_Regulatory_Guiding_Principles.pdf), Available at, <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=O J.L, 2009, 140, 0114, 0135,EN,PDF>