

Per mil $^{238}\text{U}/^{235}\text{U}$ variations in uranium ores: Evidence of fractionation by nuclear field shift?

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The ratio of uranium's two long-lived isotopes, ^{238}U and ^{235}U , has generally been considered invariant in nature with a value of $137.88 \pm 3\%$. However, previous analyses of UF_6 from uranium ores by gas mass spectrometry found small variations in $^{238}\text{U}/^{235}\text{U}$, possibly related to the geologic setting of the deposit [1]. Specifically, a bimodal distribution of $^{238}\text{U}/^{235}\text{U}$ was found where magmatic deposits have higher mean ^{235}U wt % when compared to presumably lower temperature sandstone-type deposits.

We have measured the $^{238}\text{U}/^{235}\text{U}$ in six uranium ores from both sandstone and magmatic deposits listed in [1] (provided courtesy of Smithsonian Institution). We analyzed these by MC-ICPMS using a high precision double-spike technique, utilizing $^{233}\text{U}/^{236}\text{U}$ to control for instrumental mass bias. Precision on repeat analyses of samples is better than 0.2‰ (2s). $\delta^{238}\text{U}_{\text{IRMM U-A}}$ for the two sandstone-type ores are $\approx 0.53\%$ and $\approx 0.47\%$, while the three magmatic ores average $\approx -0.47\%$. Thus, there is a consistent depletion in ^{235}U in sandstone -type ores by $\approx 1\%$ relative to magmatic ores.

The observations are consistent with an isotopic fractionation occurring between dissolved U(VI) and reduced U(IV) for sandstone type deposits (at low T) but little if any fractionation occurring as magmatic deposits form at higher T. The sense of fractionation is opposite to that found for microbial reduction of uranium in the laboratory [2] but is consistent with a nuclear field shift [3]. This is a mass-independent isotope effect of increasing magnitude with increasing atomic mass which, for uranium, can potentially exceed the mass dependent isotope effect by a factor of three [4]. The heavy isotopic composition of U in chemically reduced ore deposits is also consistent with heavy $\delta^{238}\text{U}$ signatures in other reduced settings [5].

[1] Cowan & Adler (1976) *GCA*. [2] Rademacher *et al.* (2006) *ES&T*. [3] Bigeleisen (1996) *J. Am. Chem. Soc.* [4] Schauble (2006) *AGU annual meeting*. [5] Weyer *et al.* (2008) *GCA*.

Partitioning of Rb and Sr between haplogranitic melts and aqueous fluids

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Interactions between magmas and aqueous solutions play an important role in many geological processes, e.g., volcanic eruptions, late magmatic differentiation, and formation of magmatic hydrothermal ore deposits. Fluid-melt partitioning of trace elements has been the subject of several studies, because these elements can be used as petrogenetic indicators. However, the majority of the data is based on analyses of quenched samples with associated intrinsic uncertainties particularly in the concentration in the aqueous fluid [1].

Here, we compare Rb and Sr partitioning data between haplogranitic melts and aqueous fluids determined both, by classical quench as well as *in situ* experiments. This comparison is used to better constrain the potential uncertainties associated with the classical technique. Trace element concentrations in aqueous fluids in equilibrium with melt were obtained *in situ* at elevated P-T conditions using hydrothermal diamond-anvil cells and synchrotron-radiation XRF microanalyses [2].

In situ data for synthetic haplogranitic melt and H_2O or $\text{NaCl}+\text{KCl}+\text{HCl}$ aqueous fluids were determined at 750°C and 200 to 700 MPa. Quench experiments with similar compositions were performed at 750°C and 200 & 500 MPa. Time dependent *in situ* measurements show that Rb and Sr concentrations in the fluids became constant in less than 2000 seconds at all temperatures (500 to 780°C) and indicate very rapid equilibration. The partition coefficients ($D^{f/m}$) of Rb and Sr increase with addition of $\text{NaCl}+\text{KCl}+\text{HCl}$ to the starting solution in all experiments. For Cl-bearing runs both techniques yielded consistent results. The *in situ* $D^{f/m}$ obtained in H_2O -melt runs showed a dependence on pressure, which is more pronounced for Rb than for Sr. Quench experiments, in contrast, show lower values and no effect of pressure.

[1] Adam *et al.* (1997) *Eur. J. Mineral.* **9**, 569-584.

[2] Schmidt *et al.* (2007) *Lithos* **95**, 87-102.