# Constraints on sedimentation rates from uranium diffusion 

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Uranium is a redox-sensitive element that is known to be enriched in black shales deposited in anoxic environments. While details of the reaction mechanisms by which uranium is ultimately preserved in rocks remain the subject of study, it is clear that a major factor controlling uranium accumulation is its diffusion across the sediment-water interface. Thus, box models of uranium diffusion can be used to constrain sedimentation rates in the rock record.

We measured uranium, TOC, $\delta^{13} \mathrm{C}$ and other metal concentrations in several outcrops and cores of the Devonian Woodford Shale in southern Oklahoma. Assuming the slowest sedimentation rates, model results indicate that the highest observed uranium concentrations could be fixed in the sediments in less than 6,000 years.


However, considering the preserved thickness of outcrops today, the amount of time accounted for by this model is an order of magnitude less than that constrained by biostratigraphy. These results may indicate that more complicated biogeochemical models are required to properly constrain sediment input rates. More intriguing is the possibility that this discrepancy points to previously unrecognized nonconformities in the rock record.

# The role of NaCl and $\mathrm{CO}_{2}$ on the upper critical end point in $\mathrm{SiO}_{2}-\mathrm{H}_{2} \mathrm{O}$ : <br> Insights from solubility experiments 

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Silica is a major dissolved constituent of $\mathrm{H}_{2} \mathrm{O}$-rich crustal fluids [1]; however these fluids commonly possess elevated concentrations of NaCl and/or $\mathrm{CO}_{2}$, and the effect of these components has received less attention [2]. For example, the hydrothermal melting point of quartz, and the position of the upper critical end point (UCEP) in the $\mathrm{SiO}_{2}-\mathrm{H}_{2} \mathrm{O}$ system [3, 4] should vary with the concentrations of these components. To constrain this behavior, we investigated the solubility of quartz in the systems $\mathrm{NaCl}-\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}$ at $900-1000^{\circ} \mathrm{C}$ and 15-20 kbar using hydrothermal piston-cylinder methods, with reagent NaCl and silver oxalate as NaCl and $\mathrm{CO}_{2}$ sources, respectively [2,5]. Results with NaCl show a steep initial decline in $\mathrm{XSiO}_{2}$ vs. XNaCl with a slope of -1.44 . At higher salinities, the slope levels to -0.58 . In the $\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}$ system, preliminary results suggest a similarly dramatic initial decline. To compare the two systems, XNaCl and $\mathrm{XCO}_{2}$ data were converted to water activities using models from [6] and [7] respectively. Previous studies at lower PT have shown that solubilities are consistently lower in $\mathrm{CO}_{2}-\mathrm{H}_{2} \mathrm{O}$ than in $\mathrm{NaCl}-$ $\mathrm{H}_{2} \mathrm{O}$ for a given water activity; this behavior is observed at higher PT as well. Coupling data from this study with those of previous and related studies $[2,4,5,8]$, our results require that NaCl and $\mathrm{CO}_{2}$ shift the UCEP of $\mathrm{SiO}_{2}-\mathrm{H}_{2} \mathrm{O}$ to higher T and P . Because NaCl lowers silica solubility, it must raise the UCEP to higher temperature and/or pressure. Additionally, because $\mathrm{CO}_{2}$ decreases silica solubility to an even greater extent than NaCl , this must indicate a greater shift in the UCEP to higher temperature and/or pressure with addition of $\mathrm{CO}_{2}$.
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