Cr isotope fractionation during biogeochemical reduction of Cr(VI) by Hanford native aquifer microbial communities

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Hexavalent Cr contamination in groundwater within the DOE complex has been a long-standing issue. Injection of electron donors, such as lactate, to Cr contaminated aquifers to stimulate the growth of native microbial communities, and thus promote reduction of Cr (VI) to Cr (III), has become a widely utilized remediation practice. However, whether these conditions are optimal for Cr reduction is to a large extent unknown. It has been demontrated that reduction of Cr (VI) can cause Cr isotope fractionation [1, 2]. The Cr fractionation factor changes under varying experimental conditions even with the same bacterial strain [2]. Cr isotopic measurements are more direct and effective than concentration analyses to distinguish between different reduction pathways, and also between reduction and simple dilution.

To evaluate the effects of differing electron acceptors on Cr (VI) reduction by native microbes, small-scale column experiments with homogenized material from the Hanford 100H aquifer were conducted. All columns had a continuous inflow of solutions with constant concentrations of Cr (VI), lactate, and the targeted electron acceptor (nitrate, sulfate, no electron acceptor added). Different Cr fractionation behaviors were observed under different conditions. The least extensive Cr reduction occurred in no-electron-acceptor-added columns and had the largest Cr isotope fractionation (α~0.997). The greatest Cr reduction occurred in two sulfate-containing columns that were fermenting the lactate. Samples from one such column had the smallest Cr fractionation (α~0.999). Denitrifying columns had intermediate α values. One sulfate-added (not fermentative) column showed two distinctive stages of fractionation, suggesting a change in reduction processes. Our α values mostly fall in the range 0.997-0.999, which are smaller than those observed in cell suspension experiments with *Shewanella oneidensis* and much lower lactate concentrations [2]. Reactive tranport modeling will be conducted to further evaluate the effects of various experimental parameters on Cr isotope fractionation.

[1] Ellis, Johnson & Bullen (2002) *Science* **295**, 260–262.
[2] Sikora, Johnson & Bullen (2008) *Geochim. Cosmochim. Acta* **72**, 3631–3641.

Precise $^{40}Ar/^{39}Ar$ geochronology of gas migration and accumulation

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It is very difficult to determine the exact age of natural gas emplacement because no suitable mineral for dating with common isotope geochronometers was formed during gas migration and accumulation, although illite K-Ar dating has been widely used to constrain the maximum ages of petroleum accumulation since Lee *et al*.'s [1] report. Selby *et al*. [4] demonstrated a possibility to date hydrocarbon deposits by Re-Os isotopes. Mark *et al*. [2] obtained oil migration age by UV laser microprobe $^{40}Ar/^{39}Ar$ dating of authigenic K-feldspar bearing oil fluid inclusions.

In this study, we show a novel promising approach to obtain high precision ages of gas emplacement into the Songliao Basin, NE China, by $^{40}Ar/^{39}Ar$ progressive crushing technique. The igneous quartz from the Cretaceous volcanic rocks in Yingcheng Formation (117–111 Ma) hosting the gas reservoir contains abundant K-rich secondary fluid inclusions (8.3–0.4 wt% in salinity) with high partial pressures of methane (66–9 MPa) trapped during gas emplacement. Based on our previous studies, quartz with abundant K-rich fluid inclusions provides an excellent closed system well suited for $^{40}Ar/^{39}Ar$ progressive crushing technique. Three irradiated igneous quartz samples were measured by stepwise crushing to release these secondary fluid inclusions. All three samples yielded well-defined $^{40}Ar/^{39}Ar$ isochrons with ages in close agreement, precisely constraining that the gas emplacement occurred at 42.4 ± 0.5 Ma (2SD) below the famous Daqing Oil Field in the Songliao Basin, extending possible gas reservoirs from the upper Cretaceous to the middle Eocene.

This study provides a new effective solution to gain the ages of gas emplacement. See [3] for detail.

[1] Lee M, Aronson JL, Savin SM. (1985) *AAPG Bull*. **69**(9), 1381–1385. [2] Mark DF, Parnell J, Kelley SP, Lee MR, Sherlock SC. (2010) *Geology* **38**(1), 75–78. doi: 10.1130/g30237.1. [3] Qiu HN, Wu HY, Yun JB, Feng ZH, Xu YG, Mei LF, Wijbrans JR. (2011) *Geology* **39**(5) 451–454. doi: 10.1130/G31885.1. [4] Selby D, Creaser RA. (2005) *Science* **308**(5726), 1293–1295 doi: 10.1126/science.1111081.