Mercury isotopes in Illinois Basin coal: Organic and inorganic constituents

L. LEFTICARIU[1]*, J.D. BLUM[2] AND J.D. GLEASON[2]

[1]Department of Geology, Southern Illinois University, 1259 Lincoln Dr., Carbondale, IL 62901, USA (*correspondence: lefticariu@geo.siu.edu)
[2]Department of Geological Sciences, University of Michigan, 1100 North University Ave, Ann Arbor, MI 48109, USA

Mercury (Hg) is a metal of environmental concern in coal due to its volatility, persistence, toxicity and tendency to bio-accumulate through the food chain [1]. Within coals, Hg has high affinities for both organic phases (i.e. organic-bound Hg) and inorganic phases (i.e. sulphide minerals). The occurrence and distribution of Hg in coal dictates its behaviour during coal processing and combustion, and its redistribution in combustion products.

We have investigated the Hg concentrations and Hg stable isotopic compositions of organic and inorganic constituents of the following coals from the Illinois Basin: *Herrin No. 6 and Springfield No. 5* of the Carbondale Formation and *Murphysboro and Mount Rorah* of the Spoon Formation. Our results show that the concentration of Hg is highly variable among these coals and significantly below the average for U.S. coals (170 ppb, U.S. Geological Survey COALQUAL database). Hg concentrations measured in samples of fracture-filling pyrite were two orders of magnitude higher than that measured in coal samples. Thus, Hg is dominantly associated with sulfides in Illinois coal.

Distinct Hg isotopic ratios were measured in organic and inorganic constituents of Illinois coals. The pyrite samples were isotopically unfractionated relative to the NIST 3133 Hg isotope standard. The Hg isotopic signatures of coals from the Illinois Basin overlap those of other coal samples worldwide [2] and include some of the lowest δ^{202}Hg values measured for coals (-2.7 ‰ δ^{202}Hg). Unexpectedly, each coal seam exhibits a unique range of δ^{202}Hg values. Additionally, *Herrin No. 6 and Mount Rorah* coals display negative *mass independent fractionation* (Δ^{199}Hg and Δ^{201}Hg down to -0.2‰).

These results indicate that Hg isotopes can be used to (1) fingerprint individual coal seams from Illinois Basin and (2) trace the depositional and post-depositional contributions of Hg to coals.

[1] Diehl *et al.* (2004) *Int. J. Coal. Geol.* **59**, 193–208. [2] Biswas *et al.* (2008) *ES&T* **42**, 8303–8309.

Cs sequestration into a microporous gallosilicate framework

K.M. LEFTWICH AND A.J. CELESTIAN*

Western Kentucky University, Bowling Green, KY 42101, USA (*correspondence: aaron.celestian@wku.edu)

A gallium silicate microporous framework with the zeolite CGS topology is being tested as an ion exhanger for targeted removal of Cs^+ from aqueous solutions. The CGS framework may be an ideal structure for sequestering large ionic radii cations due to elliptical and branching 10 and 8 member-rings (MR). Elliptical channels in zeolitic matierals have enhanced ion selectivity [1, 2] for cations that do not fit initially in the ellipitcal channels, and therefore must distort to accommodate the ingong cation. However, it is not know what drives the spontaneous structural transformations to accomodate these large ionic radii species.

In the as-synthesized K^+ form of the CGS structure (K-CGS), the elliptical channels cannot accommodate Cs^+ due to unacceptable short Cs-O bond distances to the framework. Therefore, the structure must distort to accommodate the guest species. This process has been observed from time-resolved X-ray diffraction ion exchange studies at NSLS Beamline X7B using 10mM CsCl at a flow rate of 0.2 mL/min. Elliptical channels in K-CGS distort and expand as Cs^+ exchanges for K^+. Exchange was completed within 10 minutes. Ion exchange seems to have involved two steps as measured from preliminary unit cell refinements: 1) unit cell expansion as Cs enters the structure, and 2) unit cell contraction as Cs may enter the branching conduits. The branching channels in CGS may also enhance ion conductivity by providing storage space away from the center of the channels so that ions are free to move in and out of the structure. This two-step ion exchange process is similar to other zeolitic materials, such as the titanosilicate CST [1], TsG-1 [2], and bernisite [3], where ion exchange was enhanced by structural distortions.

[1] Celestian *et al.* (2008) *J. Am. Chem. Soc.* **130**, 11689–11694. [2] Lee *et al.* (1999) *Chem. Mater.* **11**, 879–881. [3] Lopano *et al.* (2009) *Am. Min.* **94**, 816–826.