

## **New proxies to trace the environmental impact of hydraulic fracturing fluids**

NATHANIEL R WARNER<sup>1\*</sup>, T. DARRAH<sup>2</sup>, R. JACKSON<sup>3,4</sup>,  
R. MILLOT<sup>5</sup>, W. KLOPPMANN<sup>5</sup> AND A. VENGOSH<sup>4</sup>

<sup>1</sup>Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA

(\*correspondence: nathaniel.r.warner@dartmouth.edu)

<sup>2</sup>School of Earth Sciences, The Ohio State University, Columbus, OH 43210, USA

<sup>3</sup>Dept. of Environmental Earth System Science, School of Earth Sciences, Stanford University, Stanford, CA 94305, USA

<sup>4</sup>Division of Earth and Ocean Sciences, Nicholas School of the Environment, Duke University, Durham, NC 27708

<sup>5</sup>BRGM (Bureau de Recherches Géologiques et Minières) Orléans, France

Unconventional hydrocarbon reservoirs such as black organic-rich shales are developed through the combination of horizontal drilling and high volume slick water hydraulic fracturing (HVHF). Identifying the distinct geochemical characteristics of the injected fluids compared to the fluids associated with the target formation has important implications for possible long-term environmental impacts, hydrocarbon recovery, and wastewater disposal. Here we present a new geochemical evaluation of hydraulic fracturing flowback fluids (HFFF) from the unconventional Marcellus and Fayetteville Formations, which display geochemical fingerprints that are distinct from typical hypersaline produced waters collected from conventional oil and gas reservoir formations. The fresh water injected into the shale formations during hydraulic fracturing mixes with brine but also mobilizes sodium, lithium, and boron from exchangeable sites on clay minerals. The resulting HFFF is enriched in Na, Li, and B with distinct ranges of  $\delta^7\text{Li}$  and  $\delta^{11}\text{B}$ . Combined, the  $\delta^7\text{Li}$ ,  $\delta^{11}\text{B}$ , Li/Cl, Br/B, and B/Cl tracers constitute new diagnostic tools for delineating HFFF migration in the environment. Particularly, these tools can distinguish possible HFFF wastewater impacts compared to conventional oil and gas wastewaters, natural sources of salinity, or other anthropogenic contaminants.