Reductive weathering of black shale during hydraulic fracturing and release of barium

MUKUL SHARMA, JOSHUA LANDIS AND DEVON RENOCK*

Department of Earth Sciences, Dartmouth College, Hanover, NH 03755, USA
(*correspondence: devon.renock@dartmouth.edu)

Water used in hydraulic fracturing of black shale often contains high concentrations of barium. A major barium-containing phase, barite ($BaSO_4$), is part of drilling mud as well as occurring naturally in the black shale. However, the role of barite dissolution is unclear due to its relatively low solubility. We hypothesized that barium in produced water can be released by other phases in the shale and on a time scale relevant to fracking. We examined samples from three drill cores from the Marcellus Shale in Pennsylvania and New York to determine the possible water-rock reactions that release barium during hydraulic fracturing. Micro-XRF measurements and SEM/EDS analysis combined with chemical sequential extraction methods revealed that a majority of the Ba in the rock (55-77%) is strongly partitioned into phyllosilicate clays and is only leached from the rock by dissolution in hydrofluoric acid.

We next studied how finely-crushed shale reacts with water at T = 80 °C, low Eh, and under a range of ionic strengths to emulate the conditions that take place at depth during hydraulic fracturing. Our experimental results indicate that the amount of Ba released from the bulk rock has a positive correlation with the ionic strength of the reacting fluid. Between 5-25% of the total Ba in the rock can be leached from shale under ionic strength conditions typical of produced waters over a contact time of 7 days. We suggest that reductive weathering of black shale occurs during hydraulic fracturing due to: 1) Ba^{2+} in clays exchanging with Na^{+} and Ca^{2+} ions that are present in high concentrations in produced water, and 2) increased solubility and dissolution kinetics of barite under high ionic strength conditions. At the low Eh conditions prevalent during hydraulic fracturing the sulfate deficient water allows Ba to be dissolved into the produced water. Based on Ba yields determined from laboratory leaching experiments of Marcellus shale and a reasonable estimate of the water/rock mass ratio during fracking, we suggest that all of the Ba in produced water can be reconciled with leaching directly from the rock.