

Uranium partitioning and isotope composition in shales of the Middle Devonian Marcellus Formation

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Natural gas extraction from the Middle Devonian Marcellus Shale has raised interest in investigating the distribution and behaviour of NORM (naturally occurring radioactive material) associated with both produced water and drill cuttings from this unit. The Marcellus is a variably calcareous shale with intercalated limestone. Based on core extracted in Greene County, southwestern Pennsylvania, uranium (U) concentrations in Marcellus Formation samples range from 3 to 47 ppm. Sequential extraction experiments indicate that 30 to 95% of the U is held in the silicate fraction. Although there is a positive correlation of whole rock U concentration with TOC as observed by others, U associated with the oxidizable (organic) fraction contributes less than 25% (and usually <10%) of the total. Up to 64% of the U was found in the 1.0 N acetic acid leachate, which has implications for uranium release into the environment from relatively soluble carbonate minerals in drilling waste. The source of NORM in Marcellus produced water is primarily radium [1], the daughter product of U and Th. The low U concentrations measured in produced water samples from three Marcellus Shale gas wells (0.1 to 0.5 µg/L) may result from U reduction and precipitation as UO₂ or U₃O₈, consistent with relatively high Mn²⁺ (1-8 g/L) and Fe²⁺ (20-120 g/L) concentrations.

²³⁸U/²³⁵U ratios of Marcellus shale obtained by MC-ICPMS using the double spike method fell in a narrow range of 137.80 to 137.85, similar to other black shales. ²³⁸U/²³⁵U ratios in the carbonate fraction of calcareous shale units were in the range of marine carbonate; however carbonate cements extracted from black shale units were isotopically heavier by an average of 0.7 ‰. ²³⁸U/²³⁵U ratios in the organic matter and silicate fractions generally overlap and are lower than coexisting carbonate cement by about 0.3 ‰.

[1] Rowan *et al* (2011) USGS SciInvestRep **2011-5135**.

Isotopic and mineralogical evidence for atmospheric oxygenation in 2.76 Ga old paleosols

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Recent chemical and isotopic data from Archean marine sediments indicates that alteration of continental surfaces have contributed a substantial fraction of the flux of redox-sensitive elements (S, Cr, Mo) to the ocean several hundreds of millions of years prior to the Great Oxidation Event (GOE; between 2.45 and 2.32 Ga). However, controversies regarding the factors controlling these deliveries (increase of atmospheric oxygen, acid rock drainage, microbial activity on land) have highlighted the problems of identifying a reliable proxy of continental surface alteration during the Archean. Unlike marine proxies, which are indirect climatic records, paleosols, which form at the atmosphere-lithosphere interface, can provide direct constraints on the weathering processes at the time of formation. Here we present new sulfur isotope and mineralogical data from the reference 2.76 Ga old Mount Roe Basalt paleosols at Whim Creek (Western Australia). The data are from new lithofacies that were not documented in previous studies. These lithofacies contain a Fe³⁺-montmorillonite, calcite and sulfate mineralogical assemblage and display enrichments in Cr and Mo compared to the original basalt. Sulfur isotope analysis of microscopic sulfate inclusions preserved in Fe³⁺-montmorillonite and calcite yielded δ³⁴S, Δ³³S and Δ³⁶S values that are different from the field of mass independent (MIF) Archean sulfates. Δ³³S values overlap the field of post-Archean, mass dependent (MDF) terrestrial materials. In a Δ³³S-Δ³⁶S diagram, sulfates plot away from the MIF slope ~-1 defined by Archean samples and overlap the MDF slope of ~-7 defined by post-2.32-Ga old sulfides. The large range of δ³⁴S (up to 20‰) between different samples indicates that S-isotope heterogeneities are preserved on a small scale. Such heterogeneities are best explained by repeated cycles of microbial sulfate reduction producing sulfides followed by the re-oxidation of sulfides into sulfates during oxidative weathering and/or microbial oxidation of microbially-derived ³⁴S-depleted sulfides. These results suggest that the concentrations of free oxygen in the Late Archean climate system has increased, at least transiently, to levels similar to the GOE.