Origin of dissolved metals in produced water from the Devonian Marcellus shale, USA: Sr isotope systematics

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The horizontal drilling and hydrofracturing techniques used for extraction of natural gas from shales of the Marcellus Formation (USA) lead to production of significant volumes of high-TDS (total dissolved solids) waters that have interacted with the source shale and potentially adjacent units. Determining the source of these dissolved salts and understanding local and basinal variations in TDS have direct relevance to exploration methodologies and water management and reclamation.

A series of flowback waters have been collected from drilling operations in a geographic region spanning ~375 km, from northeastern to southwestern Pennsylvania. Most $^{87}Sr/^{86}Sr$ values fall within a narrow range, from 0.7101 to 0.7112; samples from two adjacent wells in Westmoreland County, Pennsylvania, define a second grouping (0.7120-0.7121). This bimodal distribution of flowback values could be a result of hydrofracturing water interacting with different producing members of the Marcellus Formation, or lateral (facies) variations in the isotopic composition of formation salts. The relatively tight clustering of values among geographically distant sites argues against variable influxes of brines from adjacent formations. Marcellus flowback waters contain notably elevated levels of barium and strontium (up to 12, 000 and 5, 000 mg/L, respectively, for the samples in this study). The Ba/Sr ratios of the flowback fluids measured here also vary systematically with geographic location, The combination of Ba/Sr and $^{87}Sr/^{86}Sr$ provide a method for uniquely identifying regional variations in flowback waters.

The $^{87}Sr/^{86}Sr$ ratios of Marcellus waters measured here fall well above Phanerozoic seawater values. Thus, while the Marcellus brines may have a significant seawater component, this has clearly been augmented by a high-$^{87}Sr/^{86}Sr$ source, possibly originating from dissolution of radiogenic minerals within the shale. Ongoing leaching studies of core material from the Marcellus Formation and adjacent units will provide additional insight into the origins of salts in Marcellus waters.

Evolution of andesite magma systems; Egmont Volcano, New Zealand

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A major issue in andesite magmas genesis is explaining disequilibrium crystal, matrix glass and whole rock compositions. Taranaki/Egmont is a high-K andesite volcano in the western North, Island, New Zealand, with a 200, 000 year eruption record. Thirteen recently identified and dated pre-7 ka debris avalanche deposits record the magmatic evolution of the Taranaki volcanic system. Clast compositions show a gradual enrichment in K_2O and LILE with time to high-K andesites in the Holocene. Pre-100 ka magmas include relatively primitive basalts and basaltic andesites and mineral chemistry indicates crystallisation within the lower crust or mantle. Modal rock compositions become more silicic in younger units, and the appearance of late-stage low-pressure mineral phases (high-Ti hornblende, biotite and Fe-rich orthopyroxene), suggests an increase in more evolved magmas with time. Six compositionally distinct Holocene magma batches erupted on 1500-2000 year timescales, synchronous with variations in eruptive frequency in which the largest volume (>0.5 km^3) events erupt the most evolved magmas. We suggest that andesite magmas were generated within a lower crustal 'hot zone' [1]. Matrix glasses in both xenoliths and lavas/tephras are mostly dacitic to rhyolitic in composition and, in younger lavas have a high K_2O content. These glasses may represent some of the partial melts from the 'hot zone'[2]. The disequilibrium observed in the andesites is due to the mixing of these diverse components. A complex and dispersed magma assembly and storage system developed in the upper crust where the magmas were further modified by fractional crystallisation and magma mixing and mingling [2].

[1] Annen *et al*. (2006) *J Petrol* **47**, 505–539. [2] Turner *et al*. (2011) *Geological Society of America Bulletin* (accepted for publication).