Shale gas and its environmental footprint

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The Marcellus shale is one of the largest natural gas reservoirs in the United States and, like other shale gas reserves, has been developed through advances in drilling technologies and production strategies. Concerns over potential environmental impacts have accompanied natural gas extraction around the country. We have sampled shallow groundwater systems of >200 homeowners in NE Pennsylvania and New York for brines, dissolved gases, and other attributes of water quality for the last two years. In particular, we have exampled possible relationships between water quality and distance to natural gas wells.

In our first study publishd in May of 2011 [1], we found no evidence of increase salt concentrations or fracturing fluids with distance to gas wells, but dissolved methane concentrations were 17 times higher on average for water wells found within 1km of them. Higher chain hydrocarbons (ethane, propane, and butane) were detected more often in active areas (21, 8, and 3, respectively) compared to non-active areas (3, 0, and 0, respectively), indicating a more thermogenic methane character. The carbon isotope values of methane (□^{13}C-CH4), in active extraction areas were on average less negative (-37±7 ‰) than non-active extraction areas (-54±11‰). We conclude from these, and newer follow-up results, that there are important differences in methane concentration, natural gas composition, and □^{13}C-CH_4 values in some shallow groundwater wells near natural gas extraction areas. Furthermore, the dissolved gas geochemistry nearer gas wells appears to be consistent with a more thermally mature source of organic matter. New results from additional sampling in 2011 will be presented.

[1] Osborn, Vengosh, Warner, Jackson (2011) *Proceedings of the National Academy of Sciences, U.S.A,* **108**, 8172-8176.

Mapping element concentrations and Ce^{4+}/Ce^{3+} ratios in zircon by LA-ICP-MS

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A LA-ICP-MS procedure has been developed for simultaneously generating element, element ratio and isotope ratio maps of individual zircon grains. The instrumentation used was a Photon Machines Analyte.193 laser ablation system and Agilent 7700 quadrupole ICP-MS with addition of a second rotary interface pump that doubles instrument sensitivity. The procedure involves performing lines of individual spot ablations, resulting in true spot size-limited spatial resolution. Each spot ablation is preceded by several laser cleaning pulses and a short period of flushing to remove surface contamination (from condensation and other sources). For each element, signals for each individual spot are integrated into single readings, then calibrated using an external standard (NIST 612) and an internal standard (SiO_2) for element concentration measurements, and against a zircon (GJ-1) for Pb-U isotope ratio measurement. The concentration or ratio data are then presented as colour pixel maps by assigning colours according to concentration (or ratio) using a choice of different colour assignment schemes (linear, logarithmic, percentile)

Zircon ($ZrSiO_4$) is an abundant accessory mineral in granitoid igneous intrusive rocks that are associated with porphyry and other magmatic-hydrothermal mineral deposits. Using spot sizes as small as 7 microns in diameter, Ce and the REE from Nd-Lu, Pb, Hf, Th and U can be detected routinely in zircons. Measurement of this suite of REE allows, by extrapolation, calculation of Ce^{4+}/Ce^{3+} ratios, which are a proxy for oxidation state of the source magma which has been linked to its fertility for generation of porphyry-style Cu (±Au±Mo) mineralization [1]. Distribution maps for key trace elements and Ce^{4+}/Ce^{3+} ratios in single zircons thus allow the geochemical evolution of the magmatic system, including oxidation state, to be visually documented.

The procedure is been applied to zircons from a suite of Jurassic and Cretaceous granitoid intrusions from the Canadian Cordillera, including samples from igneous host rocks to porphyry-style deposits, to determine whether systematic differences exist in the geochemical trends between mineralised and non-mineralised intrusions. Pb/U ratio and age maps for the zircons are also being generated, allowing identification of inherited cores and, potentially, multiple crystallisation ages for zircons that have had a protracted crystallisation history. Also being evaluated is whether zones with anomalous ages can be identified and whether these correlate with the chemistry of the REE, or other elements, as has been proposed [2].

[1] Ballard et al. (2002) *Contrib. Mineral. Petrol.* **144**, 347-364.
[2] Black et al. (2004) *Chem. Geol.* **205**, 115–140.