Methods for quantifying methane fluxes during shale hydraulic fracturing

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The U.S. Department of Energy currently predicts an increase of ~75% by 2035 of the total domestic production of natural gas from unconventional sources [1]. One of the unconventional methods used to an ever-increasing degree is shale gas extraction, using hydraulic fracturing and vertical drilling. However, this process is highly uncertain in terms of the magnitude of methane loss to the atmosphere during well production, storage, and transport. Methane has a significant global warming potential and a need exists to quantify the amount of fugitive gas loss during the lifetime of well operation.

We outline the current measurement techniques that could be employed to assess methane fluxes associated with hydraulic fracturing. These techniques include ground-based eddy covariance (EC) flux systems (e.g., the LI-COR 7700 open-path methane gas analyzer). EC is a continuous, fast in situ measurement technique, providing net flux of an atmospheric component at thirty-minute resolution. It can be used from a variety of platforms including tall towers and tethered balloons offering variable flux footprints depending upon implementation. Other methods include airborne platforms using small to medium size aircraft providing very large footprint and robust flux measurements. Advantages and drawbacks exist for each method depending upon the scale of measurement. Identification of methane sources is usually not possible from most flux measurements unless isotopic measurements are made in parallel. Advances in cavity ring-down spectroscopy have made isotopic measurements fast and reliable and reasonably deployable on multiple platforms including aircraft. Here we present recommendations for future measurement and assessment of fugitive methane associated with hydraulic fracturing of shale.

[1] Annual Energy Outlook 2011 Early Release Overview. DOE/EIA-0383ER(2011). Energy Information Agency, U.S. Department of Energy.

Non-traditional isotope variations at Cedar Butte volcano; insight into magmatic differentiation

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Cedar Butte (ID, USA) is a silicic volcano in the mainly basaltic Eastern Snake River Plain that produced a compositionally zoned rhyolite to basaltic andesite eruption sequence at ~400 ka. This study aims to investigate the stable isotopic compositions of Ca and Fe for selected samples from the Cedar Butte magmatic suite. Previous work shows the suite follows expectations of fractional crystallization. Despite the limited isotopic fractionations expected from non-traditional stable isotope systems in high-temperature contexts, current mass-spectrometry methods allows us to resolve significant, albeit small, isotopic variations. These tools should help us to both track and better understand differentiation mechanisms related to rock petrogenesis.

Fe isotope ratios were measured using a Nu plasma HR MC-ICP-MS (Nu Instrument, Inc.) in dry plasma mode using the sample-standard bracketing method. Results are expressed as permil $\delta^{57}Fe$ values relative to the IRMM-14 isotopic reference material. Ca isotope ratios were measured using a double spike method on a TIMS (Finnigan Triton). Calcium data are expressed as $\delta^{44}Ca$ relative to SRM915a reference material. Long-term external reproducibilities are 0.1‰ and 0.07‰ (2SD) for $\delta^{57}Fe$ and $\delta^{44}Ca$, respectively.

Total $\delta^{57}Fe$ variations in this study range from 0.10‰ to 0.62‰, and correlate with SiO_2 content as observed previously [e.g., 1, 2, 3]. Samples from basaltic to andesitic compositions do not exhibit significant $\delta^{57}Fe$ variations (from 0.10‰ to 0.19‰), whereas samples from andesitic to rhyolitic compositions show a positive correlation leading to a 0.5‰ increase of $\delta^{57}Fe$ in the most differentiated materials. Ca isotopes do not display as clear a correlation as Fe, although the most differentiated samples also tend to enrich in heavy isotopes. Total $\delta^{44}Ca$ variations range from -1.41‰ to -0.86‰, with the exception of one Ca-rich rhyolite that displays an extremely negative – and reproducible – $\delta^{44}Ca$ = -2.5‰. This sample however did not yield a comparably shifted $\delta^{57}Fe$ value. These results thus underline the ability of multiple stable isotope data to identify multiple sources and selective processes affecting the overall differentiation process. Additional information may be provided by measurements of other stable isotopes systems such as Si and Mg.

We assess 4 possible processes for explaining the isotope-differentiation relationship: 1) fractional crystallization [2]; 2) thermal migration [4]; fluid/rock interactions [1, 3], and/or partial melting/assimilation of preexisting crustal materials.

[1] Poitrasson & Freydier (2005) *Chem. Geol.* **222**, 132-147. [2] Schuessler et al. (2008) *Chem. Geol.* **258**, 71-91 [3] Heimann et al. (2008) *Geochim. Cosmochim. Acta* **72**, 4379-4396 [4] Huang et al. (2009) *Geochim. Cosmochim. Acta* **73**, 729-749.