

Tracer applications to verify carbon mineralization in Icelandic basalts

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The risks associated with geologic carbon storage can be considerably reduced by subsurface carbon mineralization.

The CARBIFIX project in Iceland is a field scale pilot study where CO₂ and H₂S emissions from the Hellisheidi geothermal power plant are dissolved in groundwater and injected into a permeable basalt formation at ~500 m depth below surface [1]. We are using non-reactive (sodium fluorescein, amidhorhodamine G, SF₃CF₃, and SF₆) and reactive (¹⁴C and ¹³C) tracers in an on-going injection project to characterize subsurface CO₂ transport and in situ CO₂-water-rock reactions. In early 2012, 170 tons of pure CO₂ tagged with ¹⁴C and SF₆ were dissolved in water and injected into a confined basalt aquifer. Samples were collected from injection and monitoring wells in evacuated serum bottles with butyl stoppers and analyzed by AMS and mass spectrometry for carbon isotopes, by fluorometry for Na-fluorescein and by gas chromatography for SF₆ and SF₃CF₃. The multi-tracer approach allows us to separate various injection experiments and differentiate between dilution and reaction. While the bulk of the injected CO₂ has not yet arrived at the monitoring wells, a fraction following a fast flowpath appeared within less than a month. δ¹³C shows an initial rise attributed to dissolution of aquifer carbonates and then a drop due to carbonate precipitation. The ¹⁴C/SF₆ ratio is lower than the injection ratio providing additional evidence for carbonate precipitation. The bulk of the injected CO₂ is expected to arrive by the summer of 2013 and we will extend the time series accordingly. Our study demonstrates the value of tracers as a monitoring, verification and accounting tool in reactive geological carbon storage systems.

[1] Gislason *et al.* (2010), *Int. J. Greenh. Gas Con.* 4, 537–545.

Robust Calibration Systems Based on Syringe Pumps for Water Vapor Isotopologue Measurements

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Advances in spectroscopic instrumentation mean that laser-based absorption spectroscopy (both direct and cavity enhanced) is increasingly used for isotopic measurements in environmental sciences. For studies involving water, this technique offers the advantages of speed and non-destructive sampling, allowing for new applications in water vapor measurements [e.g. 1] and for the support or replacement of mass spectroscopy in studies of ice cores [e.g. 2]. In both uses, instrument accuracy is tied to instrument calibration and therefore dependent on the availability of suitable calibration systems. We describe here a new calibration technique based on syringe pumps for producing air streams of known and constant water content and isotopic composition. Syringe pumps offer advantages over previous methods such as capillary flash-evaporation, water vapor "bubbling", or microdrop generation [e.g. 2,1,3], including greater control and reliability. We show the stability and time response of two calibration systems, built at the University of Chicago and the J. Fourier University of Grenoble and designed for high and low flow rates (0.1 -10 slm) and a water vapor dynamic range of 3-10,000 ppm. We discuss the optimization of parameters such as pressure, injection rate step shape, temperature and hydrophobic coatings. The designs are robust and readily modified for instrument-specific configurations, suggesting they may find wide use in the community.

[1] Sayres, D. S., *et al. Rev Sci Inst.* **80**, 2009. [2] Gkinis, V., *et al. Atm Meas Tech.* **4**, 2011. [3] Iannone, R. Q., *et al. J. Atmos. Ocean. Tech.* **26**, 2009.