

Modelling gas-fluid-mineral interactions in a CO₂ injection analogue site with noble gases

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We carried out an artificial noble gas tracer injection experiment in a CO₂ EOR project in a depleted oil field in the USA. In this experiment, 2 STP litres of ³He and 2 STP litres of ¹²⁹Xe were injected together with the EOR CO₂ stream. Samples were collected both from the CO₂ injector and 4 monitoring wells before, during and after injection.

Natural background of ³He/⁴He and ¹²⁹Xe/¹³²Xe ratios in fluid sampled from this field are 0.07Ra and 0.98 respectively. Measured spiked CO₂ stream has ³He/⁴He and ¹²⁹Xe/¹³²Xe ratios of 49.0Ra and 23.94 respectively. Tracers were detected in monitoring wells both updip and downdip of the injector in a short period after the tracer injection. This is completely different from a simple PHREEQC model prediction that is based on one-dimensional tracer dispersion in a dual porosity column. It reflects the complexity of the reservoir system. Although tracers are present in monitoring wells, the peak tracer ratios are at a level that is orders of magnitude lower than the injected ratios. Simple mass balance calculation assuming phase equilibrium between gas and groundwater shows that water volume involved in this system is 3-4 orders of magnitude higher than the gas volume. This is not reasonable and groundwater alone cannot account for observed tracer concentrations and ratios. Other processes that could affect tracers present in monitoring wells include multi-phase interaction, dissolution into oil, diffusion and adsorption into immobile reservoir porosity, etc. In this presentation, we discuss models that take into account these processes in this complex reservoir system to explain observed data. This work demonstrates huge potential of exploiting artificial noble gases in crustal fluid studies.

Silicon isotopes as a new tool to identify the main cause of the field-lab apparent discrepancy of feldspar dissolution rates

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In 2004, Zhu, Blum, and Veblen proposed a new hypothesis for explaining the apparent discrepancy between lab-measured and field-estimated feldspar dissolution rates [1]. They identified the coupling of dissolution and precipitation reactions as the main contributor to the apparent discrepancy. In the intervening nine years, we have tested this hypothesis by conducting a series of batch experiments at elevated temperatures [2-5] and numerical simulations of coupled dissolution and precipitation reactions [4, 6]. The results show that taking into account of reaction coupling is able to reduce the gap between the field and lab rates by about two orders of magnitude at elevated temperatures of 200-300 °C [4]. A chapter in volume 70 of *Review in Mineralogy and Geochemistry* [7] has summarized the historical development of the topic and its role in the overall picture of water-rock interaction.

A field study of Si isotopes of groundwater, feldspars, and secondary clays demonstrated the promise of Si isotopes as a new tool to unravel the coupled reactions [8]. We are now employing the new tool for laboratory experiments. A methodology paper on using Si isotopes was just published [9]. This presentation will discuss results of new experimental data, as well as the potentials and pitfalls of this new tool.

[1] Zhu *et al.*, in *Water-Rock Interaction*, R.B. Wanty and R.R.I. Seal (Ed) 2004, A.A. Balkema: Saratoga Springs, New York. 895-899.[2] Fu *et al.*, *Chemical Geology.*, 2009. **91**(3): 955-964. [3] Zhu and Lu, *GCA*, 2009. **73**(11): 3171-3200. [4] Zhu *et al.*, *GCA*, 2010. **74**(14): 3963-3983. [5] Lu *et al.*, *Applied Geochemistry*, 2013. **30**: 75-90 [6] Ganor *et al.*, *Environmental Geology*, 2007. **53**(3): 599-610. [7] Zhu, in *Thermodynamics and kinetics of water-rock interaction*, E.H. Oelkers and J. Schott, Editors. 2009, Mineralogical Society of America. 533-569. [8] Georg *et al*, *GCA*, 2009. **73**(8): 2229-2241.[9] Gruber *et al.*, *GCA*, 2013. **104**: 261-280.