

The geological storage of CO₂: Quantification of natural gas/ groundwater interaction

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The storage of anthropogenic CO₂ in geological reservoirs remains one of society's preferred options for reducing the global emission of greenhouse gases. While there are several types of environment under investigation, including depleted oil and gas reservoirs, adsorption onto uneconomical coalbed surfaces and deep saline aquifers, it is the latter that has the potential to cope with the mass of CO₂ to be injected into the ground. Whatever the geological target, the security of the injected CO₂ must be assured both for efficacy and public confidence. Because CO₂ is both a reactive gas and highly soluble in groundwater understanding the fate of the injected CO₂ is not simple as this may be secured in the form of precipitated carbonate or remain mobile as either a free gas phase or dissolved in the groundwater.

Nature has provided natural analogues. Volcanic CO₂ has been injected into a variety of reservoirs, differing both in their structure and reservoir lithology. We review the most recent advances we have made from case studies across the USA, Europe and China. We show how using a combination of noble gases and stable isotopes that we can constrain the hydrological environment into which these magmatic gases have been injected. We show that CO₂ removal from the gas phase is directly related to the degree of water in contact in all case studies. We show that in many of these natural analogues we can resolve and quantify the competing carbon sinks of dissolution in the groundwater from precipitation as a carbonate phase and conclude that carbonate precipitation is only a minor carbon sink in all analogue studies to date and probably not occurring at all in carbonate lithologies.

Enrichment of the PGE in magmatic sulfide melt

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Despite decades of research, enrichment of magmatic sulfides in the platinum-group elements (PGE) is understood only in broad terms. The single most important parameter is the sulfide/silicate partition coefficient D , a concentration ratio of PGE in sulfide relative to PGE in silicate and a measure of the chemical affinity of an element toward sulfide. Another parameter is the R factor [1], a measure of the mass ratio of silicate to sulfide melt. Its invention is based on the reasoning that high D s can only be effective if an immiscible sulfide melt droplet comes into physical contact, and equilibrates with, maximum volumes of silicate melt, to collect chalcophile elements including the PGE. Typical fluid-dynamic situations allowing high R factors to be achieved are situations of magma mixing in layered intrusions or melt conduits when exsolved sulfide droplets are carried around in suspension in vigorously convecting silicate melts [2].

It is not unusual though that magmatic sulfides may have high PGE contents without the obvious involvement of an R factor. Peach *et al.* [3] analyzed Ir, Pt, and Pd in sulfide droplets in rapidly quenched MORB and found enrichments in Pd that do not fall short of the Pd enrichment in Merensky sulfides of the Bushveld complex. Presumably, during MORB emplacement fluid-dynamic situations are not favorable for high R factors to be reached. We show that the PGE content of a sulfide melt is controlled by the mechanism by which PGE are dissolved in silicate melt. We are determining the solubility of Pd in S-bearing, S-undersaturated basaltic silicate melt at controlled f_{O_2} and f_{S_2} to quantify the proportion of Pdⁿ⁺ dissolved as PdS_{n/2} compounds. Early results indicate that in absolute terms, the influence of S²⁻ on bulk Pd solubility in silicate melt is modest because in basalts close to sulfide saturation O²⁻ ligands are about 200 times more abundant than S²⁻ ligands. In relative terms, however, and for the PGE tenor of a sulfide melt, the PGE proportion associated with S²⁻ is a critical factor. For example, the Pd contents in the MORB sulfides [3] afford that prior to sulfide unmixing, about half of the Pdⁿ⁺ cations dissolved in silicate must have been associated with S²⁻. Hence, when sulfide saturation is reached, the PGE fraction dissolved in the silicate melt structure as MS_{n/2}, as well as all PGE associated with anions of other chalcogenes and non-metals with preference to PGE (i.e. As, Sb, Te, and Bi), will be sequestered to the sulfide in preference to MO_{n/2} compounds. PGE enrichment in a magmatic sulfide melt, in the R factor model visualized as a combination of high D with high R , may in reality be a measure of the degree of association of PGE with S²⁻ and other chalcogenes in the sulfide-undersaturated silicate melt.

- [1] Campbell & Barnes (1984) *Canad. Miner.* **22**, 151-160.
[2] Cambell *et al.* (1983) *J. Petrol.* **24**, 133-165. [3] Peach *et al.* (1990) *Geochim. Cosmochim. Acta* **54**, 3379-3389.