Solubility and mineral storage of CO_2 in basalt

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The long-term security of geologic carbon storage is critical to its success and public acceptance. Much of the security risk associated with geologic carbon storage stems from its buoyancy. Gaseous and supercritical CO_2 are less dense than formation waters providing a driving force for it to escape back to the surface via fractures, or abandoned wells. This buoyancy can be eradicated by the dissolution of CO_2 into water prior to, or during its injection into the subsurface. The dissolution will further enhance mineral storage of CO_2 especially if injected into silicate rocks rich in divalent metal cations such as basalts and ultra-mafic rocks.

We have demonstrated the dissolution of CO_2 into water during its injection into a rock formation leading to its geologic solubility storage in less than 5 minutes. This process was verified via the successful injection of over 170 tons of dissolved CO_2 into porous basaltic rocks located 400-800 m below the surface at the CarbFix [1,2,3] field injection site in SW Iceland. Rock dissolution, dilution, and dispersion, caused the pH and alkalinity of the injected water to increase. Concomitantly, the concentration of most dissolved elements increased and carbonate minerals became saturated. Conservative tracers and ^{14}C labelled CO_2 were mixed into the injected gas and water stream to monitor the subsurface transport and to assess the degree of subsurface carbonation.

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Dating mantle metasomatism: A new tool (U/Pb LIMA titanate) and an impostor ($^{40}Ar/^{39}Ar$ phlogopite)

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Precise dating of fluid processes in the Earth's mantle remains a major challenge for geoscientists. The U/Pb and Ar/Ar dating techniques have both been used in an attempt to constrain the timing of mantle metasomatic events; however, the Ar/Ar results have proven contentious [1]. Here we compare the $^{40}Ar/^{39}Ar$ ages obtained for large phlogopite grains from 7 mantle xenoliths from the 84 Ma Bultfontein kimberlite (Kimberley, South Africa), with U/Pb ages from metasomatic zircon and LIMA minerals coeval with phlogopite.

LIMAs are unusual titanates that occur in phlogopite-rich metasomatised peridotites [2]. LIMA minerals are enriched in incompatible elements (e.g., LILE, LREE, HFSE), with high U (250-400 ppm) and Pb (200-700 ppm) contents. U/Pb geochronology on LIMA minerals is limited by the low U/Pb ratios and high common Pb. In this study, the U, Th and Pb isotopes of LIMA minerals from three mantle xenoliths were measured by *in-situ* LA-ICP-MS. Common Pb values were determined from isotope dilution MC-ICP-MS measurements of coeval clinopyroxene grains. LIMA U/Pb ages are ~ 170-180 Ma, in agreement with a U/Pb age of 184±2 Ma obtained for a single zircon from one of the LIMA-bearing xenoliths. These results suggest a link between mantle metasomatism and Karoo magmatism in southern Africa [3].

Ar/Ar step-heating analyses of phlogopite grains were conducted using a new generation ARGUSVI multi-collector mass spectrometer. All the phlogopite samples yielded much older $^{40}Ar/^{39}Ar$ ages (up to 780 Ma) than coexisting zircon and/or LIMA minerals. We attribute these anomalously old Ar/Ar ages to the presence of excess ^{40}Ar in the metasomatic fluid that crystallised phlogopite [4]. We conclude that the $^{40}Ar/^{39}Ar$ phlogopite technique cannot be used to date mantle metasomatism.

[1] Phillips (2012) *Precambr Res* **208**, 49-52. [2] Haggerty (1983) *GCA* **47**, 1833-54. [3] Konzett *et al.* (1998) *EPSL* **160**, 133-145. [4] Phillips & Onstott (1988) *Geology* **16**, 542-546.

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