

U-Th-Pb-He double-dating of zircon from the diamondiferous Ellendale lamproite pipe, Western Australia

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Zircon, like diamond, is a highly refractory mineral, resistant to physical and chemical weathering – and therefore, if zircon can be geochemically linked to the process of kimberlite/lamproite eruption, then it could be used as a new diamond indicator mineral [1]. In theory, ancient crustal xenocrysts should yield U-Th-He ages that are reset to eruption age if their residence time in the magma was prolonged. To test this hypothesis we applied SHRIMP U-Th-Pb and ALPHACHRON U-Th-He double-dating methods [2] to zircon grains from the Miocene Ellendale lamproite pipe and from the surrounding country rock.

The U-Th-Pb-He double-dating results indicate that all of the lamproitic zircon analysed is of xenocrystic origin. SHRIMP ²⁰⁷Pb/²⁰⁶Pb ages of the zircon grains ranges from Carboniferous to Archaean in both populations (440-2522 Ma for lamproitic zircon and 350-3248 Ma for country rock zircon). For the helium system, zircon from high temperature lamproite volcanic facies (volcanic dike and olivine-phlogopite tuff) have a unimodal U-Th-He age population of 18.9 ± 0.1 Ma (n=60) and are distinct from the older U-Th-He ages (250-650 Ma) for country rock zircon.

These data indicate that the lamproite magma entrained crustal zircon xenocrysts en route from the mantle to the surface. During transit the temperatures were high enough for the helium to completely diffuse out of the zircon crystal such that helium only began accumulating following diatreme emplacement and cooling ~19 Myr ago. Zircon within the diamondiferous lamproite tuffs and dyke has a unique U-Th-Pb-He signature, such that erosion of these units should produce a distinctive suite of detrital zircons with Miocene (U-Th)/He ages. These results indicate that helium dating of detrital zircon has application in diamond exploration.

[1] McInnes *et al.* (2009) *Lithos* **112S**, 592–599. [2] McInnes *et al.* (2008) *GCA* **72**(12), A614.

C and H isotope systematics of microbial methane accumulations in coalbeds and fractured shales

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Microbial methane is generated via multiple metabolic pathways in surface to deep subsurface organic-rich environments, including acetate fermentation and CO₂ reduction. It is important to distinguish between these two pathways if microbial methanogenesis is to be stimulated *in situ* for new energy resources and/or these geologic reservoirs are targeted for CO₂ sequestration.

Carbon and hydrogen isotopes of co-produced CH₄, CO₂, and formation waters have long been employed to distinguish between acetate fermentation and CO₂ reduction [1, 2]. We provide evidence that these isotopic signatures may not be as straight forward as previously thought; instead they may reflect other hydrobiogeochemical processes, besides metabolic pathways. For example, natural gas and formation waters from the Antrim Shale (Michigan Basin) have C and H isotope values indicative of CO₂ reduction [3], yet recent microbial studies show the presence of both acetate and CO₂ utilizing methanogens [4].

We revisit the controls on C and H isotope systematics of microbial gas accumulations in fractured shales and coalbeds world-wide using published datasets of natural gas and associated formation waters. Initial results show that $\delta^{13}\text{C}$ values of CO₂ and CH₄ are significantly modified by the extent of methanogenesis (i. e. early versus late stage) under open versus closed system conditions. In addition, $\delta^{13}\text{C}$ values of CH₄ and CO₂ may be altered by sulfate reduction coupled to methane oxidation. Hydrogen isotope values of CH₄ may be more reflective of formation water δD values, rather than metabolic pathways. More studies are needed to directly link metabolic pathway to isotopes within deep subsurface methanogenic environments.

[1] Schoell (1980) *Geochim. Cosmochim. Acta* **44**, 649–661. [2] Whiticar *et al.* (1986) *Geochim. Cosmochim. Acta* **50**, 693–709. [3] Martini *et al.* (1998) *Geochim. Cosmochim. Acta* **62**, 1699–1720. [4] Waldron *et al.* (2007) *Appl. Environ. Micro.* **73**, 4171–4179.