

Accelerated carbon sequestration in mine tailings using elevated $p\text{CO}_2$

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Mineralization of atmospheric CO_2 within hydrated Mg-carbonate minerals occurs passively in ultramafic mine tailings via weathering of Mg-silicates [1]. If this process were accelerated, large mines may have the capacity to sequester millions of tonnes of CO_2 annually, providing the potential to offset the greenhouse gas emissions of mining. Recent evidence from laboratory experiments and reactive transport modelling indicates uptake of atmospheric CO_2 into solution is rate limiting [2]. An increase in CO_2 partial pressure may accelerate carbon sequestration by increasing dissolved inorganic carbon (DIC) and enhancing primary mineral dissolution due to increased acidity.

The effect of elevated $p\text{CO}_2$ on carbonation rate was examined experimentally to mimic process water chemistry and temperature conditions in tailings at the Mount Keith Nickel Mine (MKM), Western Australia. N_2 and CO_2 mixtures, ranging from 10% to 100% CO_2 , were sparged into 3.0 L alkaline slurries containing 5% brucite [$\text{Mg}(\text{OH})_2$]. Subsequent experiments will examine carbonation of serpentine, which is more abundant in MKM tailings but dissolves more slowly in aqueous solutions. System mass, pH, temperature and gas composition were monitored throughout the experiment. Samples were analyzed for DIC, Mg concentration, mineralogy and carbon content of solids. Nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] completely replaced brucite within 10 hours with 100% CO_2 gas and within 100 hours with 10% CO_2 gas. This corresponds to an increase in brucite carbonation rate from ~ 0.007 to ~ 0.07 g CO_2 /g brucite/hour. PHREEQC geochemical modelling using experimentally derived mineral dissolution rates indicates that serpentine dissolution would exhibit a similar acceleration at elevated $p\text{CO}_2$ conditions. Modelling of experimental conditions indicates that equilibrium between the gas and aqueous phases is not attained during sparging of CO_2 -rich gas. Thus there is potential to further accelerate carbonation.

Brucite dissolution provided sufficient buffering capacity for carbonate mineral formation despite a significant pH shift to near neutral conditions in response to CO_2 injection. The carbonation process therefore not only sequesters CO_2 , but also neutralizes process water alkalinity. At the mine scale, complete carbonation of brucite at MKM would sequester a total of 1.2 to 3 Mt CO_2 .

[1] Wilson *et al.* (2009), *Econ. Geol.* **104**: 95-112. [2] Wilson *et al.* (2010), *Environ. Sci. Technol.* **44**: 9522-9529.

Jack Hills zircon Lu-Hf revisited

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Our in situ Lu-Hf analyses of Hadean zircons [1,2] revealed surprising results, including the presence of unradiogenic $^{176}\text{Hf}/^{177}\text{Hf}$ close to solar system initial (Hf_0) and those with highly positive $\epsilon_{\text{Hf}(T)}$ suggestive of their origin from a long-term depleted source. The latter population, however, was not observed in our follow-up study (or even later efforts by others). As these results have profound implications for the early history of BSE, we have revisited these issues with new in situ Lu-Hf analyses of Hadean zircons from Jack Hills (JH), Western Australia. These analyses were undertaken on an expanded suite of rocks from the region, including a paragneiss adjacent the 'Blob' granite. In situ Lu-Hf analyses using a NEPTUNE LA-ICPMS-MC confirm the presence of large negative $\epsilon_{\text{Hf}(T)}$ deviations and re-open the possibility of significant positive deviations. Specifically, we re-analyzed zircon ANU125 11.3, earlier found to be within error of Hf_0 , at multiple locations and replicated the earlier datum within uncertainty. Using currently adopted CHUR parameters, these data collectively require the source of this zircon to have separated from BSE by 4.45 Ga at the latest (assuming Lu/Hf=0) and more likely by 4.5 Ga ($^{176}\text{Lu}/^{176}\text{Hf}=0.015$). The paragneiss zircons displays uniform $^{176}\text{Hf}/^{177}\text{Hf}$ but Hadean grains contain younger domains such that matching of age to Lu-Hf systematics is less certain. If the Hadean ages and measured $^{176}\text{Hf}/^{177}\text{Hf}$ reflect closed system behaviour, then $\epsilon_{\text{Hf}(T)}$ deviations up to +18 are possible. Alternatively, these data could be evidence for the homogenisation of zircon $^{176}\text{Hf}/^{177}\text{Hf}$ within the source rock. Focussed Lu-Hf studies of 3.9-3.5 Ga JH zircons show a general diminution of $\epsilon_{\text{Hf}(T)}$ deviations by ~ 4 Ga, suggestive of vigorous continental crust-mantle re-cycling, although evidence of highly negative $\epsilon_{\text{Hf}(T)}$ continues to 3.6 Ga. We thus infer that a geochemical reservoir resembling the modern continental crust formed by ca. 4.5 Ga, perhaps leaving a depleted signature in a sufficiently large portion of the upper mantle to be later sampled by other JH zircons. Numerous geochemical investigations of Hadean zircons reveal their origin in a continental crust-like environment. Thermo-barometric results for Jack Hills zircons and their inclusions imply low conductive heat flows suggestive of their formation under a suppressed heat flow condition. Thus the single most compelling model for their formation is also the simplest: re-working of an initially tonalitic flotation crust by a process similar to that operating at modern convergent margins.

[1, 2] Harrison *et al.*, 2005, 2008,