



Investigating the influence of mineral dissolution and precipitation on oxygen isotope ratio ($\delta^{18}\text{O}$) of CO_2 -rich groundwater in Daylesford, South East Australia

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Abstract

The ability to identify water interaction with CO_2 is critical for CCS (Carbon Capture and Storage) site monitoring. The isotopic composition of the injected CO_2 provides a tracer for gas migration in the subsurface and interaction with water. The occurrence of CO_2 -rich springs in Daylesford, southeast Australia, presents an opportunity to study the potential effects of CO_2 on groundwater, as an analogue to an unlikely event of CO_2 migration out of a storage reservoir.

The water- CO_2 oxygen equilibration relationship can be used as a monitoring tool for CO_2 migration. It has been successfully used in CO_2 -EOR (enhanced oil recovery) (Johnson et al., 2011) and pilot CO_2 storage sites (Kharaka et al. 2006; Gilfillan et al., 2016) to monitor the movement of injected CO_2 plume; and confirmed in laboratory experiments (Johnson & Mayer 2011, Becker et al., 2015). Similarly, changes in the oxygen isotope ratio ($\delta^{18}\text{O}$) in natural shallow aquifers where CO_2 is migrating to groundwater from depth has been observed, for example in CO_2 springs in Italy (Cinti et al. 2011), Spain (Cerón et al., 1998), Portugal (Marques et al., 2000) France (Pauwels et al., 2007) and South Africa (Harris et al., 1997). Here we investigate how CO_2 influences the oxygen isotope ratio ($\delta^{18}\text{O}$) of groundwater in Daylesford.

Mineral springs in Daylesford have high Ca^{2+} , Mg^{2+} , Na^+ and bicarbonate contents. Numerous faults dissecting the area likely facilitate the upwelling of deep seated CO_2 -rich fluids that mix with the shallow water. Spring water is distinctively depleted in ^{18}O , in contrast with the local precipitation water (Figure 1).

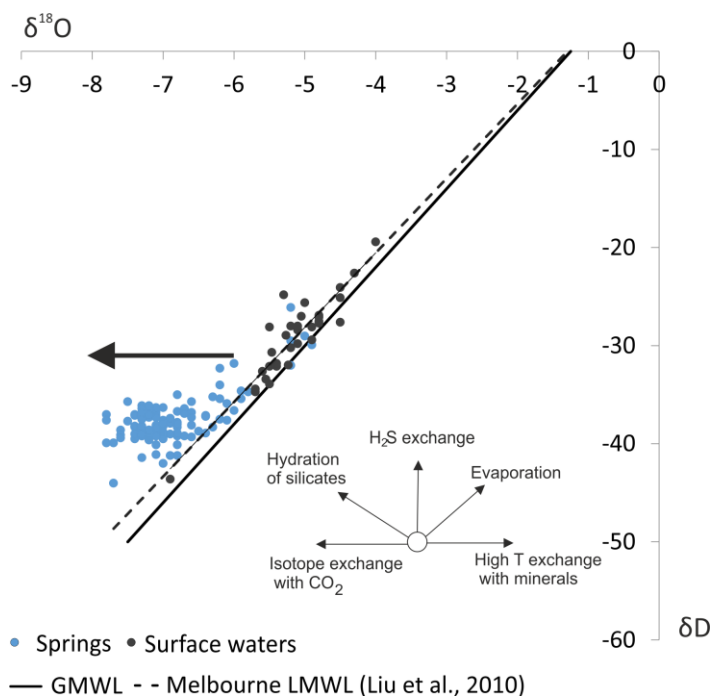


Figure 1. Oxygen versus hydrogen isotope ratio in spring and surface waters from Daylesford mineral springs (Modified? from Cartwright et al., 2002). Mineral springs are ^{18}O depleted relative to the LMWL and GMWL (local and global meteoric water line, respectively).

CO_2 presence in the system can lead to ^{18}O depletion in water by either:

- i) Promoting low-temperature primary mineral dissolution and secondary mineral precipitation reactions preferentially consuming ^{18}O .
- ii) CO_2 -water equilibrium oxygen isotope exchange.

Under equilibrium conditions, secondary minerals such as kaolinite preferentially incorporate more ^{18}O during precipitation and hence leave the remaining water ^{18}O -depleted, if reaction rates are sufficient (Kloppmann et al. 2002). Mineral dissolution and precipitation reactions were simulated using geochemical modelling software PHREEQC (Parkhurst & Appelo 1999) and the geochemical dataset from the mineral springs published in Cartwright et al. (2002) to test if dissolution of anorthite, albite and forsterite and precipitation of clay minerals could explain the observed water ^{18}O depletion.

Geochemical reaction simulations demonstrate that the fraction of oxygen involved in silicate dissolution and clay precipitation represents only up to 0.01% of total oxygen in the system. The model eliminates the possibility of mineral reaction influencing the water $\delta^{18}\text{O}$. This provides evidence that oxygen isotope equilibrium exchange governs water $\delta^{18}\text{O}$. Consequently, our study confirms similar findings of an observed water- CO_2 oxygen equilibration relationship in CO_2 -EOR and CO_2 storage sites, in laboratory experiments and in other natural CO_2 springs all around the world, and therefore demonstrates the feasibility of using oxygen isotopes to trace CO_2 migration in the shallow subsurface. Currently, further work is being pursued to investigate this relationship. Samples of water and CO_2 have been collected for oxygen isotope analysis to test if the two phases are in equilibrium.

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