

## Kinetics of CO<sub>2(g)</sub>-H<sub>2</sub>O<sub>(l)</sub> isotopic exchange, including <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O

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The analysis of mass 47 isotopologues of CO<sub>2</sub> (mainly <sup>13</sup>C<sup>18</sup>O<sup>16</sup>O) is established as a constraint on sources and sinks of environmental CO<sub>2</sub>, complementary to δ<sup>13</sup>C and δ<sup>18</sup>O constraints, and forms the basis of the carbonate 'clumped isotope' thermometer. This measurement is commonly reported using the Δ<sub>47</sub> value — a measure of the enrichment of doubly substituted CO<sub>2</sub> relative to a stochastic isotopic distribution. Values of Δ<sub>47</sub> approach 0 (a random distribution) at high temperatures (≥ several hundred degrees C), and increase with decreasing temperature, to ~1 ‰ at 25 °C.

While the thermodynamic properties of doubly substituted isotopologues of CO<sub>2</sub> (and, similarly, carbonate species) are relatively well understood, there are few published constraints on their kinetics of isotopic exchange. This issue is relevant to understanding both natural processes (e.g., photosynthesis, respiration, air-sea or air-groundwater exchange, CO<sub>2</sub> degassing from aqueous solutions, and possibly gas-sorbate exchange on cold planetary surfaces like Mars), and laboratory handling of CO<sub>2</sub> samples for Δ<sub>47</sub> analysis (e.g., re-equilibration in the presence of liquid water, water ice or water adsorbed on glass or metal surfaces).

We present the results of an experimental study of the kinetics of isotopic exchange, including changes in Δ<sub>47</sub> value, of CO<sub>2</sub> exposed to liquid water between 5 and 37 °C. Aliquots of CO<sub>2</sub> gas were first heated to reach a random distribution of its isotopologues and then exposed at low pressure for controlled periods of time to large excesses of liquid water in sealed glass containers. Containers were held at 5, 25 and 37°C and durations of exchange ranging from 5 minutes to 7 days. To avoid the formation of a boundary layer that might slow exchange, the tubes were vigorously shaken during the period of exchange. At the end of each experiment, CO<sub>2</sub> gas was recovered from the head space of the reaction vessel, purified and analyzed for its Δ<sub>47</sub>, δ<sup>13</sup>C and δ<sup>18</sup>O by gas source isotope ratio mass spectrometry.

Equilibrium was reached for both δ<sup>18</sup>O and Δ<sub>47</sub> after durations of few tens of hours. δ<sup>18</sup>O values at equilibrium were consistent with known fractionation factors for the CO<sub>2</sub>-H<sub>2</sub>O system. The evolution of δ<sup>18</sup>O and Δ<sub>47</sub> with experiment duration was fitted with an exponential rate law, yielding rate constants equal to each other (within error), averaging 0.18 h<sup>-1</sup> at 5°C and 0.29 h<sup>-1</sup> at 25°C. We calculate an activation energy for this isotopic exchange reaction of 16kJ/mol. By comparison, Mills and Urey (1940) measured the rate of <sup>18</sup>O exchange between CO<sub>2</sub>(aq) and water to have a rate of 11 h<sup>-1</sup> at 25 °C and an activation energy of 71.7 kJ/mol. Our finding of a slower rate and lower activation energy is consistent with the rate limiting step of our experiment being the CO<sub>2(g)</sub>—CO<sub>2(aq)</sub> exchange. Our experiments also define the path through δ<sup>13</sup>C—δ<sup>18</sup>O—R<sup>47</sup> composition space (where R<sup>47</sup> is the ratio of mass 47 to 44 isotopologues) followed by CO<sub>2</sub> gas during exchange with water. The stochastic distribution is a curved surface in composition space, hence changes in composition of CO<sub>2</sub> during exchange with water may, in some circumstances, yield distinctive co-variations in Δ<sub>47</sub> and δ<sup>18</sup>O. This may be relevant for the study of vital effects and other natural processes in which CO<sub>2</sub> and DIC species depart from local isotopic equilibrium.

## Unravelling the paragenesis at one of Australia's highest-grade gold deposits

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Australia's currently producing highest-grade gold deposit, (ave. 19.7g/t Au), the Archean Wattle Dam deposit, is located in the Yilgarn Craton of Western Australia. Despite its obvious importance, very little is understood about its formation. In the current study we report on a paragenetic framework for the deposit, mineral zoning, conventional optical petrography, SEM and stable isotope data of carbon, oxygen and sulphur. These data record important characteristics of ore-forming fluids and aid with the development of accurate genetic and exploration models.

The Wattle Dam deposit is hosted within a 350m thick amphibolite grade ultramafic unit which is bounded by a 400m thick metasedimentary unit to the west [1]. The alteration envelope surrounding the main lode is gradational and extends up to 10m. The Wattle Dam deposit is atypical as it lacks quartz veining and a low gold-grade envelope surrounding the main mineralisation normally associated with other Archean gold deposits [1].

A paragenetic study of the ultramafic rocks reveals a peak metamorphism assemblage consisting of actinolite, hornblende and plagioclase followed by a patchy calcite overprint of the peak metamorphism assemblage and by retrograde metamorphism clinocllore. These assemblages were overprinted during the main alteration event which culminated with the creation of the Wattle Dam gold deposit. The main alteration event consists of the precipitation of early calcite ± pyrite veins followed by tschermakitic amphiboles, biotite, clinocllore (possibly enriched in Fe<sup>3+</sup>) and by late coarse-grained gold nuggets (quartz-free), pyrrhotite, pentlandite and breithauptite (NiSb) in veins. Dolomitisation of calcite veins and serpentinisation and talcification of the ultramafic rock were observed post-mineralisation.

Stable isotope values vary between -5.5 to -2.7‰ (VPDB) for δ<sup>13</sup>C<sub>cal2</sub>, +10.7 to +15.0‰ (VSMOW) for δ<sup>18</sup>O<sub>cal2</sub> and +3.85 to +5.23‰ (VCTD) for δ<sup>34</sup>S<sub>py</sub>, distal to the deposit while elevated δ<sup>13</sup>C<sub>cal2</sub> (-0.3‰) and δ<sup>18</sup>O<sub>cal2</sub> (+18.1‰) were observed proximal to the deposit within the main lode. These elevated values combined with the presence of pyrrhotite, the lack of clear alteration selvages around gold nuggets and the lack of quartz within the main lode are consistent with a reduced vapour-rich, relatively water-poor environment in which CO<sub>2(g)</sub> is partially reduced to CH<sub>4(g)</sub> during the main-stage of alteration.

[1] Hutchison (2010) *Gravity Gold Conference*, Bellarat 22-23 Sept.