

THE BEHAVIOR OF ISOTOPES DURING THE DISSOLUTION OF CARBONATES BY PHOSPHORIC ACID

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PROJECT OBJECTIVES

- To understand the behavior of the clumped isotope proxy (Δ_{47} values) during the dissolution of carbonates by phosphoric acid and consequently improve the understanding of the application of the clumped isotope proxy.

PROJECT RATIONALE

The stable C and O isotopic analysis of CO₂ released from carbonates has become a standard tool in the study of numerous geological and biological processes since the early 1950s. The experimental method involves the release of CO₂ through the dissolution of carbonate in ortho-phosphoric acid (McCrea, 1950) (equation 1).



This acid was chosen by McCrea, in preference to others such as nitric acid or sulfuric acid, for a variety of reasons, including its low vapor pressure and consistent isotopic exchange between the oxygen in the acid and the CO₂ produced in the reaction with carbonate. Despite these properties which have seen its use persist for over 50 years, phosphoric acid contains oxygen in its structure and the reaction itself produces three compounds, all with oxygen. As a consequence, there is significant oxygen isotopic fractionation associated with the reaction (Sharma and Clayton, 1965). This study will reexamine the oxygen and clumped isotopic exchange between CO₂ and phosphoric acid by means of a series of experiments in which stochastic and non-stochastic CO₂ will be equilibrated with phosphoric acid over periods of weeks as well as over times that are more representative of times used in carbonate reactions.

BACKGROUND

Phosphoric acid (H₃PO₄) is normally supplied at a nominal concentration of 88 %. In order to lower the vapor pressure, reduce the amount of H₂O in the acid, and thus make it suitable for reacting with carbonates, P₂O₅ can be added and/or the acid can be heated. However, as the process proceeds the acid undergoes polymerization reactions forming various forms of poly-phosphoric acid and water (Fig. 1).

In considering the possibility of isotopic exchange of ¹⁸O and the ¹³C¹⁸O species during the exposure of phosphoric acid to CO₂ there are several possible points at which fractionation could take place. First, isotopic exchange could take place between the CO₂ and the H₂O already present in the acid. During the polymerization reactions water is produced and this water is then

utilized to produce additional phosphoric acid. Water equilibrated in this last step would then re-exchange with the CO₂. Equilibrium established at this point would be dependent upon the temperature. During excessive heating of the phosphoric acid, P₂O₅ and excess H₂O are produced, also possible points of isotopic exchange.

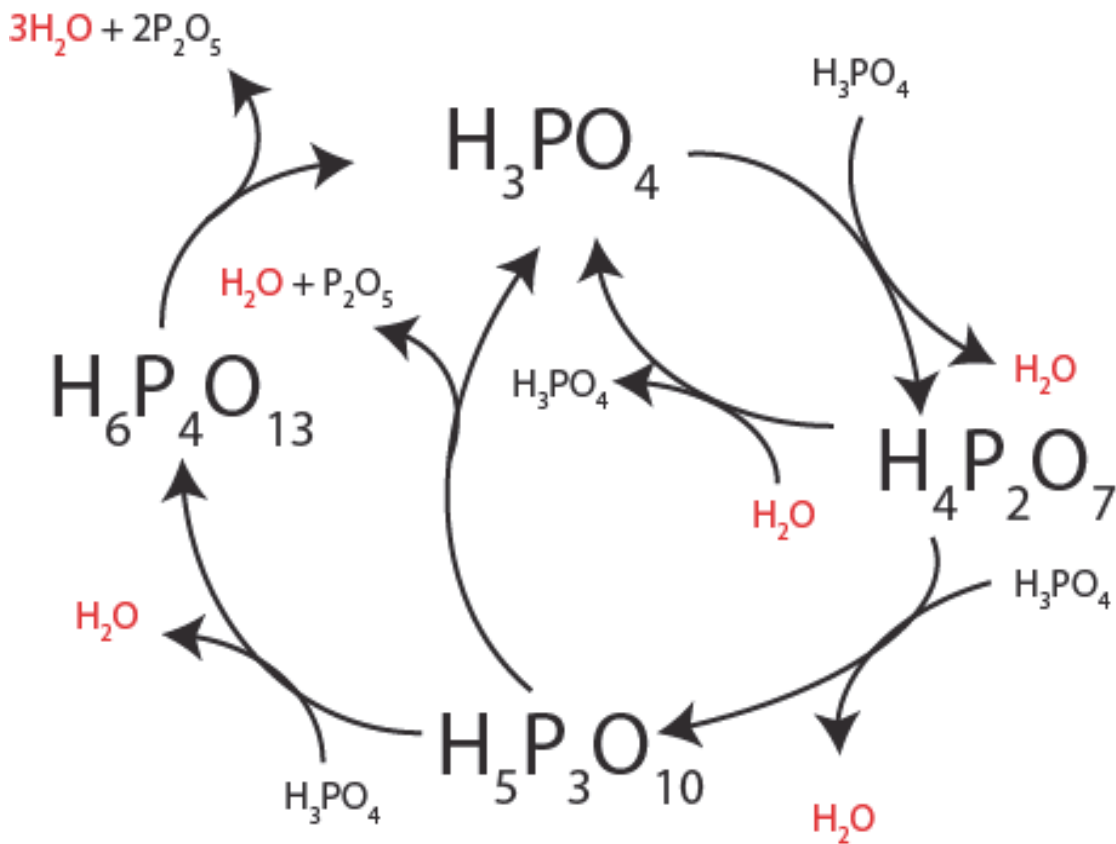


Figure 1: Possible pathways of for the production of poly phosphoric acid and the creation of water during the preparation of 'strong' phosphoric acid.

SCOPE OF WORK

Three experiments are proposed.

Experiment 1: In this experiment phosphoric acid, with a specific gravity (sg) of either 1.98 or 1.88, will be placed in Pyrex tubes with an aliquot (~1 μM) of one of three different CO₂ gases. At predetermined times the tubes will be removed and the CO₂ extracted and cleaned using the standard procedures in our laboratory (Murray et al., 2016).

Experiment 2: Aliquots of CO₂ from the three tank gases will be allowed to equilibrate in our normal reaction area over acid at 90°C with a sg of 1.98 for periods of between 5 and 120 minutes. A limited number of experiments will be also carried out using an acid temperature of 25°C. In addition, aliquots of Tank A and C that are heated to 1000°C will also be equilibrated with the 1.98 acid for varying lengths of time. Normally during this equilibration period, the

acid is stirred using our usual protocol for the reaction of carbonate samples. Some of the experiments will not be stirred. In some experiments, a blank reaction vessel without acid will be substituted. After the equilibration is complete, the CO₂ will be cleaned in the normal manner.

Experiment 3: Calcite samples precipitated at temperatures between 5 and 75°C, and therefore possessing a range of Δ_{47} values between 0.57 and 0.80‰, will be reacted at 25°C using the normal protocol as outlined by Murray et al. (2016). The procedure at 25°C will be identical to that carried out at 90°C with the exception that ~180 minutes will be used for each reaction, as opposed to 30 minutes at 90°C. These last experiments are designed to examine the difference in exchange as a function of temperature.

SIGNIFICANCE

It is our contention that the processes outlined above will lead to important variations in the Δ_{47} values measured in carbonates. At 90°C, which is the common reaction temperature, the Δ_{47} value of CO₂ in equilibrium with water in the acid will be 0.619‰. Hence samples with inherently lower Δ_{47} values, carbonates produced at high temperatures, will exchange with the water producing a lower temperature than they should. Conversely, carbonates with higher Δ_{47} values, colder carbonates, will tend to manifest higher temperatures. We further contend that these differences will vary between laboratories based on the design of the carbonate extraction systems as well as the method of preparing the phosphoric acid.

REFERENCES

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