

Control of growth rate on Li/Ca ratio of calcite - An experimental approach

A. Föger^{1,2}, V. Mavromatis^{2,3}, F. Konrad², A. Leis¹, M. Dietzel²
 anja.fueger@jr-aquaconsol.at



INTRODUCTION & METHOD

Lithium ions from seawater is known to be incorporated into marine carbonates, e.g. in brachiopod shells. Partitioning and stable isotope fractionation of Li might therefore be qualified for studying the variation of environmental conditions in seawater over geological timescales. In order to understand the Li incorporation behavior during carbonate mineral formation, well constrained inorganic precipitation experiments are necessary to identify the influence of parameters controlling partitioning during crystal growth. In this study, we performed Li co-precipitation experiments with calcite at 25 °C using a mixed flow reactor. In this setup, two separate solutions are mixed together using a peristaltic pump at controlled flow rate (Fig. 1).

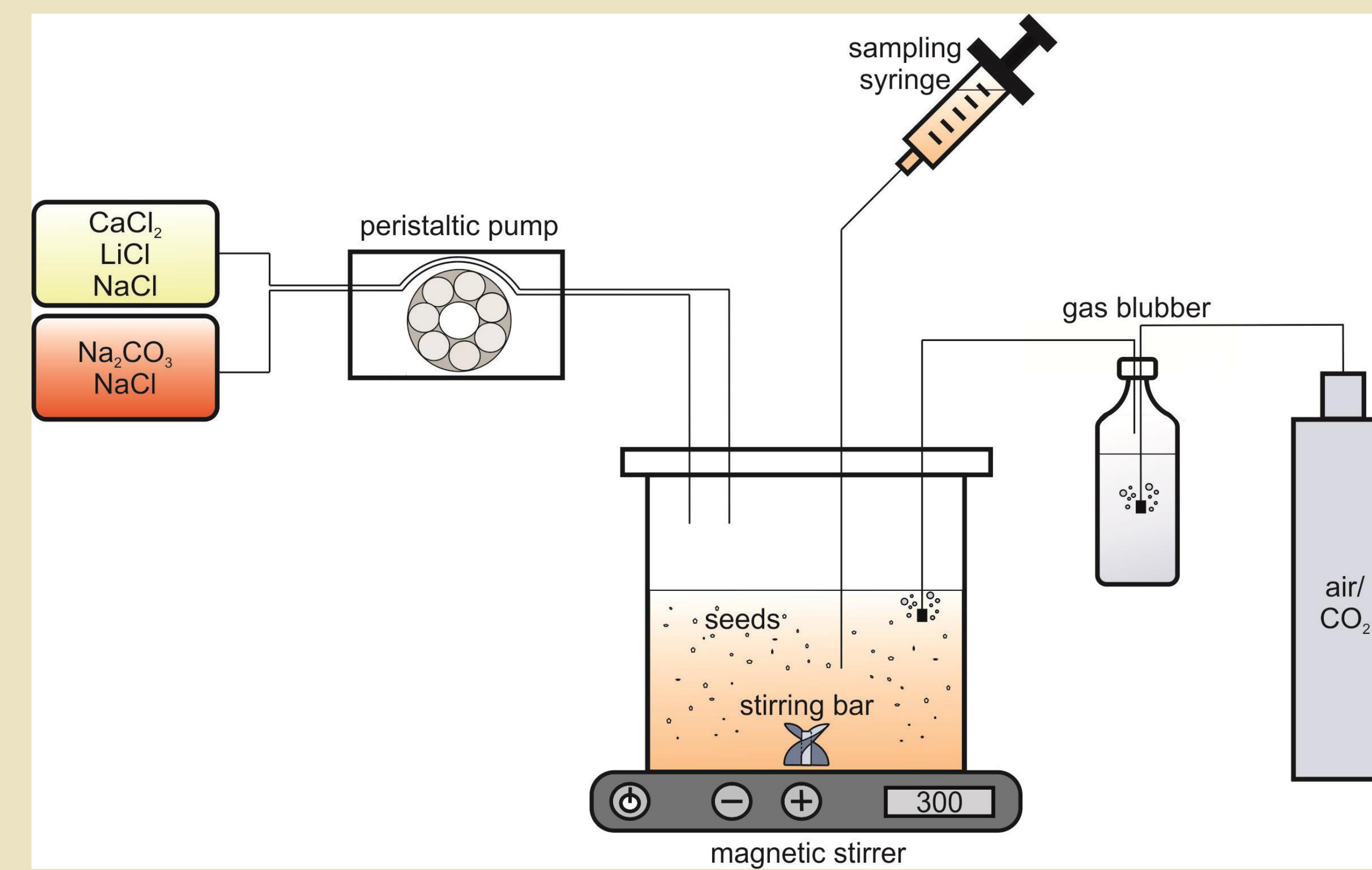


Fig 1. Experimental Setup.

REF.

[1] Wright et al. (2001) *Phys. Chem. Chem. Phys.*, **3**, 839-844

SEM ANALYSIS

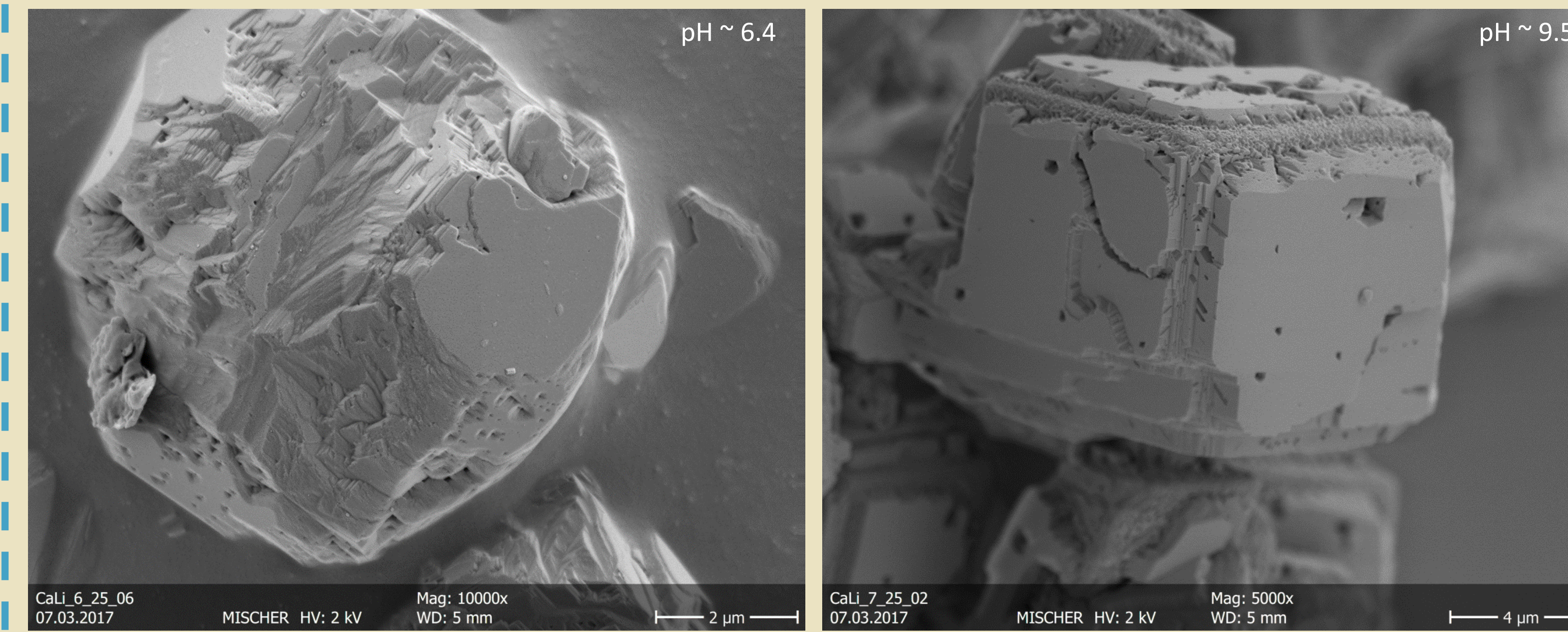


Fig 3. Scanning electron microphotographs of our synthetic samples at different pH.

STEADY-STATE CONDITIONS

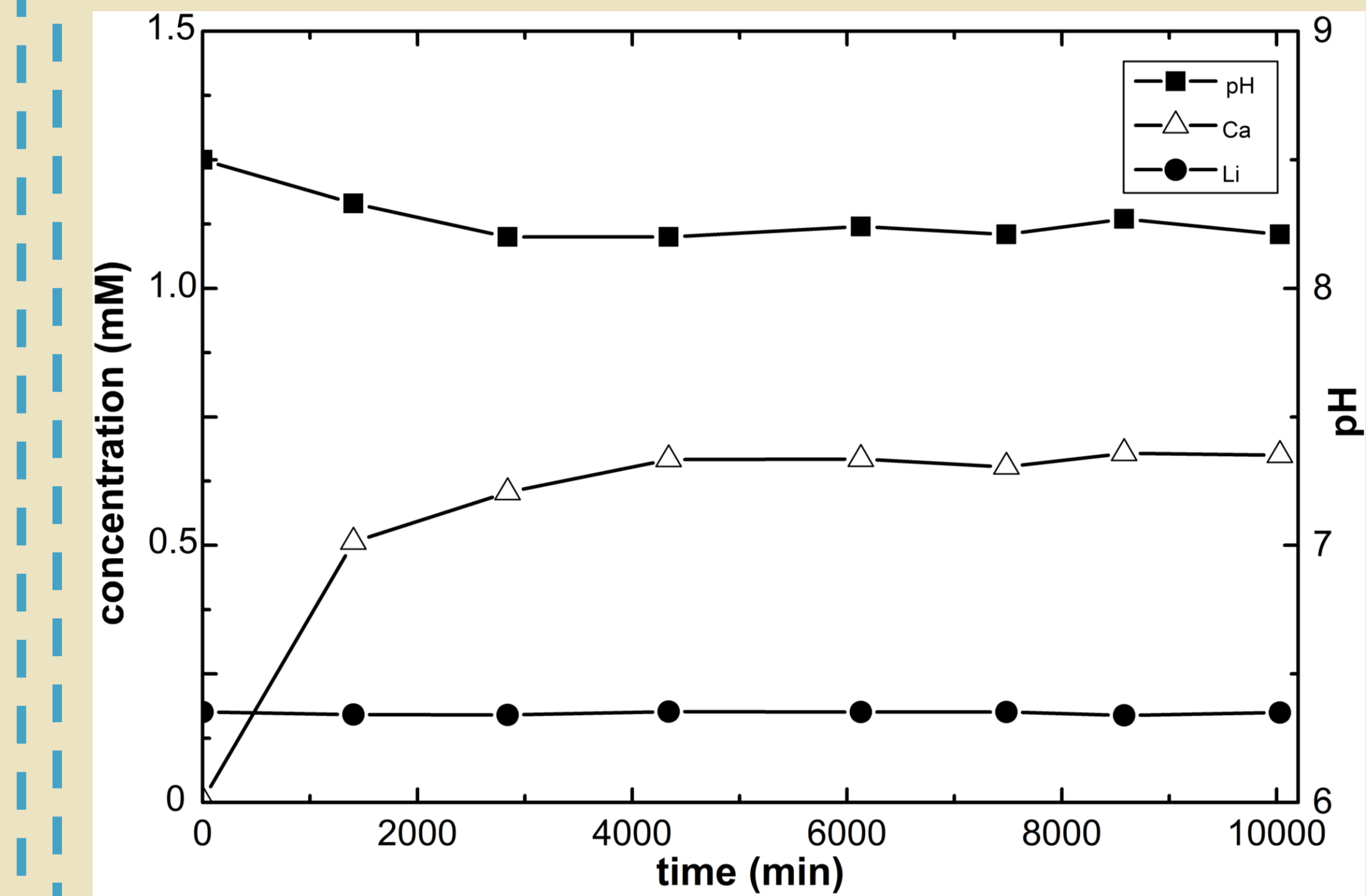


Fig 4. Concentrations of Ca and Li and evolution of pH over reaction time for an experiment with a flowrate of 120 mL/d. Analytical uncertainty is included in symbol size.

The time to attain steady-state conditions depends on the Ca concentration in the solution. Steady-state condition with respect to aqueous Ca concentration within the experimental runs was reached after around 3000 min, whereas steady-state with respect to aqueous Li concentration was achieved over the whole duration of the experiment.

PRECIPITATION RATE & PH DEPENDENCE

The incorporation of Li into calcite does not show an obvious dependence on the precipitation rate (Fig. 5), whereas pH (Fig. 6) seems to play a crucial role during the incorporation of Li in calcite in our experiments. Interactions between dissolved aqueous species and the calcite surface are reported to be affected by changes in the surface charge of calcite as a function of pH [1]. Following this, the Li incorporation increases proportional to Ca during the formation of carbonate layers with increasing precipitation rate at pH 8.4. With increasing pH the Ca content in the solution decreases, whereas the Li content remains the same. This finding, the pronounced relationship between the distribution coefficient and the pH, might be controlled by pH dependent solid surface characteristics and aqueous speciation effects, that has still to be resolved.

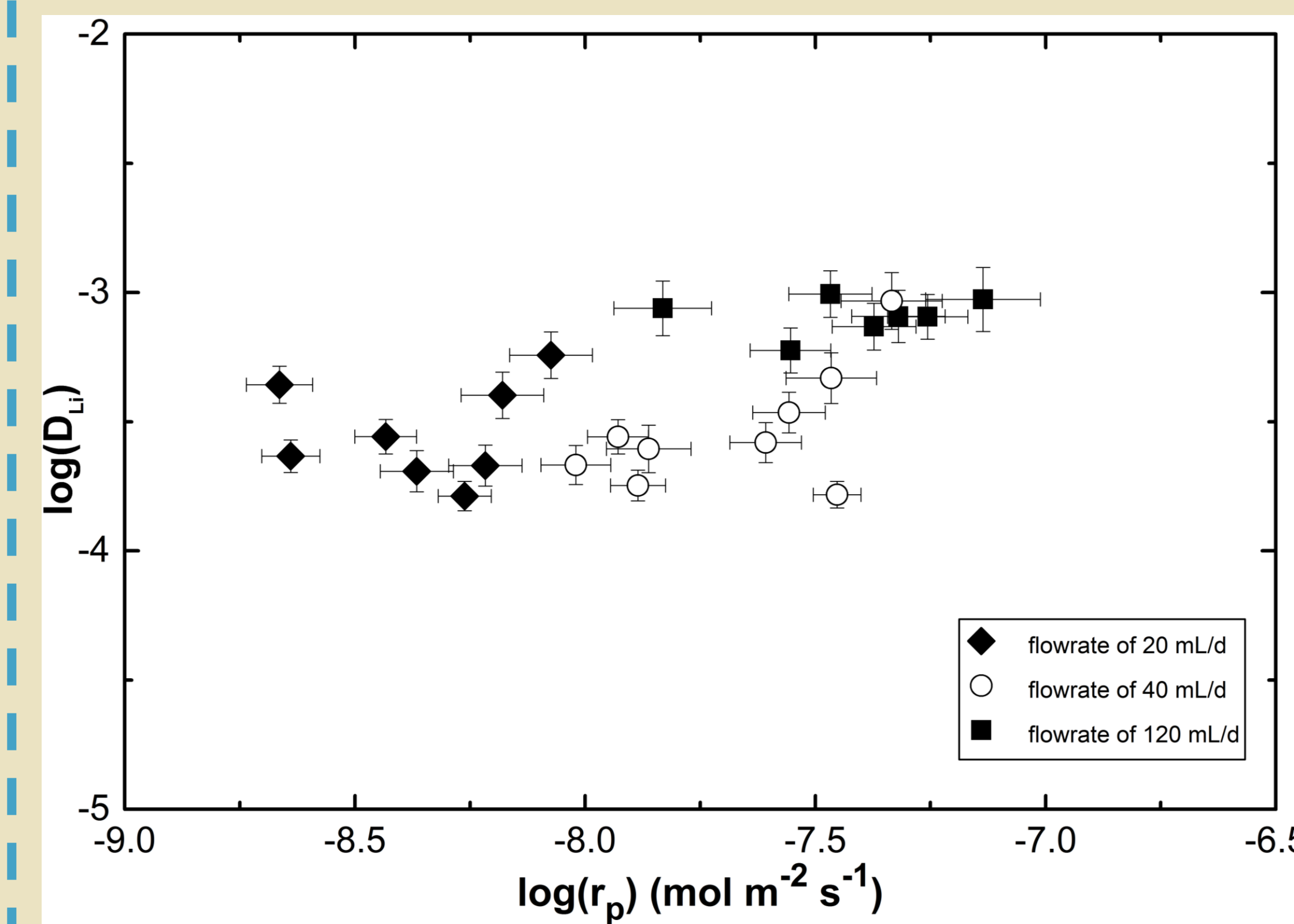


Fig 5. Li distribution coefficient ($D_{Li} = (Li/Ca)_{calcite} / (Li/Ca)_{aq}$) between calcite and solution as a function of calcite growth rate (pH ~ 8.3).

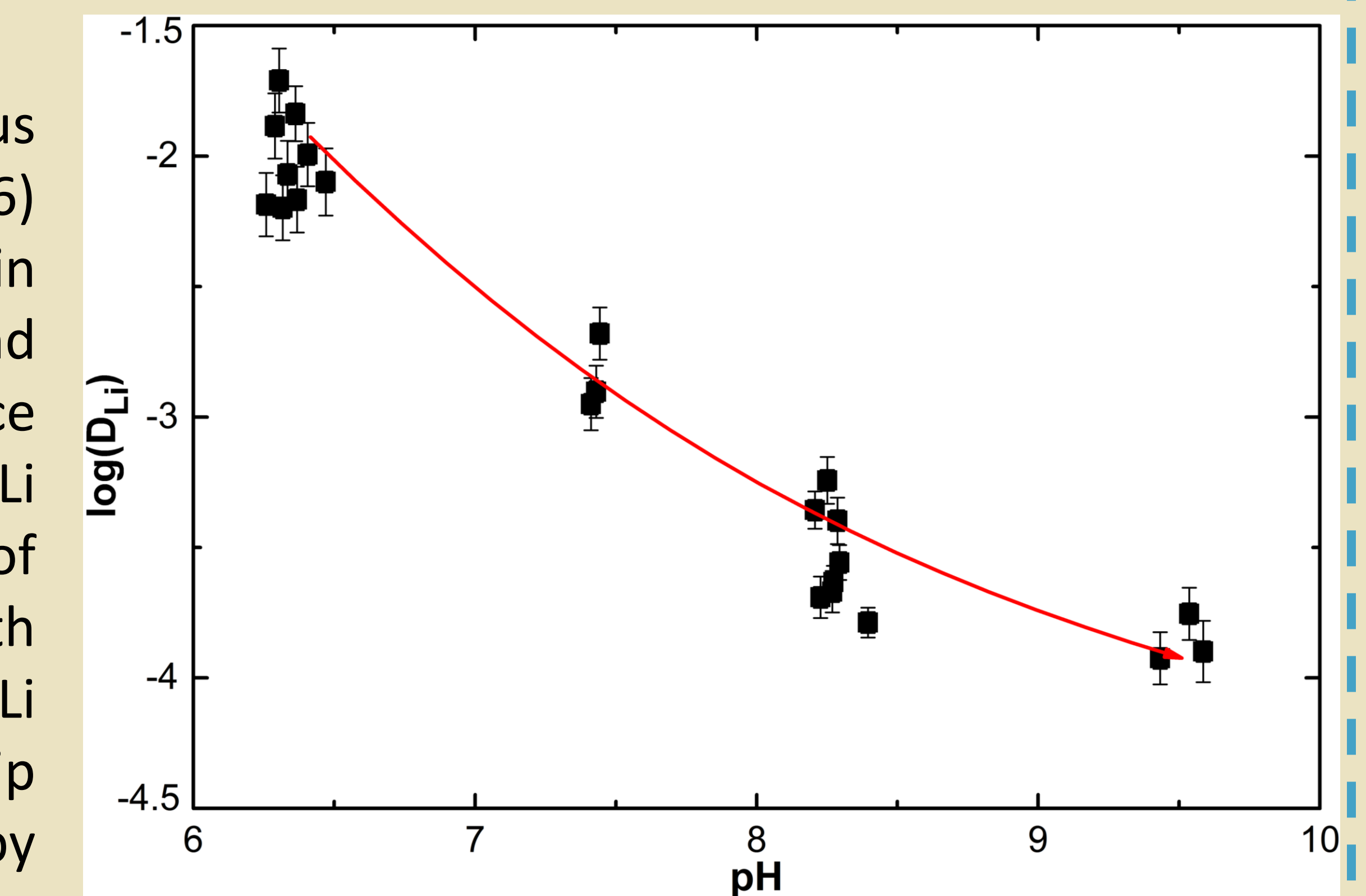


Fig 6. Li distribution coefficient between calcite and aqueous solution as a function of pH.

