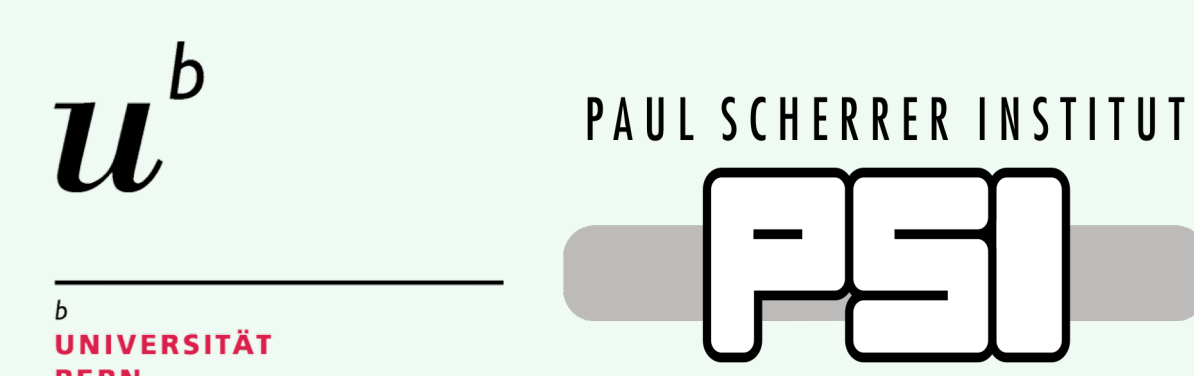


# Effect of $Pb^{2+}$ , pH and ionic strength on nucleation of calcium carbonate

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## Motivation

One of the most promising methods for the safe and sustainable disposal of anthropogenic  $CO_2$  is the fixation of  $CO_2$  into carbonate minerals (Matter et al., 2011). The mechanism of such a reaction, however, is not well understood and its slow kinetics could be a handicap for the implementation of silicate mineral carbonation as an efficient method for  $CO_2$  capture and storage (Roza Llera et al., 2021). In this regard, a thorough knowledge of the geochemical processes involving the formation and stability of carbonate phases is essential (Di Lorenzo et al., 2017). Furthermore, anthropogenic lead contamination is an environmental issue that affects soil and water quality and endangers living organisms in a number of surface and subsurface ecosystems (Nriagu & Pacyna, 1988). Therefore, this study derives fundamental experimental parameters that could be used to improve water treatment and carbon storage technologies.

## Aims and Methods

This study deals with the precipitation of  $CaCO_3$  in presence of  $Pb^{2+}$ . A comparison between the nucleation of  $CaCO_3$  in a pure system and in presence of lead (Ca/Pb = 100) was obtained. Furthermore the influence of two crucial variables (pH and IS) was studied to provide experimental information about the kinetics of Ca and Pb coprecipitation over a broad range of conditions. A variety of techniques were used (SEM-EDX, XRD, FTIR) and in particular a titration system by Metrohm.

### Schematic representation of titration experiment

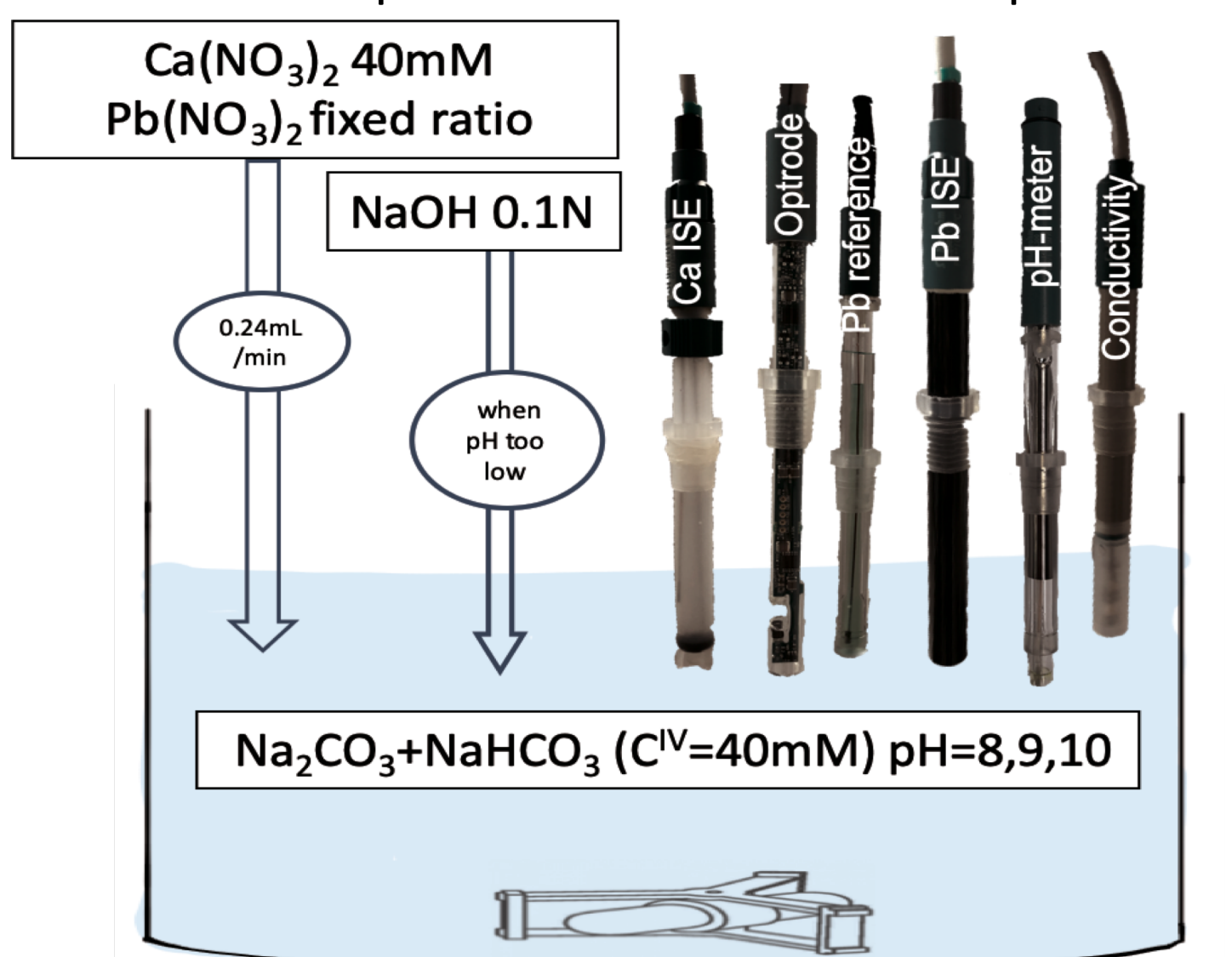


Fig.1: Titration system with six electrodes

### Titration experiments

- $CaCO_3$  nucleation studies in Pb-free solutions and in presence of  $Pb^{2+}$  (Ca/Pb=100).
- An automated titration system Metrohm (OMNIS) was used.
- Experiments under varying pH (8, 9 and 10) and ionic strength (0.05, 0.1 and 1M).
- $KNO_3$  was added to fix the ionic strength of the initial solution.
- A mixture of  $Na_2CO_3$  and  $NaHCO_3$  as carbon source.
- The formed solids were filtered ( $\phi = 0.45 \mu m$ ) under low vacuum for phase identification and Ca/Pb ratio.

## Results and Discussion

### Effect on nucleation of ionic strength and pH

At constant pH an increase in induction time with increasing ionic strength was observed. On the other hand increasing pH at constant ionic strength decrease the induction time. The dependency of ionic strength in relation to the induction time could be explained by the fact that ionic strength lowers the activity coefficient and thus more calcium was needed in the system for nucleation to occur. Further, ions in solution form ion pairs, which decrease the concentration of 'free' ions and therefore lower the possibility to form the solid phase.

### Dependency of ionic strength and pH on induction time

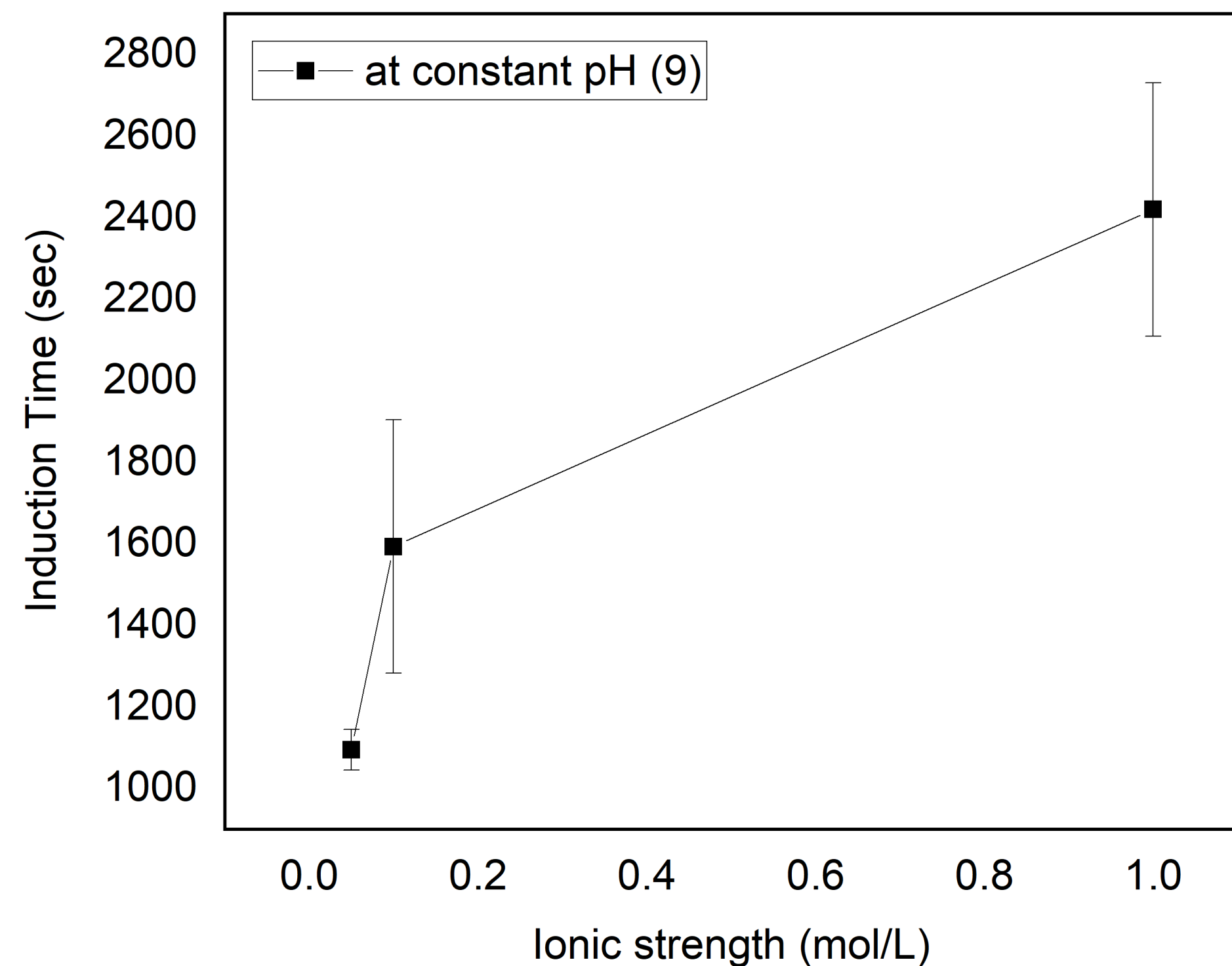


Fig.2: Induction time at constant pH 9

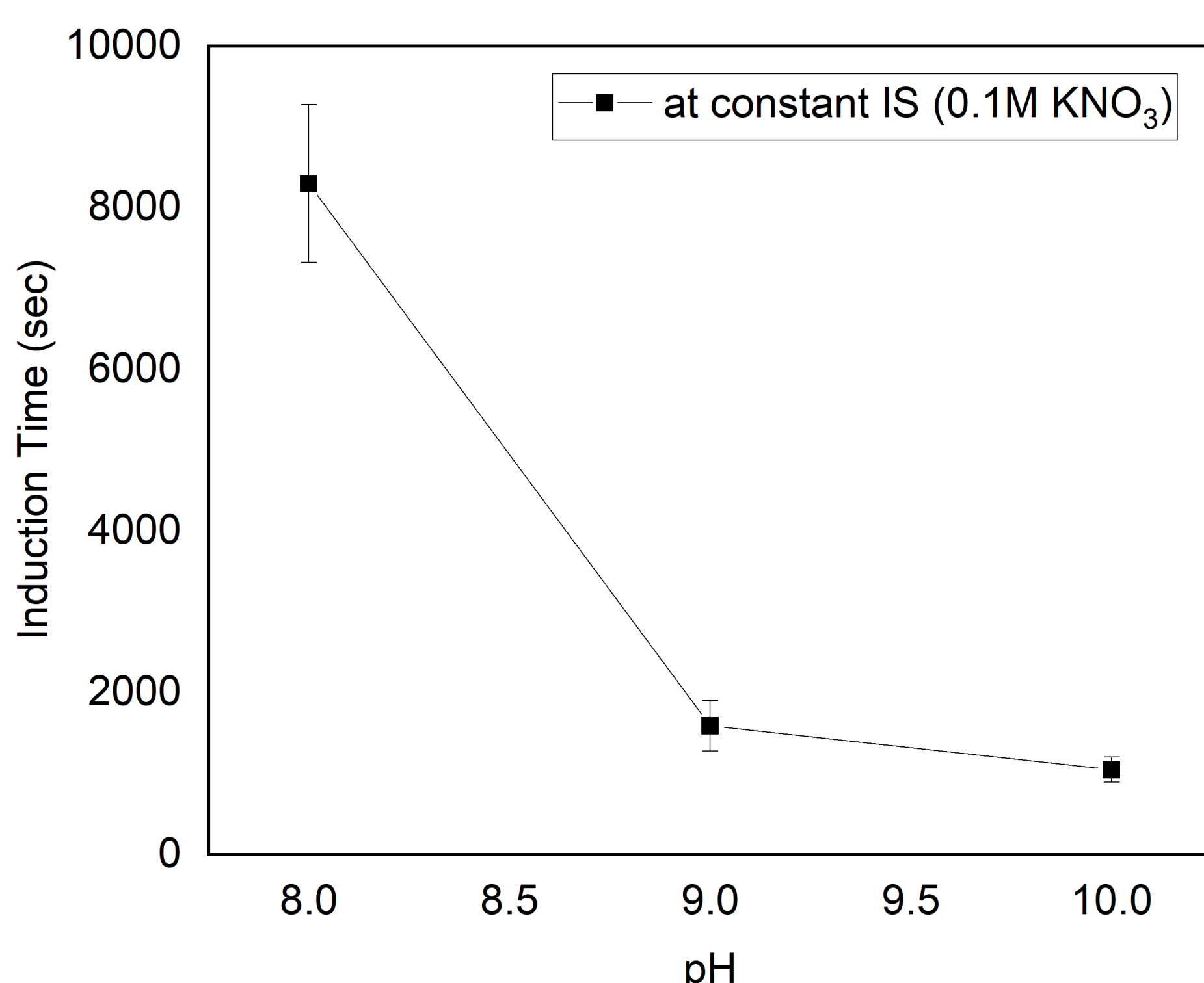
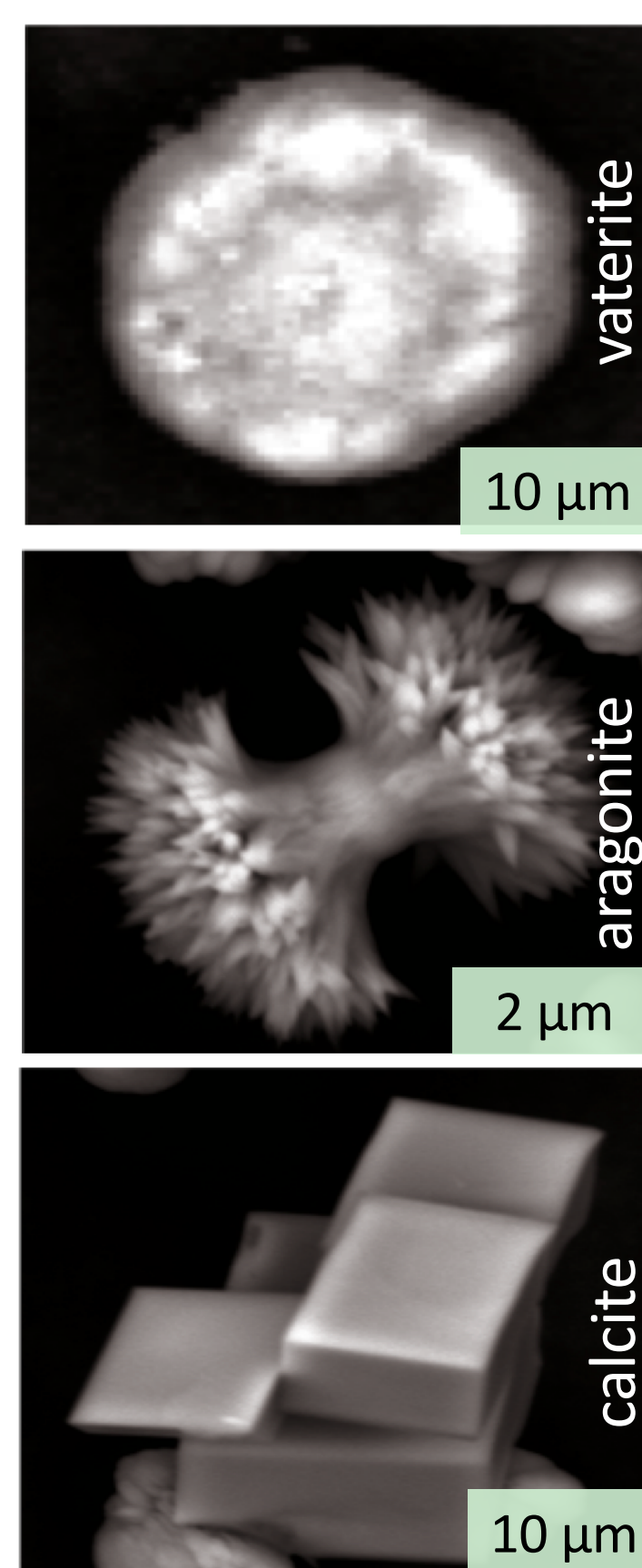


Fig.3: Induction time at constant ionic strength



## Correlation between induction time and saturation index

It is well known that saturation state of carbonate minerals is strongly dependent on pH. With increasing pH the saturation index increases as well. This behaviour is in agreement with the carbonate speciation in water. At high pH values the dominant species is  $CO_3^{2-}$  that is required to form  $CaCO_3$  at supersaturation. Therefore, saturation indices are observed to be higher with increasing pH.

### Saturation indices and induction time as a function of pH and ionic strength

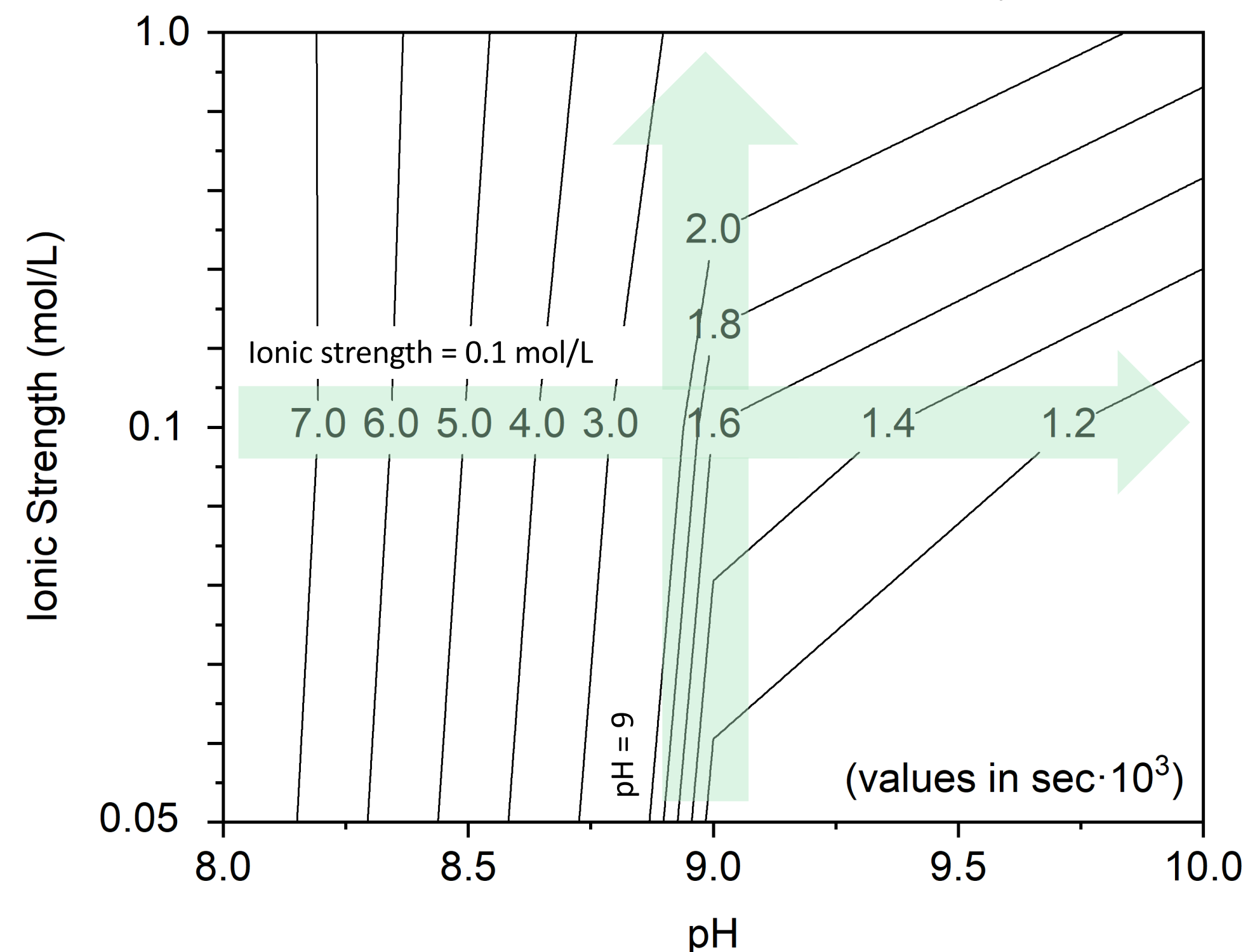


Fig.4: 3D plot of induction time varying pH and IS; Green arrows corresponds to Fig.2 and Fig.3

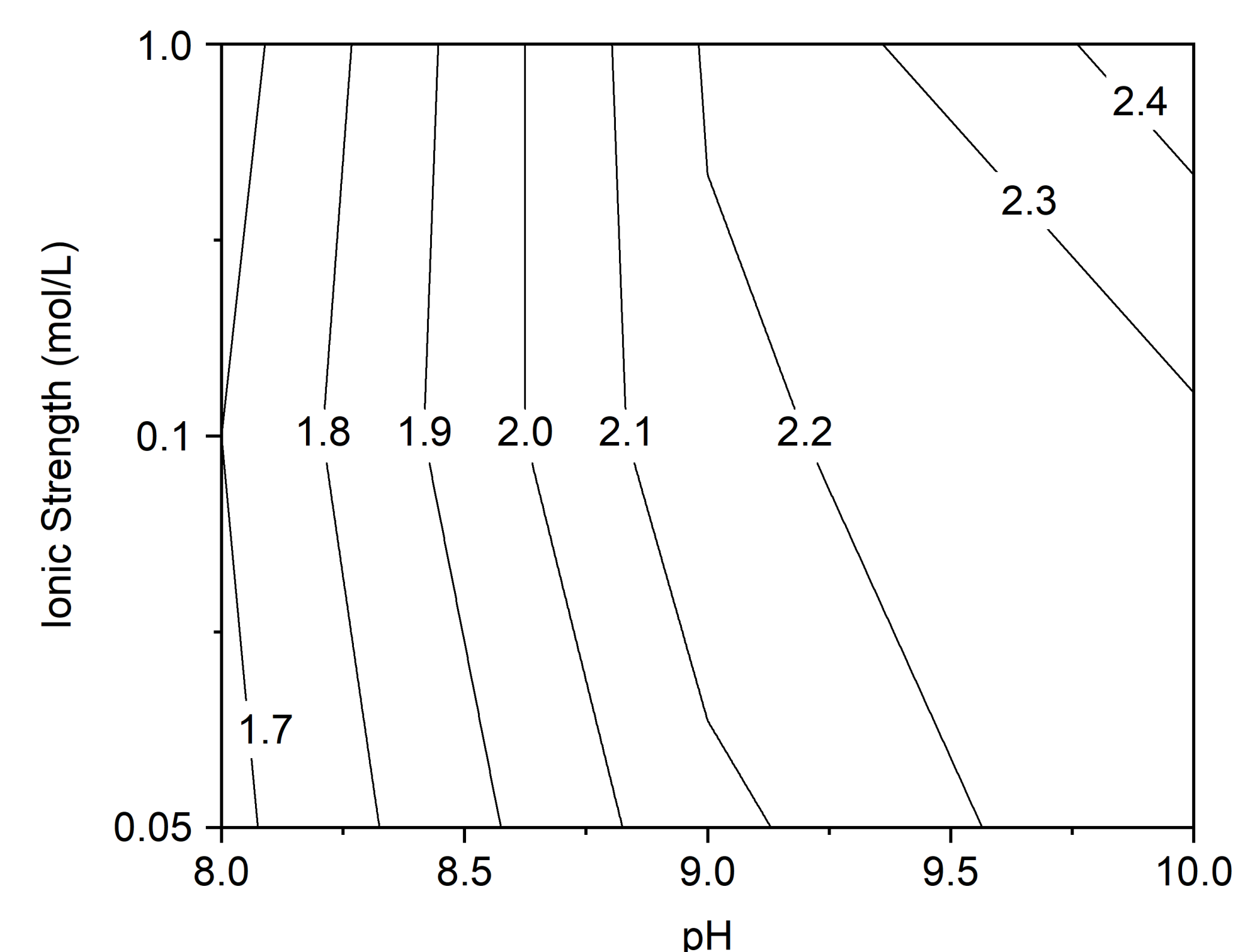


Fig.5: Saturation indices varying pH and IS for the pure calcite system

## $Pb^{2+}$ uptake by calcium carbonate

Three different carbonate minerals were identified in solid products from experiments containing lead. These crystalline phases have different affinity for  $Pb^{2+}$  incorporation. At the lowest ionic strength there is no preferential partitioning of  $Pb^{2+}$  into any crystalline phase. At intermediate ionic strength the only phase that seems to uptake preferentially  $Pb^{2+}$  is aragonite. Aragonite is isostructural with cerussite, which would explain the relative high  $Pb^{2+}$  incorporation at low ionic strength. At high ionic strength we do not detect aragonite anymore, but both phases detected (calcite and vaterite) show significant preferential incorporation of  $Pb^{2+}$ . Vaterite (globular habit) with its expanded structure allowed big ions like  $Pb^{2+}$  to fit inside the structure. Calcite (rhombohedral habit) despite its dense structure, has managed to uptake some  $Pb^{2+}$  at high ionic strength.

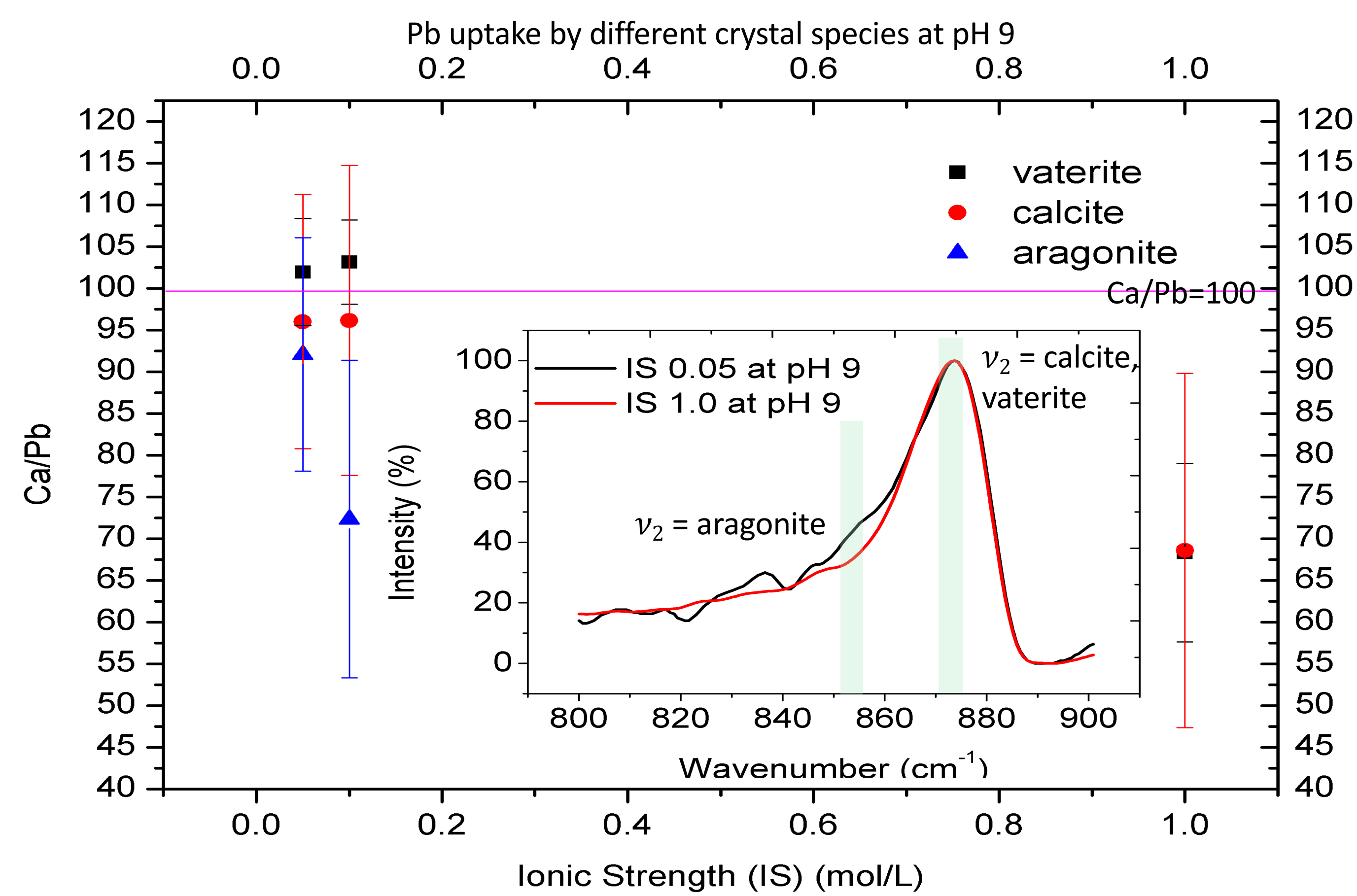


Fig.6:  $Pb^{2+}$  uptake by carbonate phases and FTIR-Spectra

## Conclusions

- High ionic strength and low pH result in high induction time concerning the nucleation of calcium carbonate
- Saturation indices increase with increasing pH of the solution. The effect of ionic strength on the critical saturation indices is less evident.
- Uptake of  $Pb^{2+}$  is different among the polymorphs of calcium carbonate
- Due to the different structures of the carbonate phases, preferential  $Pb^{2+}$  incorporation was observed: aragonite > vaterite ≥ calcite

## Outlook

Further characterization of the products with additional techniques (FTIR, XRD) will be conducted to quantify the relative proportion of the different phases, thus to understand their importance for  $Pb^{2+}$  uptake. From these quantitative results the influence of trace elements, like Pb, on the polymorphism of  $CaCO_3$  will be assessed. This is a crucial experimental parameter necessary to ensure safety, efficiency and long-term stability aiming at geological carbon storage.

## References

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