PUBLISHABLE SUMMARY

PROJECT OBJECTIVES

The main goal of this project was to carry out an in depth study of the effects of boron in the chemistry and crystallization of calcium carbonates.
This project aimed to answer the following questions:

1) What is the role of borate in $CaCO_3$ crystallization and how does it affect the kinetics and mechanisms of calcite growth?
2) What is the effect of borate on the surface properties of calcite?
3) How do the different mechanisms of $CaCO_3$ crystallization affect surface attachment, incorporation and isotopic fractionation of boron (B^{10}/B^{11} ratio) in calcite and aragonite?

In order to answer the questions above, the project was structured in 4 work packages:

[Months 1-6] Crystallization of $CaCO_3$ from solution in the presence of borate.
[Months 7-16] Growth of calcite in the presence of borate ions.
[Months 17-20] Synchrotron-based study: $CaCO_3$ crystallization in the presence of borate; study of calcite surface properties.
[Months 21-24] Boron isotope measurement in calcite formed at different temperatures and pH.

WORK PERFORMED SINCE THE BEGINNING OF THE PROJECT

During the first year of this project I deepened my understanding of X-ray electron spectroscopy (XPS) and pair distribution function (PDF) techniques in general by working with the data and also in collaboration with colleagues at the Nano Science Center who have deep knowledge about these techniques. I have learn how to interpret the data I collected on the uptake of borate on calcite surfaces and how to evaluate the effect of this ion on the local structure of amorphous calcium carbonate. Besides, I have been introduced to other techniques I had never used before, like transmission electron microscopy (TEM), atomic force microscopy (AFM) and UV-Vis spectrophotometry. In particular:

- Crystallization from solution experiments were carried out and excellent data on the effect of borate on polymorph selection, crystallization kinetics and pathways of $CaCO_3$ minerals.
- Structural characterization of poorly-ordered precursor phases (amorphous $CaCO_3$) grown in the presence of borate ions was carried out.
- Calcite was also grown from solution and data on the uptake on borate has been successfully obtained.
- Furthermore, as both boron and carbon speciation are strongly affected by pH, some collaboration studies were carried out in order to understand the effect of pH in ACC formation and also in calcite surface speciation in collaboration with members of the NanoGeoScience group.

MAIN RESULTS ACHIEVED SO FAR

Results show that the morphology, stability and polymorph distribution of calcium carbonate polymorphs and the amount of borate uptaken by $CaCO_3$ are different as function of temperature and initial B/Ca ratios in the aqueous solutions. Our data unambiguously suggests that amorphous $CaCO_3$, a poorly-ordered and metastable precursor phase that forms prior to crystalline $CaCO_3$ formation, has a very important role in the evolution of the reaction. The transformation of ACC into calcite always takes place via vaterite in the pure system at different temperatures (7.5 – 25 °C), and my data indicates that the combined variations of temperature and initial B/Ca ratios are the key to change the evolution of the reaction. The vaterite-calcite transformation usually takes place by dissolution-recrystallisation. In borate-bearing solutions, the rate of this dissolution-reprecipitation process was controlled by temperature and the surface area of the calcite. Experiments showed that crystalline $CaCO_3$ morphologies changed progressively at decreasing temperatures and increasing borate. The analysis of borate uptaken by calcite and ACC showed that at constant temperature, the content of borate in calcite increased proportionally to the initial B/Ca ratio in solution (Figure 1). In contrast, when the initial B/Ca ratio was constant, the boron content in calcite was inversely proportional to temperature.

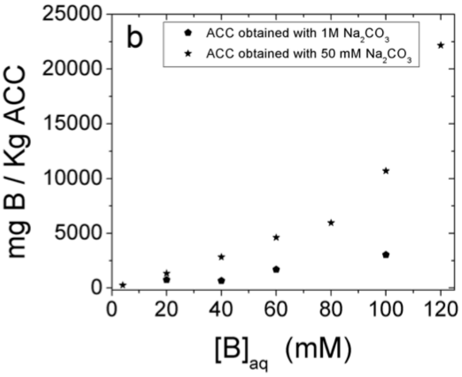

Fig. 1: update of borate by amorphous calcium carbonate (ACC).

Structural characterization of ACC has show that the structure at the local scale of ACC is strongly modified when borate ions are present in solution (Figure 2). This data is preliminary and further evaluation is being carried out at present.

Furthermore, collaboration work with NanoGeoScience group members on the effect of pH in ACC formation and also in calcite surface speciation has shown that ACC lifetime, composition and structure at high pH is different than ACC formed from a pure system at lower pH because of the incorporation of OH^- ions into its structure [1]. Also, on calcite surface, our results have demonstrated that the pH where adsorbed bicarbonate converts to carbonate is 3 pH units lower than for bicarbonate deprotonation to carbonate in solution [2].

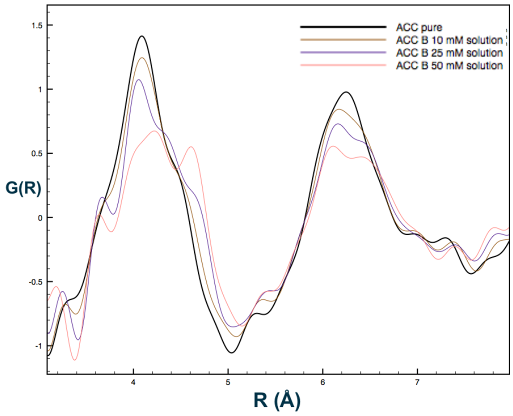

Fig. 2: preliminary pair distribution function data showing the effect of borate on ACC structure.

Finally, with this project I have also developed a method to synthesize nanocalcite with very high surface area, a challenge that has been addressed by many researchers during the last years but has not been successfully solved. This methodology will be published during 2016-2017 as a communication in a journal about materials science or crystallization processes.

EXPECTED FINAL RESULTS AND THEIR POTENTIAL IMPACT AND USE

The early termination of the NanoCArB project (month 18 of 24) due to starting a new job at the Trinity College Dublin (University of Dublin) will not affect negatively the publication outcome. I expect to publish results in the next following months. Two full manuscripts and a short communication manuscript are in production and will be submitted to open-access journals. This research will: *i*) improve the methodology to use B isotopes as paleo-pH proxies to interpret the effects of ocean acidification and climate change; *ii)* provide a suitable method to remove borate from wastewaters using calcium carbonates. *iii)* provide a suitable method to suppress or slow down $CaCO_3$ scaling in pipes.

References

[1] Andersson, M., **Rodriguez-Blanco, J.D.**, Stipp, S.L.S. (2016) Is bicarbonate stable in and on the calcite surface? Geochimica et Cosmochimica Acta, 176, 198-205. doi:10.1016/j.gca.2015.12.016

[2] Tobler, D.J., **Rodriguez-Blanco, J.D.**, Sørensen, H.O., Stipp, S.L.S., Dideriksen, K. (2016) Effect of pH on Amorphous Calcium Carbonate Structure and Transformation. Crystal Growth & Design, 16, 4500–4508. DOI: 10.1021/acs.cgd.6b00630

Project website: https://jrodriguezblanco.wordpress.com/projects/nanocarb/