

# Experimental determination of hydromagnesite precipitation rates and their implication for carbon storage

Ulf-Niklas Berninger<sup>1,2,\*</sup>, Guntram Jordan<sup>2</sup>, Eric H. Oelkers<sup>1,3</sup>

<sup>1</sup>Géosciences Environnement Toulouse, CNRS-UPS, 14 av. Édouard Belin, 31400 Toulouse, France.

<sup>2</sup>Department für Geo- und Umweltwissenschaften, LMU, Theresienstr. 41, 80333 München, Germany.

<sup>3</sup>Department of Earth Sciences, UCL, Gower Street, WC1E 6BT London, United Kingdom.

The precipitation rates of carbonate minerals are of current interest due to their potential role in carbon storage. Carbon storage via carbonate mineral precipitation appears to be particularly favored in basaltic and ultra-mafic rocks due to their abundance in divalent cations such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Whereas anhydrous calcium carbonates readily precipitate at ambient temperatures, the precipitation of the anhydrous Mg carbonate mineral magnesite is apparently inhibited at temperatures below  $\sim 80^\circ\text{C}$ . At lower temperatures, the precipitation of hydrous Mg carbonates like hydromagnesite ( $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) is favored.

Hydromagnesite precipitation rates were measured in closed-system reactors at far to near to equilibrium conditions in  $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$  bearing aqueous solutions at pH from 8.5 to 11 and temperatures from 22.5 to  $75^\circ\text{C}$ . Resulting rates ( $r$ ) were fit following the method described by Harouiya et al. [1] using

$$r = k \cdot (1 - \Omega^\sigma)^n$$

where  $k$  denotes the surface area normalized rate constant,  $\Omega$  refers to the saturation state of hydromagnesite,  $\sigma$  represents Temkin's coefficient [2] ( $\sigma = 0.2$ ), and  $n$  designates the reaction order ( $n = 1$ ). Determined pH  $\sim 9$  rate constants are 8.5, 8, and  $7 \cdot 10^{-9} \text{ mol/m}^2/\text{s}$  at 22.5, 50 and  $75^\circ\text{C}$  respectively.

Forsterite is commonly thought of as the best source of the divalent metal cations required to create carbonate minerals due to its worldwide abundance. Forsterite forward dissolution rates after normalization to its Mg content are  $\sim 2$  orders of magnitude slower than corresponding hydromagnesite precipitation rates. This observation indicates that, in contrast to the carbonation of forsterite to form magnesite, the limiting step of the carbonation process to form hydromagnesite from forsterite is the relatively slow dissolution of forsterite. As dissolution rates of forsterite are not increased by changing saturation state at far-from-equilibrium conditions [3] or substantially by the addition of organic ligands [4] it seems likely that the most efficient way of accelerating this overall process would be by increasing forsterite reactive surface areas (e.g. by increased grinding).

[1] Harouiya et al. (2007) *Chem. Geo.* **244**, 554-568.

[2] Temkin, M. (1963) *Dolk. Akad. Nauk SSSR* **152**, 782–785.

[3] Oelkers, E. H. (2001) *Chem. Geol.* **175**, 485-494.

[4] Declercq et al. (2013) *App. Geochem.* **39**, 69-77.

# A METHOD FOR ELIMINATING SULFIDE INTERFERENCE ON SILICA COLORIMETRIC ANALYSIS

*Fernando L. Berro Jiménez<sup>1</sup>, Matteo Lelli<sup>2</sup>, Giorgio Virgili<sup>3</sup>,  
Ilaria Minardi<sup>3</sup>, Luigi Marini<sup>4</sup>*

<sup>1</sup>West System s.r.l., Via Don Mazzolari 25, I-56025, Pontedera (PI), Italy: f.berro@westsystem.com

<sup>2</sup>CNR Institute of Geoscience and Earth Resources (CNR-IGG), Via Moruzzi 1, I-56124, Pisa, Italy

<sup>3</sup>West System s.r.l., Via Don Mazzolari 25, I-56025, Pontedera (PI), Italy

<sup>4</sup>Consultant in Applied Geochemistry, Via A. Fratti, 253, I-55049, Viareggio (LU), Italy

The mitigation of silica scaling and the correct disposal of separated geothermal liquids require *inter alias* frequent analysis of dissolved silica, which can be performed by means of the molybdate colorimetric method (yellow form). Several interferences are known in the colorimetric determination of silica. In particular, reducing substances determine partial conversion of yellow silicomolybdate to the blue form. Among the reducing substances, sulfide species are probably the most important in geothermal environments. Their interference must be suppressed when silica determination has to be performed immediately after collection, whereas sulfide species may disappear without any treatment during long-term sample storage.

Two different approaches were tested to suppress sulfide interference on the silicomolybdate method of silica determination: (1) oxidation of sulfide species to elemental sulfur and (2) conversion of the sulfide species to H<sub>2</sub>S and stripping by air bubbling.

Based on the experiments carried out in this work, sample acidification to pH 2 and air bubbling represent the most effective and simplest treatment to remove sulfide species, thus suppressing their interference on the colorimetric analysis of dissolved silica using the silicomolybdate method (yellow form).

It is surprising that such a simple way to solve this crucial problem has not been described in the geothermal scientific literature, as far as we know. For example, the classical textbook of Ellis and Mahon (1977) reports that “if sulfide or sulfur dioxide are present, the silicomolybdic acid turns green”, without offering any solution to this problem. No mention is given on H<sub>2</sub>S interference on colorimetric silica determination in the well-known report by Giggenbach and Goguel (1989). Boiling an acidified sample is suggested for sulfide removal by the APHA, AWWA, WEF (1999) Manual. However, heat treatment may cause undesirable effects, such as water loss and precipitation of solid phases. The only possible but uncommon problem of the technique proposed in this communication is the O<sub>2</sub>-driven oxidation of reduced species (e.g., divalent iron) with consequent precipitation of solid phases (e.g., oxyhydroxides of trivalent iron) and increase in turbidity. Use of nitrogen or another unreactive gas instead of air solves this possible problem.

# DEVELOPMENT OF AN AUTOMATIC SYSTEM TO MONITOR SILICA CONCENTRATION IN GEOTHERMAL WATERS

*Fernando L. Berro Jiménez<sup>1</sup>, Giorgio Virgili<sup>2</sup>, Ilaria Minardi<sup>2</sup>,*

*Matteo Lelli<sup>3</sup>, Luigi Marini<sup>4</sup>*

<sup>1</sup>West System s.r.l., Via Don Mazzolari 25, I-56025, Pontedera (PI), Italy: f.berro@westsystem.com

<sup>2</sup>West System s.r.l., Via Don Mazzolari 25, I-56025, Pontedera (PI), Italy

<sup>3</sup>CNR Institute of Geoscience and Earth Resources (CNR-IGG), Via Moruzzi 1, I-56124, Pisa, Italy

<sup>4</sup>Consultant in Applied Geochemistry, Via A. Fratti, 253, I-55049, Viareggio (LU), Italy

Monitoring of silica concentration in geothermal waters is important to mitigate silica scaling in pipelines and other surface installations of geothermal power plants as well as in re-injection wells. In fact, precipitation of amorphous silica represents the main obstacle for the exploitation of geothermal aqueous solutions coming from high-temperature geothermal reservoirs (Gunnarsson and Arnorsson 2005, *Geothermics*, 34, 320-329). Previous considerations motivate the development of an automatic system to monitor silica concentration in geothermal waters through the molybdate colorimetric method, measuring the absorbance of the yellow-colored silicomolybdate complex.

The sample is mixed with Acidified Deionized Water (ADW) into the reactor as soon as possible to avoid occurrence of silica precipitation. Both the sample and ADW are pumped into the reactor using two peristaltic pumps whose flows are suitably adjusted to obtain the desired dilution factor. Nevertheless, the amounts of sample and ADW are weighted by a high-precision balance and obtained weights are processed by a laptop computer to compute the dilution factor with sufficient precision.

Since sulfide species determine partial conversion of the yellow silicomolybdate to the blue form, they have to be eliminated when silica determination is performed immediately after collection as in the present case (Berro et al. 2014, *Mineral. Mag.*, submitted). Therefore, ADW is used not only to dilute the sample but also to obtain a pH close to 2. At this pH value, all dissolved sulfide species are present as H<sub>2</sub>S, which is stripped by air bubbling.

Afterwards, a known volume of ammonium molybdate solution is added to the reactor using a peristaltic pump and the solution is stirred for a few seconds. After 12 minutes, which are needed for the complete development of the yellow color, the aqueous solution is continuously pumped by a peristaltic pump through a Z-form flow cell with an optical path length of 410 mm.

One edge of the path length is connected to a light bulb whereas the opposite edge is connected to a spectrophotometer by two optic fibers. The absorbance values measured by the spectrophotometer at different wavelengths are acquired by the laptop computer and processed to compute silica concentration. A standard solution is analyzed after a selected number of samples to check the calibration curve. The obtained silica concentration is stored in a CSV file and displayed as a function of time.

# Adsorption of $\text{MgCl}_2$ and $\text{CaCl}_2$ on illite as seen with cryogenic X-ray photoelectron spectroscopy (cryo-XPS)

S. Jelavić\*, N. Bovet, S.L.S. Stipp

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark

\* [stanislav.jelavic@nano.ku.dk](mailto:stanislav.jelavic@nano.ku.dk)

Illite is one of the most important clay minerals in oil-bearing rocks because it can act as a cement, that reduces the flow rates of pore fluids, and it is very reactive, as a consequence of high surface area and electrical charge density. Understanding the mechanisms of adsorption of common cations and anions found in formation waters and brines on illite is essential for predicting the response of oil reservoirs during water flooding for oil recovery. The formation of clay minerals as a secondary phases during the reaction of  $\text{CO}_2$  charged waters is also of interest in carbon capture and storage (CCS) because clay formation consumes cations intended for carbonate mineral formation.

Cryo-XPS is a method for studying chemical composition and the bonding environment of elements at the solid-solution interface because it detects photoelectrons excited from the topmost layers of atoms of the interface [1, 2]. In batch experiments, we prepared and equilibrated illite (CMS standard IMt-1, fraction  $<2\ \mu\text{m}$  separated by centrifugation) in  $\text{MgCl}_2$  and  $\text{CaCl}_2$  solutions at a range of concentrations (1, 6, 12, 25, 50 and 125 mM) and fast froze the centrifuged wet paste directly in the spectrometer's antechamber using a liquid nitrogen cooled stage. The difference between Cl 2p electron binding energies between the fast frozen specimens and those dried under ultra-high vacuum demonstrates that the electrical double layer has been preserved and can be observed directly. The surface excess of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  were measured and the organisation of cations and anions within the electrical double layer could be observed. Because of the stronger preference of the illite surface for  $\text{Ca}^{2+}$  over  $\text{Mg}^{2+}$ , lower ionic strengths of  $\text{Ca}^{2+}$  solutions are needed for  $\text{Cl}^-$  to become less dominant ionic specie on the surface compared to  $\text{Cl}^-$  in  $\text{Mg}^{2+}$  solutions.

This study is continuation of efforts to understand the influence of clay minerals on oil recovery. Skovbjerg et al. [3] showed that the presence of clay minerals can alter the wettability of the pore surfaces in reservoir rocks by selectively adsorbing some components from the oil and the water used to push oil to the production well but the exact mechanism of this process is still not well understood. Wettability of pore surfaces is also of interest in systems where scaling is an issue or where reaction of  $\text{CO}_2$  with the porous medium is desired.

[1] Shchukarev, A., Sjöberg, S. (2005), *Surface Science*, **584**, 106-112

[2] Shchukarev, A., Boily, J.-F., Felmy, A.R. (2007), *Journal of Physical Chemistry C*, **111**, 18307-18316

[3] Skovbjerg, L.L., Hassenkam, T., Makovicky, E., Hem, C.P., Yang, M., Bovet, N., Stipp, S.L.S. (2012), *Geochimica et Cosmochimica Acta*, **99**, 57-70

# Multiscale mapping of physical properties from 3D nanotomograms

D. Jha <sup>1</sup>, H. O. Sørensen <sup>1</sup>, D. Mütter <sup>1</sup> and S.L. S. Stipp <sup>1</sup>

<sup>1</sup>Nano-Science Center, Department of Chemistry, University of Copenhagen,  
Universitetsparken 5, 2100 Copenhagen Ø, Denmark

The study of porous materials, with an aim of determining physical properties, offers information that can be used to solve many of the real world challenges society faces today. Pore size distribution and pore network strongly influence the flow properties as well as the mechanical behaviour of the porous materials. This is important for understanding the flow of groundwater in aquifers, movement of contaminants in soil, production of oil in porous reservoirs, the flow of solutions through filtration membranes and must be understood if geological storage of CO<sub>2</sub> is to be considered. Synchrotron based high resolution tomography can reveal fine structures in porous media but at quite high resolution, the field of view is restricted. On the other hand, lower resolution tomograms give a wider field of view but compromise the contrast of micro and nanostructures in the sample.

To overcome this, we collected data at a range of resolution by linearly translating the sample along the conical beamline at ID 22, ESRF, France. Three dimensional (3D) tomograms obtained at each resolution were aligned and registered with subpixel accuracy to ensure that the same exact region was characterised. This method creates a discrete sequence of data where high resolution and wide field of view are combined. It also eliminates the influence of uncertainties that are generated from locally different micro and nanostructures and allows us to develop a method for interpolating between physical observables over a range of length scales. The trend derived from the whole set of tomograms provides information for deciding what resolution might be optimal for investigating a certain type of flow or a particular porous media structure analysis.

[1] Yu Ren *et al.* (2013), *Nature Communications*, 4-2015

[2] Z. Liang, *et al.* (2000), *Chemical Engineering Science*, 55-22, p 5247-5262

[3] B. Srinivasa Reddy, Biswanath N. Chatterji (1996), *Image Processing, IEEE Transactions on*, 5-8, pp.1266,1271

[5] We thank Finn Engstrøm for providing the chalk samples. The work was funded by Maersk Oil and Gas A/S and the Danish National Advanced Technology Foundation (P<sup>3</sup> Project), the Danish Council for Independent Research (via DANSCATT) and the European Commission (ITN FP7-MINSC).

# **Silica precipitation inside a geothermal heat exchanger reduces production of thermal energy: case study from the Hellisheiði geothermal power station**

*Daniela B Meier<sup>1</sup>, Einar Gunnlaugsson<sup>2</sup>, Ingvi Gunnarsson<sup>2</sup>, Nagitha Wijayathunga<sup>3</sup>, Caroline L Peacock<sup>1</sup>, Liane G Benning<sup>1</sup>*

<sup>1</sup>Cohen Geochemistry Group, School of Earth and Environment, University of Leeds, Leeds LS2 9JT, United Kingdom (eedbm@leeds.ac.uk)

<sup>2</sup>Reykjavik Energy, Baejarhals 1, 110 Reykjavik, Iceland

<sup>3</sup>Institute of Medical and Biomedical Engineering, School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

According to a recent report [1] only around 223 TWh of geothermal energy, both electricity and thermal energy, were produced in 2012. Besides high exploration, development and running costs, the development of geothermal resources is often limited by corrosion and scaling problems. One of the most common scaling problems in geothermal power stations world-wide is the precipitation of amorphous silica. However, there is still no universally applicable solution to mitigate silica precipitation because our understanding of the pathways and mechanisms of silica precipitation under conditions prevalent in geothermal power plants (i.e. high temperatures and high flow rates) is still in its infancy.

Here we present results from a study of silica precipitates that formed inside the heat exchanger unit used for the production of thermal energy at the Hellisheiði power station in SW Iceland. Amorphous silica precipitated over ~ 6 months from a fast flowing (400 l/s), 120°C hot solution containing around 800 ppm of SiO<sub>2</sub>. The precipitates that were removed during a routine cleaning operation were dried and characterized for composition and structural features.

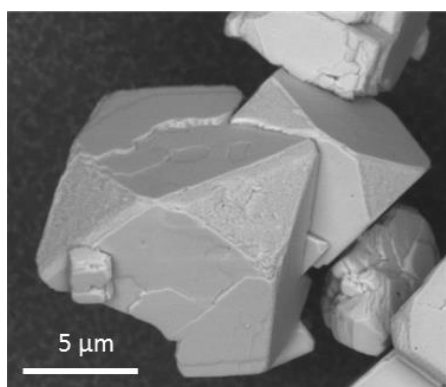
All precipitates were nearly pure amorphous silica as confirmed by X-ray diffraction and FTIR spectroscopy. Scanning electron microscopy revealed that precipitates were composed of individual spheres 0.5 to 20 µm in diameter. These small individual spheres were cemented together into larger, up to 1 mm spherical aggregates by the continual polymerization of monosilicic acid (H<sub>4</sub>SiO<sub>4</sub>). These aggregated structures had a total specific surface area of ~ 0.24 m<sup>2</sup>/g. Interestingly, nuclear magnetic resonance measurements revealed a low overall porosity of ~ 8%, but with a high proportion of pores in the nm-range, and only ~ 17% of the pores reaching ~ 0.2 µm. The silica precipitates showed very intricate three-dimensional structures that were analysed by X-ray computed tomography. Information about the 3D resolved structure of samples combined with the bulk analyses helps us quantify and likely also model better the formation processes and allows us to assess the impact of these precipitates on fluid flow through the heat exchanger. Reduction in flow due to precipitation impacts the production of thermal energy at Hellisheiði power station and both compositional and structural knowledge about these precipitates can help mitigate the costly scaling problem.

# Calcite growth inhibition: Clues for designing an amino acid based inhibitor

*G. Montanari<sup>1</sup>, L. Lakshatanov<sup>1</sup>, N. Bove<sup>1</sup>, K. Dalby<sup>1</sup> and S. Stipp<sup>1</sup>*

<sup>1</sup>Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark  
(\*giulia.montanari@nano.ku.dk)

Calcite scaling is a common problem for industrial processes where variations in water temperature or composition change the saturation state of the solid. Calcite scaling can lead to high maintenance costs and too frequent shut downs because of clogged pipelines. Additives can be used to reduce the formation of scale but these are expensive and can pose a problem for water quality. In the natural environment, acidic proteins are commonly used by organisms to control the shape of biogenic calcite, such as for mollusk shells. Proteins regulate growth and morphology, producing natural composite materials with resilient structures. Carboxylic and amino groups form the strongest bonds with the calcite surface sites. Amino acids are the basic units of the complex biomineralising protein matrix and they present the same functional groups in a much shorter chain length. The aim of this work was to investigate and quantify the effect of amino acids on calcite growth, using constant composition experiments [1]. Our goal was to improve understanding about the function of amino acids and to explore their use as additives against precipitation. We chose aspartic acid (Asp), the main component of Asp-rich proteins, glycine (Gly), the most simple amino acid, as well as polymers consisting of each of them, in order to relate molecule structure to the degree of inhibition. Asp has one carboxyl unit more than Gly, and polymers contain several functional groups in a chain. We found the Asp (poly)-amino acids to be better inhibitors for calcite precipitation than Gly. The concentrations that were needed decreased as the polymer chain length increased. The presence of carboxyl groups was essential for high surface interaction and adhesion was best when the distance between the carboxyl units along the chain fit the spacing of the surface sites. XPS (X-ray photoelectron spectroscopy) detected Asp and Gly polymers in the top 10 nm of the calcite surface, and SEM (scanning electron microscopy) show that in all cases morphology of edges and corners is changed (Figure 1). Our results suggest that an ideal inhibitor for calcite scaling would contain carboxylic groups located in a linear chain. Surface sites matching, electrostatic interactions and chain length are important parameters to be considered.



**Figure 1:** Crystal step edges roughen after introduction of 0.4 mM Asp to the calcite precipitating system.

[1] Lakshatanov et al. (2011), *Geochim. et Cosmochim. A.* **75**(14), 3945-3955.

# **Evaluation of common hydrological tracers in porous rocks through flow through column experiments**

*Prathap Moola<sup>1, 2</sup>, Andri Stefánsson<sup>1</sup>, Bergur Sigfússon<sup>2</sup>*

<sup>1</sup> Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland (snp3@hi.is)

<sup>2</sup> Reykjavík Energy, Baejarhálsi 1, 110 Reykjavík, Iceland

Tracer testing plays an important role in geohydrology and are used to study for instance groundwater flow and groundwater reservoir characteristics. Colored compounds or dyes are among common tracers used in such tests. The ideal tracer for groundwater hydrology should be non-reactive, i.e. not decompose or react with the surrounding rocks. In this study the chemical behavior of common hydrological tracers in porous rocks were studied experimentally at 25°C. Six common hydrological tracers were investigated. These were amino G acid, amino rhodamine G, fluorescein, naphthionic acid, rhodamine B and pyranine in porous rocks consisting of basaltic glass, quartz or rhyolite and at pH 3, 6.5 and 9. Flow through column experiments were conducted: The columns were filled with homogenous porous material of fixed grain size 45-125µm. Experimental solutions without tracer were pumped at fixed flow rates through the column until stable baseline was obtained. Subsequently, experimental solution with tracer was injected for 20 minutes at the same flow rate followed by experimental solution without tracer. The tracer concentration was monitored at the outlet of the column using spectrophotometer and a breakthrough curve generated. The measured breakthrough tracer curves were compared to theoretical 1-D reactive transport simulations calculated using the PHREEQC program (Parkhurst and Appelo, 1999). Based on the results, the tracers may be chemically non-reactive and/or reactive. Three groups were observed, tracers that are reactive under all conditions, tracers that are always non-reactive and tracers that are either reactive or non-reactive depending on pH and rock type. The tracers that were observed to be reactive showed indications of adsorption and desorption. The results suggest that some of the tracers commonly used in ground water tracer tests are not suitable under all conditions as they may react with the rocks of the groundwater system. The least reactive tracers from this study will be used to follow pore volume changes in future experiments.



# **The effects of time and acid supply on olivine alteration - an experimental study**

*Jan Přikryl\* & Andri Stefánsson*

Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavík, Iceland (\* [jap5@hi.is](mailto:jap5@hi.is))

The CO<sub>2</sub> cycle has been affected by anthropogenic emissions with influence on global climate. One of the possible long-term reductions of atmospheric CO<sub>2</sub> is sequestration by mineralization in the crust. Among suitable rocks for the mineral trapping are mafic and ultramafic rocks and olivine is within the main constituents of such rocks. Its dissolution releases divalent Mg<sup>2+</sup> and Fe<sup>2+</sup> ideal for carbonate formation.

Laboratory batch-type experiments were conducted to study olivine alteration in CO<sub>2</sub> rich solutions. The experiments were carried out at 150°C and saturation water vapor pressure in titanium reactors, at close to neutral pH, CO<sub>2</sub> concentration between 10 and 30 mmol/kg, using forsterite (93%) from Åheim Olivine Pit-Norway. The reaction progress and olivine alteration was subsequently studied using the solution chemistry and alteration mineralogy. The laboratory experiments were further supported by reaction path modeling. Upon water-rock interaction forsterite rapidly dissolved in the CO<sub>2</sub> rich solutions and leached divalent cations. Within 24 hours secondary mineral formation was observed. The most common minerals precipitated were magnesite and chrysotile along with brucite, ferroan magnesite and siderite. The CO<sub>2</sub> concentrations were observed to decrease upon reaction time indicating CO<sub>2</sub> mineralization. Experiments with higher initial CO<sub>2</sub> concentrations required longer time until CO<sub>2</sub> decrease was observed. According to the experimental results and the reaction modeling olivine progressively dissolved forming secondary minerals and solutes. The exact reaction path was found to depend on solution composition, pH and reaction progress (time). Initially the pH is buffered by CO<sub>2</sub> and characterized by H<sup>+</sup> uptake and elemental release during olivine dissolution. Upon progressive rock dissolution secondary minerals like carbonates become saturated and mineralized. This results in decreased CO<sub>2</sub> concentration and eventually increase of the solution pH accompanied with Mg-silicate mineral formation.

# How carbon-chains could help mitigate mineral scaling

Taher Rabizadeh, Caroline L. Peacock, and Liane G. Benning

Cohen Geochemistry Laboratory, School of Earth and Environment, University of Leeds, UK LS2 9JT

(eetr@leeds.ac.uk)

In several industrial processes that rely on water handling systems (e.g., oil or geothermal energy production, water desalination), the precipitation of mineral scales leads to costly problems including pipeline or membrane clogging. The use of additives to retard mineral formation is a promising approach to mitigate industrial scaling, but the two main requirements for a ‘good’ inhibitor [1], namely their efficiency at low concentrations and their biodegradability (green inhibitors), are only poorly constrained.

Here we report results from a study on the nucleation and growth kinetics, as well as the structure and morphology of calcium sulfate scale minerals that were precipitated in the presence and absence of low concentrations (0-20 ppm) of ‘green’ additives of carboxylic and polyepoxysuccinic acids. Nucleation and growth reactions from solution were followed *in situ* and in a time-resolved manner through changes in turbidity and conductivity, while the solid products were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The results indicate a clear interdependency between additive type and concentration and induction time for the formation of calcium sulfate phases. In the case of carboxylic acids, at equivalent concentrations the most effective inhibition (longer induction time) was achieved with citric acid followed by maleic and tartaric acid [2]. Compared to the additive free system, the presence of 20 ppm of tartaric, maleic and citric acid increased the induction time from 6 min to 9, 16 and 25 minutes. However, by far the most effective inhibitor was polyepoxysuccinic acid, which outperformed all carboxylic acids and at 20 ppm delayed the induction of the reaction to 260 min. This additive clearly inhibited mineral precipitation by at least 40 fold compare to the additive free  $\text{CaSO}_4$  system.

When the solids that caused the turbidity were analysed, the XRD patterns revealed that in all cases at the beginning of the reaction the hemihydrate bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) precipitated first. With time and depending on additive concentration the hemihydrate bassanite transformed to the dihydrate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) but a clear link between additive type and additive concentrations and bassanite stabilization was evident. Imaging the solid intermediates and end products also demonstrated that some of the additives also changed the shape and size distribution of the solid products, however these effects are still under study.

[1] Lioliou *et al.* (2006), *Journal of Colloid and Interface Science* **303**, 164-170

[2] Rabizadeh *et al.* (2014), *Mineralogical Magazine*, in review

# Si isotope fractionation during the dissolution of quartz, opal-CT, diatomite, and amorphous SiO<sub>2</sub>

Thomas RINDER<sup>1</sup>, Eric H. OELKERS<sup>1,2</sup> And Thomas ZAMBARDI<sup>3</sup>

<sup>1</sup>GET/CNRS, 14 avenue Édouard Belin, 31400, Toulouse, FRANCE (rinder@lmtg.obs-mip.fr)

<sup>2</sup>Earth Sciences, UCL, Gower Street, London, UNITED KINGDOM

<sup>3</sup>Dpt. of Geology, Univ. of Illinois Urbana-Champaign, IL, USA

During CO<sub>2</sub> sequestration in Iceland acidic solutions are injected into basaltic rocks, promoting dissolution and shifting the pH up allowing the formation of secondary carbonates. However such a pH increase will also favour the reprecipitation of Fe and Al dissolved from the primary minerals – a process which might negatively influence the rates of mineral carbonation by the formation of passivating Al/Fe-hydroxide coatings on the dissolving phases. The accompanied adsorption of Si on these hydroxides produces a positive shift in the Si isotopic signatures of the remaining solution [1]. Therefore fluid Si isotopic signatures might be applied to monitor injection sites, identify the formation of such detrimental secondary phases and help to take suitable countermeasures.

In an attempt to quantify this fractionation process opal-CT, quartz, diatomite, and amorphous SiO<sub>2</sub> were dissolved at 70 °C and pH 3 and 9 in closed system batch reactors (I = 0.1) for up to several months, allowing reprecipitation as the solutions reach equilibrium. The isotopic composition of the Si released from quartz is identical within uncertainty to that of the dissolving mineral. In contrast, the Si initially released from opal-CT, diatomite and amorphous SiO<sub>2</sub> dissolution at pH 3 is isotopically light but that initially released at pH 9 is isotopically heavy compared with the solid and this fractionation is significantly higher in samples containing aluminium. With time, the Si isotopic composition of the fluid phase at pH 9 converges attaining a stationary state with  $\delta^{30}\text{Si}$  values between 0 to 0.3‰ heavier than the initial solid, as the the dissolved Si concentration approaches equilibrium. The observation that a single steady-state aqueous fluid-solid Si fractionation value is attained by distinct pathways depending on fluid pH is consistent with the two way transfer of material during dissolution as equilibrium is approached [2]. Moreover, the distinct Si fractionation behaviour observed for aluminium containing and pure phases may provide a useful tool for monitoring reprecipitation processes in carbon injection sites.

[1.] Delstanche, S., et al. (2009), *Geochimica et Cosmochimica Acta*, **73**(4): p. 923-934.

[2.] Pearce, C.R., et al. (2012), *Geochimica et Cosmochimica Acta*, **92**(0): p. 170-183.

## Study of BaSO<sub>4</sub> crystallization by TEM

Cristina Ruiz-Agudo <sup>(1)\*</sup>, Christine V. Putnis <sup>(1)</sup>, Encarnación Ruiz-Agudo <sup>(2)</sup> and Andrew Putnis <sup>(1)</sup>

(1) Institute for Mineralogy, University of Münster, Corrensstrasse 24, 48149 Münster, Germany.

(2) Department Mineralogía y Petrología, Universidad de Granada, Fuentenueva s/n, 18071 Granada, Spain

\*c\_ruiz02@uni-muenster.de

Precipitation of barite (BaSO<sub>4</sub>) causes major problems in numerous industrial processes. In oil recovery, barite scale forms as a result of the mixing of injection water (mainly seawater) and formation water (water in the pores of the reservoir rock). Barite can be problematic due to its low solubility and hardness and so can affect oil recovery with subsequent high costs. The mechanisms of barite nucleation and growth at the early stages are still unclear and this poses a problem in the design of preventive methods to reduce the damaging consequences associated with scale formation. The addition of trace amounts of additives that inhibit barite precipitation is the most used strategy to reduce scale formation. The effectiveness of these inhibitors depends on numerous parameters, such as pH, temperature and concentration. Inhibitors can affect different stages of the precipitation process (e.g. blocking active growth sites at the surface, sequestering the scale-forming metal ion, influencing the type of amorphous phase or crystalline polymorph formed, as well as promoting solid-cluster formation (Gebauer et al., 2009)).

Numerous recent studies on the precipitation of several minerals, e.g. calcite (Gebauer et al., 2008), gypsum (Van Driessche et al., 2012), magnetite (Baumgartner et al., 2013) and iron oxyhydroxide (Li et. al 2012) have been shown to precipitate following a non-classical crystallization process. The aim of our present work was to gain a better understanding of the early stages of BaSO<sub>4</sub> precipitation with the objective of choosing the most suitable inhibitors to reduce barite scale formation. With this purpose, barite was precipitated by mixing BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> solutions. The process was quenched with ethanol at different times and the particles obtained were observed ex-situ using Transmission Electron Microscopy. We found the initial formation of nanometer-size (5-10 nm) particles that fuse in an oriented way to form larger particles. Two hierarchical levels of aggregation were observed: first, the aggregation of 5-10 nm particles to form larger, but still nanometer-sized (20-60 nm) particles. In a second stage, these latter particles aggregate (200-500 nm) and later transform into larger single crystals. No evidence of an amorphous precursor phase previous to crystalline barite was found. Our findings have implications for the design of scale prevention methods, especially in the selection of the most suitable scale inhibitor.

- Gebauer D., Cölfen H., Verch A. and Antonietti M. (2009) The multiple roles of additives in CaCO<sub>3</sub> crystallization: a quantitative case study. *Adv. Mater.* 21, 435–439.

- Gebauer D., Völkel A. and Cölfen H. (2008) Stable prenucleation calcium carbonate clusters. *Science* 332, 1819-1822.

- Van Driessche A.E.S., Benning L.G., Rodriguez-Blanco J. D., Ossorio M., Bots P. and García-Ruiz J. M. (2012) The role and implications of bassanite as a stable precursor phase to gypsum precipitation. *Science* 336, 69-71.

- Baumgartner J., Dey A., Bomans P. H. H., Le Coadou C., Fratzl P., Sommerdijk N. A. J. M. and Faivre D. (2013) Nucleation and growth of magnetite from solution. *Nature* 12, 310-314.

- Li D., Nielsen M.H., Lee J.R.I, Frandsen C., Banfield J.F. and De Yoreo J.J.(2012) Direction-Specific Interactions Control Crystal Growth by Oriented Attachment. *Science* 336, 1014-1018.

# Precipitation of CaCO<sub>3</sub> in microemulsions

Tomasz M. Stawski\*,<sup>1</sup> Adriana Matamoros Veloza,<sup>1</sup> Teresa Roncal-Herrero Teresa,<sup>2</sup>  
Roland Kröger,<sup>2</sup> Liane G. Benning<sup>1</sup>

<sup>1</sup>School of Earth & Environment, University of Leeds, LS2 9JT, UK (\*[t.m.stawski@leeds.ac.uk](mailto:t.m.stawski@leeds.ac.uk));

<sup>2</sup>Department of Physics, University of York, York, YO10 5DD, UK

Calcium carbonate is probably the most ubiquitous functional biomineral in nature. Its biomineralization by microscopic organisms underpins a vast array of Earth system processes, including carbon cycling. Living organisms direct the precipitation of CaCO<sub>3</sub> from simple aqueous ions with an unprecedented level of control. For example, the cocolithophores that mineralize CaCO<sub>3</sub> plates do so in vesicles produced in the Golgi apparatuses of their cells. The plates exhibit a high level of structural complexity and reproducibility. These microstructures indicate complicated, but controlled chemical routes between dissolved ions and final morphologies. If only chemists were able to elucidate and mimic, the mechanisms of such biomineralization, not only would we gain knowledge about some of the most important processes that support a big array of marine planktonic life forms, but we would also acquire a powerful tool to *engineer* inorganic materials.

Wet-chemical routes for inorganic nanoparticles utilising water-in-oil microemulsions increasingly gain interest in colloid chemistry. They offer a confined reaction environment ideal for synthesis of nanoparticles of low polydispersity and well-defined shapes. Water-based micelles stabilised by an interface surfactant are typically 1-10 nm in diameters and each can carry dissolved salt ions and exchange their contents upon collision. Thus, they are well-suited for mimicking the nanoscale mineral precipitation at the polar/non-polar interface. We use such microemulsions as a bioinspired nanoreactor system for mineralization of e.g. coccolith frustules. We follow reactions between two separate initially clear microemulsions, one containing Ca<sup>2+</sup> and the other CO<sub>3</sub><sup>2-</sup> ions and quantified the gradual development of a white precipitate using *ex situ* and *in situ* high-resolution imaging, diffraction and scattering.

The results from the *ex situ* methods revealed stabilised nano-sized (Ø ~10 nm) particles of low-polydispersity forming larger aggregates (Ø ~250 nm). However, the morphology of the particles when quantified *in situ* (i.e., micellar mixtures in the liquid phase) was considerably different. Time-resolved and *in situ* small angle X-ray scattering demonstrated that the particles grew through a slow but progressive agglomeration of ion-carrying micelles to larger mass-fractal-like stable structures of high fractal dimension (Ø ~ 100 nm,  $D_f > 2.8$ ). This *in situ* scattering data when combined with liquid-cell TEM results suggested that upon destabilization of the mass-fractal-like structures, a transformation from initially stable micelle-sized structural units to larger particles took place.

By combining these results with the fact that an individual micelle can accommodate in its water core only a limited number of reacting ions, we hypothesize that these micellar mass-fractal-like aggregates likely contain only liquid-like CaCO<sub>3</sub> complexes stabilised by the confinement and interfaces and not CaCO<sub>3</sub> solid particles *per se*. Only once the micellar large aggregates are destabilized is crystallization induced.

# Evaluation of barite solubility data at oil reservoir conditions using the Pitzer ion interaction approach

*B.Y. Zhen-Wu<sup>1</sup>\*, K. Dideriksen<sup>1</sup>, D.A. Belova<sup>1</sup>, S.L.S. Stipp<sup>1</sup>*

<sup>1</sup> Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen, Denmark

(\*email: biyun.zhen@nano.ku.dk)

Barite ( $\text{BaSO}_{4(s)}$ ) can precipitate as scale in production wells when sea water is injected into a reservoir to enhance oil recovery. Scaling is a problem in pipes and in the pores of reservoirs. We reviewed data for barite solubility at ionic strength ranging from 0 to 5 molal, temperature, from 25 to 250 °C, and pressure, from 1 to 500 bar. Our intention was to assess the consistency of the Pitzer.dat database in the geochemical speciation code PHREEQC (Version 3) and the Multiscale code (Version 8) by comparing calculated values with published experimental solubility data. Our results with both databases showed that at 1 bar, the differences for barite solubility increase as ionic strength increases, reaching differences of as much as 23 to 41%. Notably, the discrepancies increase with the database of PHREEQC at temperatures above 80 °C. The difference between calculated and measured solubility as a result of change in pressure (at 95 °C and 4 molal) is relatively small with the PHREEQC database (14-26%) but it is significant with the Multiscale database (88-110%).

More detailed calculations of barite solubility and activity coefficients for barium ( $\text{Ba}^{2+}_{(aq)}$ ), sulphate ( $\text{SO}_4^{2-}_{(aq)}$ ) and mean barium sulphate ( $\text{BaSO}_{4(aq)}$ ) in sea water and formation water brines were made at the conditions typical for oil reservoirs. At 150 °C and 350 bar, the differences in activity coefficient calculated with the two databases for  $\text{Ba}^{2+}_{(aq)}$  range as much as 12% but for both  $\text{SO}_4^{2-}_{(aq)}$  and mean  $\text{BaSO}_{4(aq)}$ , they vary by as much as 50%. The Pitzer binary ion interaction parameters compiled in the databases for  $\text{BaSO}_{4(aq)}$  are either estimated from thermodynamic data for  $\text{CaSO}_{4(aq)}$  or set to a value of zero. Our study makes it clear that the Pitzer ion interaction parameters for the barite system require reassessment. A critical analysis is needed to determine the causes of the large discrepancies, especially for the sulphate activity coefficient.