Feasibility of In Situ Sequesteration of Toxic Metals in Flowback Water from Hydraulic Fracturing.

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Introduction

- Subsurface fluids produced as wastewater in hydrofracturing activities, particularly from shale formations, are resulting in significant amounts of produced toxic and radioactive metal contaminants, [1-5] such as barium and radium.

- Barium (Ba^{2+}) is a toxic metal present in some produced oil and gas field waters at levels of several thousand mg/L,[6,2] far exceeding the EPA Maximum Contaminant Limit (MCL) of 2 mg/L.

- Radium is the primary Naturally Occurring Radioactive Material (NORM) in these fluids.[3,4] Some produced water from wells in the Marcellus shale (PA) contain up to 18,000 pCi/L dissolved radium (Ra^{2+}),[6] far exceeding the MCL of 5 pCi/L.

- Barite ($BaSO_4$) 'scales' in wellhead and borehole equipment can also be radioactive due to radium incorporation.[2]

Figure 1. Barite scale in a pipe used to carry oil. (http://theoildrum.com)

- Current practice is to treat the contaminants in produced waters on the surface, but municipal and industrial water treatment plants are not currently equipped to deal with some of the contaminants.[7] Instead of above-ground treatment, a possible strategy may be to induce precipitation of mineral phases containing the contaminants directly in the subsurface, reducing treatment of flowback water at the surface.

What are the sources of the metals?

- Barite is present in Marcellus shale and related formations as nodules, veins, replacement crystals. Its sulfur and oxygen isotope ratios don't match seawater. Its source could be from hydrothermal springs during early diagenesis and has been remobilized.[8]

- Radium is a product of radioactive decay of uranium, which in turn is enriched in shales, likely caused by the shale's reducing environment (uranium reduction causes precipitation of UO_2) and high organic matter (which complexes uranium).
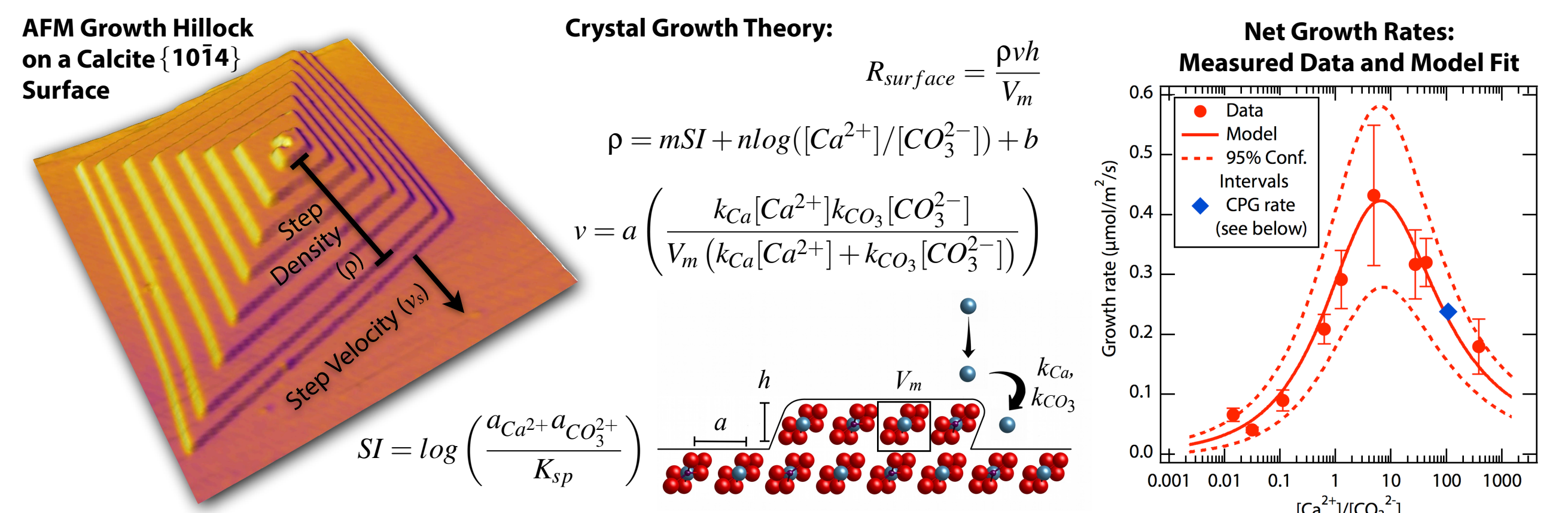
Can we induce precipitation to reduce toxic metals?
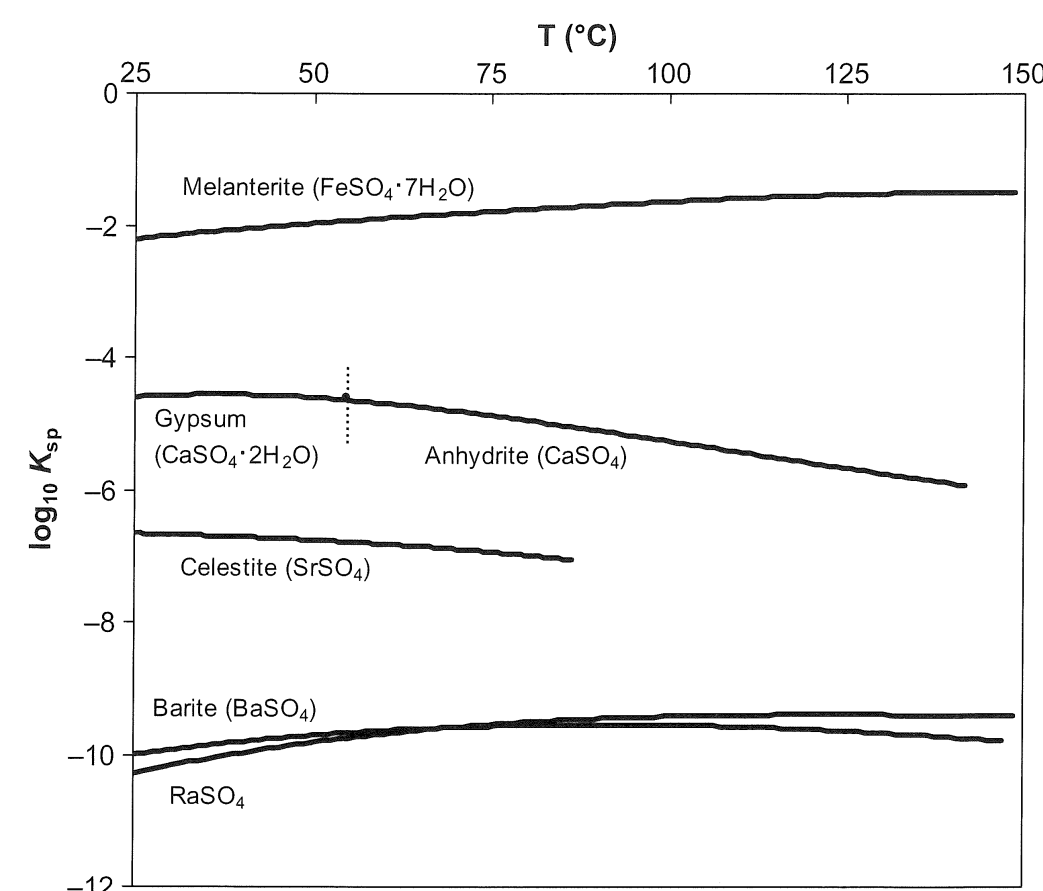
Figure 2. Logarithm of the solubility product (K_{sp}) of sulfate minerals as a function of temperature. Barite and $RaSO_4$ have very low solubilities.[9]
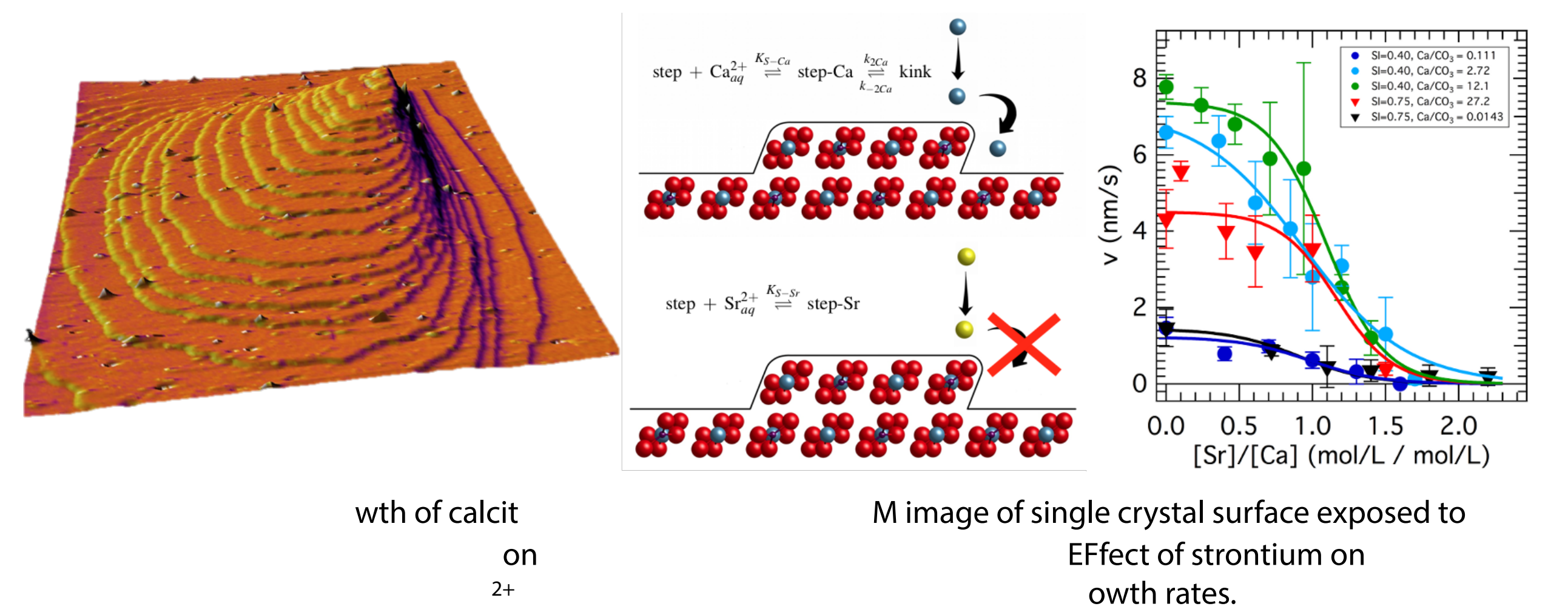
- Barium and radium sulfates have very low solubilities (Figure 2).

- Radium readily substitutes for barium in barite. The mobility of Ra^{2+} is entirely dominated by a disordered $(Ra,Ba)SO_4$ barite phase.[10]

- Evaporation followed by crystallization has been used as an above-ground treatment strategy, but not for hydraulic fracturing flowback water.[11] This method has high energy costs and large capital costs.[5]

- These costs may be reduced substantially for in situ sulfate mineral precipitation. This is due to the low solubilities of barium and radium sulfates, and that the flowback waters are high in cations but low in sulfate, indicating sulfate concentration is limiting precipitation (Table 1).

- In situ sequestration has been proposed for other types of contamination, e.g., strontium and uranium.[12,13]

- The key for in situ precipitation is the rate of reaction. A precipitation that occurs too rapidly after injection will clog porosity near well screens and reduce permeability,[14,15] a precipitation rate that occurs too slowly will not remove the contaminants before the flowback water is brought to the surface. This will lead to scale formation and require above-ground treatment.

- Precipitation rate depends on both saturation state and the aqueous cation-to-anion ratio (Figure 3).[16,17]

- Traditional geochemical models don't account for this, they only consider saturation state.

Table 1: Example Flowback Water Compositions[5]

Constituent	Low[2] (mg/L)	Medium[2] (mg/L)	High[3] (mg/L)
Total dissolved solids	66,000	150,000	261,000
Total suspended solids	27	380	3200
Hardness (as $CaCO_3$)	9100	29,000	55,000
Alkalinity (as $CaCO_3$)	200	200	1100
Chloride	32,000	76,000	148,000
Sulfate	ND[5]	7	500
Sodium	18,000	33,000	44,000
Calcium, total[4]	3000	9800	31,000
Strontium, total	1400	2100	6800
Barium, total	2300	3300	4700
Bromide	720	1200	1600
Iron, total	25	48	55
Manganese, total	3	7	7
Oil and grease	10	18	260
Total radioactivity	ND[5]	ND	ND

Case Study: Calcite growth rates.

$$R_{surface} = \frac{\rho v h}{V_m}$$

$$\rho = mSI + nlog([Ca^{2+}]/[CO_3^{2-}]) + b$$

$$v = a\left(\frac{k_{Ca}[Ca^{2+}]k_{CO_3}[CO_3^{2-}]}{V_m\left(k_{Ca}[Ca^{2+}] + k_{CO_3}[CO_3^{2-}]\right)}\right)$$

$$SI = log\left(\frac{a_{Ca^{2+}}a_{CO_3^{2-}}}{K_{sp}}\right)$$

Figure 3. New mineral precipitation model.[18] **Left)** Growth rates of $CaCO_3$ are measured on single crystals using the atomic force microscope (AFM). The velocities and densities of monomolecular steps are measured. **Center)** These are combined into a model that predicts rates of growth per unit surface area. **Right)** Measured data points and model prediction, along with 95% Confidence Intervals and growth rate in porous media.

- Process-based precipitation models can successfully predict the dependence of growth rate on changing cation-to-anion ratio.

- Other ions in solution can poison growth of certain phases, e.g., strontium inhibits growth of $CaCO_3$ when the $[Sr^{2+}]/[Ca^{2+}] \gtrsim 1$ (Figure 4). **Will flowback water compositions inhibit growth of $(Ra,Ba)SO_4$?**

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M image of single crystal surface exposed to EFfect of strontium on owth rates.

- How do the components of the fracturing fluid affect precipitation rates? These include viscosity modifiers, scale inhibitors, proppants etc. Scale inhibitors in particular will likely not be possible to use for an in situ precipitation technique. **How will this affect scale formation of other phases (such as $CaCO_3$)?**

The effects of pores on precipitation.

- Precipitation in porous media may be affected by the size of the pores in which the precipitation is occurring (Figure 5). Permeability will be most impacted by precipitation in larger pores. **How will precipitation be affected in shales?**
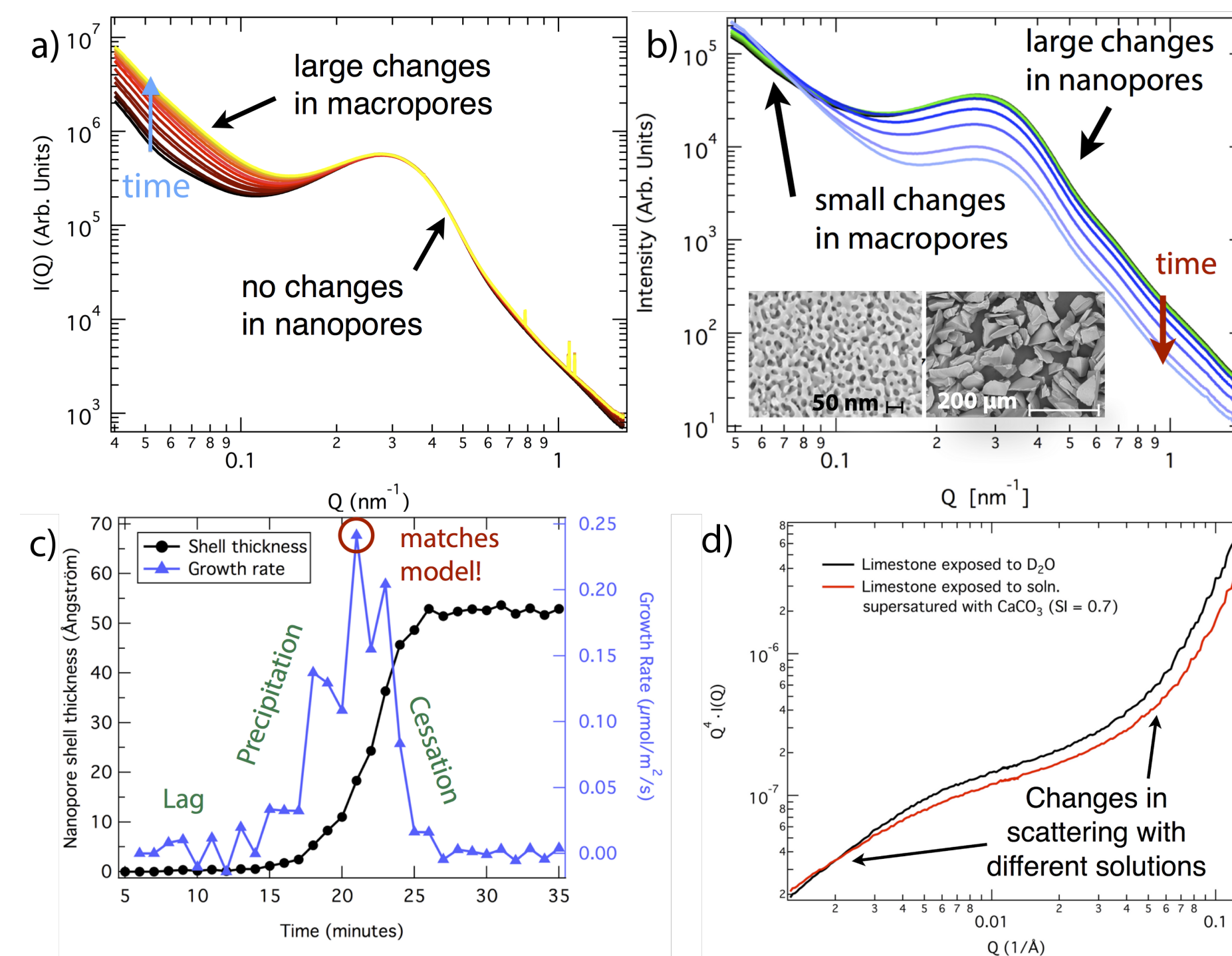
Figure 5. Small Angle X-ray and Neutron Scattering (SAXS, SANS) of $CaCO_3$ precipitation in pores.[20] **a)** SAXS data in controlled pore glass (CPG), an amorphous silica with well defined nanopores and intergranular spaces (macropores). **b)** CPG functionalized with a anhydride-terminated self assembled monolayer, known to promote nucleation. Precipitation is observed in nanopores. **c)** Modeling of results from **b**, whose maximum rate matches AFM model (Figure 4). **d)** SANS of precipitation in limestone, which behaves similarly to **b**.

Summary

- While preliminary data is encouraging, many questions remain before the feasibility of in situ precipitation can be established. These include the effects of other dissolved species in the flowback water, the composition of the flowback water itself, and the effects of pores.

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