

Supplement: Effect of laser induced heat on celestine dissolution

Typical temperature increase for a laser power of 300 mW lies between 50°C to 100°C depending on the nature of sample Johansson et al [1]. Consequently, the temperature rise for a 50mW laser can be expected to vary between 5°C to 10°C, we therefore considered a temperature increase of 7°C during our evaluation below. To assess the effect of the laser-induced heat on celestine dissolution in our experiment, we consider a cube-shaped celestine crystal with an edge length of 10 μm and an initial volume $V_0 = 1000 \mu\text{m}^3$, which is allowed to dissolve in pure water. We evaluate the temporal evolution of the ratio of the volume of the crystal at a given time V_t to the initial volume V_0 , considering the kinetic parameters (i.e. reaction rates) for celestine dissolution reported in Dove and Czank[2]. In this calculation, a roughness factor of 0.16 was assumed to fit the V_t/V_0 of celestine in experiment A reported in Fig. 6. A roughness factor (i.e. ratio of reactive surface area to actual surface area) <1 is mainly explained by the hydrological accessibility.

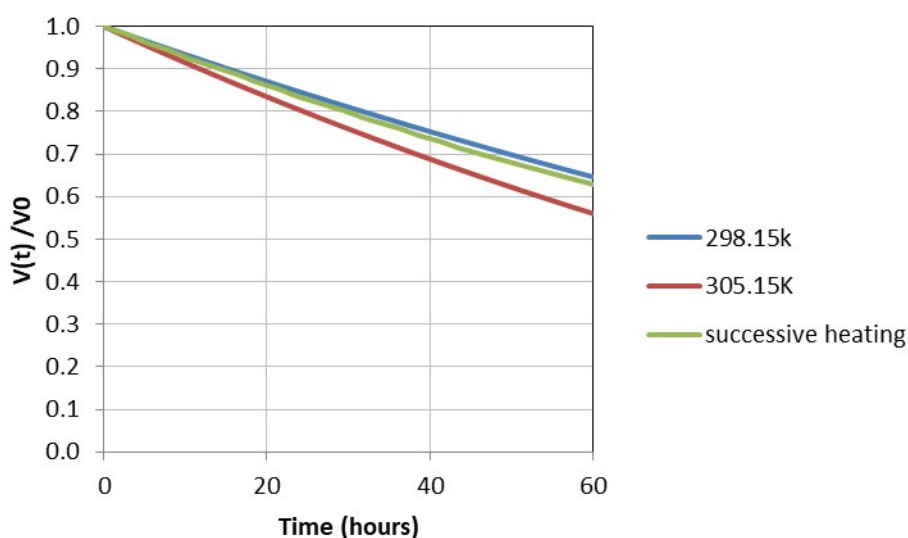


Fig. S1: Dissolution of a cube-shaped celestine crystal (initial edge length 10 μm) at 298.15 K and 307.15K as function of time, expressed a ratio between the volume at time t (V_t) and the initial volume (V_0). [1]. The successive heating refers to the alternating temperatures room temperature and temperature of 305.15K (during the mapping).

As shown in Fig. S1, a fictitious temperature increase of 7 °C would increase of the volume of 13.7% over a period of 60 hours. However, our repeated Raman mappings lasted only for 100 minutes within the experimental duration of 60 h; therefore the experiment was not constantly heated. If we consider the 8 Raman mappings conducted for experiment A and successively alternating temperatures and thus dissolution kinetics, we obtain an increase in dissolution on a single grain of 2.7% compared to constant temperature conditions, which is acceptable. Although the Raman tomography required a much longer time (9 h), the impact on celestine dissolution is thought to be marginal, because the measurements were conducted at the beginning of the experiment, when the pore solution was already saturated with respect to celestine and at the end of the experiment, respectively, when the pore solution was stagnant (no leaching process). Overall, the slight enhancement of celestine dissolution due to the temporal temperature increase induced by the Raman measurements is deemed not to be significant in

the evaluation of the porosity and the total volumes of the minerals present in the system after reaction.

Reference

- 1 Jonas Johansson, Staffan Pettersson, Lynne S. Taylor, Infrared imaging of laser-induced heating during Raman spectroscopy of pharmaceutical solids, *Journal of Pharmaceutical and Biomedical Analysis*, Volume 30, Issue 4, 2002, 1223-1231, ISSN 0731-7085, [https://doi.org/10.1016/S0731-7085\(02\)00461-2](https://doi.org/10.1016/S0731-7085(02)00461-2).
- 2 P. M. Dove and C. A. Czank, *Geochimica et Cosmochimica Acta*, 1995, **59**, 1907-1915.