## EFFECTS OF BACTERIAL SIDEROPHORE AND BIOFILM SYNTHESIS ON SILICATE MINERAL DISSOLUTION KINETICS: RESULTS FROM EXPERIMENTS WITH TARGETED MUTANTS. M. D.

Van Den Berghe<sup>1</sup>, A. J. West<sup>1</sup> and K. H. Nealson<sup>1</sup>. <sup>1</sup>Department of Earth Sciences, University of Southern California (3651 Trousdale Pkwy, Los Angeles, CA, 90089, <u>mdvanden@usc.edu</u>).

With metal ions forming the catalytic center to countless critical biochemical reactions, it might be expected that the emergence of continuous, selfsustaining autocatalytic reactions that form life is linked to early interactions between mineral substrates and sorbed organic compounds [1,2]. Biomoleculemineral sorption interfaces are further suggested to enhance mineral dissolution and elemental release [3]. Notably, many microorganisms synthesize siderophores, organic compounds with extremely high ironbinding affinities, in order to isolate iron and improve its acquisition. However much remains unknown about siderophores' role in the release of iron contained in silicate minerals, and thus their impact on dissolution kinetics [4]. Many bacteria also form thick, redoxactive biofilms on mineral surfaces in order to create micro-environments favorable for growth, which role is also unclear with respect to silicate mineral dissolution [5]. These combined effects however suggest active mechanisms of nutrient acquisition directly from mineral phases, processes so far largely overlooked and poorly understood. Constraining siderophore and biofilm influences on mineral phases therefore has the potential to answer long standing questions about the biological controls on silicate weathering, the metabolic potential driving bacteria-mineral interactions, as well as the limits of life in ocean and sub-surface environments, and the coevolution of life and Earth.

Our current research is aiming to characterize and quantify the effects of bacterial siderophore and biofilm synthesis on the dissolution kinetics of silicate minerals. We have adopted a new approach to this problem, using targeted gene deletion mutants on environmentally relevant bacteria (S. oneidensis and P. aeruginosa) in order isolate specific metabolic effects on bacteria-mineral interactions. Batch experiments with S. oneidensis wild type (MR-1) and a siderophore synthesis gene deletion mutant strain, both grown in iron-deplete minimal media amended with olivine as sole source of iron, show a pronounced growth penalty for the siderophore deletion mutant. P. aeruginosa can however synthesize centimeter-thick, multi-layered redox-active biofilms, and preliminary experiments with wild type (PA-14) and a siderophore synthesis gene deletion mutants, also grown in iron-deplete minimal media amended with olivine, show no growth penalty for the gene deletion mutant. Dissolved silicon concentrations, measured as a proxy for olivine dissolution, also increased in growth experiments for both *P*.

aeruginosa strains. Both *P. aeruginosa* and *S. oneidensis* wild types also show higher growth and dissolved silicon concentrations when grown in glass flasks as opposed to Polytetrafluoroethylene flasks, suggesting they are facilitating active dissolution of the glass flasks.

These results strongly suggest that mineral phases can act as a substrate supporting bacterial growth, and that siderophores can act as an effective mechanism for bacteria to dissolve and acquire micronutrients directly from mineral, and even glass, phases. Thick, multilayered, redox-active biofilms can also have abrasive qualities that can lead to mineral dissolution and nutrient release, supporting microbial growth even in the absence of siderophores. The precise mechanisms involved in biofilm-driven mineral dissolution may include extra-cellular electron shuttles such as phenazines, and secondary metabolites such as lactate, pyruvate, malonate or ketogluconic acid, all products of glucose metabolism and fermentation [5], known to act as effective surface sorbents [6]. Such metabolites may be found in very high concentrations in biofilms and may further contribute to mineral dissolution. These experiments thus point to the potentially high importance of biofilms as possible hot-spots of mineral dissolution. Our ongoing research will further characterize and quantify these processes through advanced metabolomics and imaging experiments, as well as identify them in the natural, limiting environment of oceanic crustal fluids.

## References:

- 1 Belmonte, L. and Mansy, S.S. (2016) *Elements* 12, 413–418
- 2 Hazen, R.M. and Sverjensky, D.A. (2010) *Cold Spring Harb. Perspect. Biol.* 2, a002162–a002162
- 3 Kraemer, S.M. (2005) *Rev. Mineral. Geochem.* 59, 53–84
- 4 Dhungana, S. and Crumbliss, A.L. (2005) *Geomicrobiol. J.* 22, 87–98
- 5 Glasser, N.R. et al. (2014) Mol. Microbiol. 92, 399–412
- 6 Stumm, W. (1995) *Aquatic Chemistry* 244 (Huang, C. P. et al., eds), pp. 1–32, American Chemical Society.