

Geochemical complexity and emerging organisation in alkaline lakes

RAPHAEL PIETZSCH^{1,2} AND NICHOLAS J. TOSCA³

¹University of Oxford

²Petrobras

³University of Cambridge

Presenting Author: pietzsch@ymail.com

Natural systems are often highly complex. Cascading events arising from kinetic effects may be conserved and propagated through time, generating self-organised macroscopic patterns [1]. However, thermodynamics is never violated. It is simply that multiple competing forces often induce natural systems to slowly evolve from one point to another constrained within sub-systems imparting fewer degrees of freedom. This can be symbolically seen as troughs and peaks in a multidimensional landscape [2]. In other words, natural systems are usually only allowed to move to its closest point of local equilibrium [1]. A good tangible example is the “simple” CaCO₃-aqueous system in supersaturated, alkaline lake environments, clearly far from equilibrium with respect to some CaCO₃ polymorphs. In these settings, supersaturated calcite does not seem to precipitate directly [3]. Instead, its metastable precursor phases, monohydrocalcite (MHC) or amorphous CaCO₃ phases usually form first. Furthermore, other metastable precursors, such as aragonite and vaterite, may be prevented to form entirely [4], reflecting the chemical conditions of the solution and thereby the degrees of freedom accessible to the system. In our study, we expand on these observations and undertake a comprehensive database mining comprising the fluid chemistry of alkaline lakes from around the world and test experimentally the effects of supersaturation (Ω) and inhibitor concentration (ΣPO_4) aiming to reproduce the observed trends in natural environments. Our investigations are corroborated with theoretical predictions and empirical observations that have shown crystal growth and specific polymorphs respectively, to develop and to form under well-defined ranges of supersaturation and concentration of other interfering ions [5]. However, challenges to improve experimental and theoretical kinetic predictions remain. Particularly, reducing uncertainties and acquiring better estimations of interfacial free energies of various face specific and CaCO₃ polymorph phases will aid in determining the effects of “contingencies”, such as in heterogenous growth or nucleation from solution, which define the macroscopic expression of the final mineral products.

[1] Prigogine (1978), *Science* 201, 777–785. [2] Walther (2020), *Adv Mater* 32, 1905111. [3] Fukushi & Matsumiya (2018), *ACS Earth Space Chem* 2, 735–744. [4] Myszka et al. (2019), *RSC Advances* 9, 18232–18244. [5] Knight et al. (2023), *GCA* 12942.