Geochemical and bacterial evidence for 9800 years of meromixis and euxinia in alpine Lake Cadagno

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Lake Cadagno is a meromictic high-alpine lake in the southern Alps of Switzerland (1921 m asl, 0.26 km^2, max. water depth 21 m). The inflow of sulfate-rich waters from subaquatic springs located in dolomitic bedrock results in a permanent chemocline at 10 to 13 m water depth with sulfidic conditions in the hypolimnion [1]. As yet, it is unknown how far back in time euxinia has prevailed in the Lake Cadagno water column, maintaining a diverse anaerobic community of bacteria at and below the redox-transition zone.

Here, we present results documenting the lake's redox-state evolution through the Holocene period using sediment cores (10.5 m) that cover the past ~12,000 years and applying sedimentological, geochemical and molecular analyses.

Trace metal analysis by XRF core scanning and ICP-MS measurements documents the transition from oxic conditions after the lake formation (~12,000 cal yr BP) to sulfidic conditions at 9800 cal yr BP. Part of this transition is a ~1000-year period with enhanced accumulation of Mn (up to 5.9 wt% of Mn) in the sediments, indicating an intermediate oxygenation state with fluctuating redox conditions. We propose that the high Mn concentrations are the result of Mn^{2+} leaching from the sediments during reducing conditions and subsequent rapid precipitation of Mn-oxide minerals during episodic and short-term mixing events. Thereafter, a stable chemocline formed and sulfidic conditions, documented in the sediments by high Mo burial rates (Mo concentrations of up to 470 ppm) [2], prevailed until modern times without any lasting hypolimnetic oxygenation. The onset of euxinia probably corresponds in time to the actuation of the subaquatic springs after the last glacial termination.

The evidence of a stable and persistent chemocline over ~10 kyr in Lake Cadagno offers the framework to study the evolution of anaerobic bacterial communities in an extreme lacustrine environment that could serve as an equivalent for conditions in ancient oceans.

[1] Del Don *et al.* (2001) *Aquat. Sci.* **63**, 70-90. [2] Dahl *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 144-163.

A general quasi-chemical solution model for ordered many-component systems

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As first principles quantum mechanical techniques have developed to take advantage of increasing computational power, theoretical mineral physicists have begun to turn their attention toward more realistic systems with greater compositional complexity. While it is now possible to use density functional theory to calculate Gibbs energies of both crystal and liquid solutions composed of many compositional end-members, we will forever be limited by the exponential growth of the parameter space with each added component. Resigned to only sparsely sampling such large many-dimensional composition spaces, we must therefore rely on accurate, and ideally predictive, solution models to interpolate into the large intervening spaces between data points.

In this talk, we will present a new quasi-chemical model that can be used to accurately describe the Gibbs energy surface for many component solutions in addition to providing a physically-based method for projecting into the interior of the many-component space. Our model is a union and extension of the work presented on the polynomial solution model in Saulov (2006) and on the modified associates model in Saulov (2009) [1, 2]. In particular, we have adapted this quasi-chemical model, which is carefully constructed to avoid violating entropy constraints, and applied it to describe the locally ordered regions of solutions. By fitting the model to data along the bounding binaries of the system, we can estimate the non-ideal Gibbs energy cost associated with having local n-body regions in the solution of mixed composition. We have further developed and fully generalized a probabilistic projection method, extending Saulov (2006) to many dimensional systems with Gibbs energy surfaces of realistic complexity, which uses the derived set of binary models to project inside the ternary, quaternary, or higher dimensional space. Because the model is physical rather than merely geometric, it has considerably more predictive power than other commonly used projection methods like the Kohler or Muggianu models [3]. Also, we incorporate a statistically rigorous probability weighting scheme, which straightforwardly produces error estimates on the resulting Gibbs energy surface while enabling mixed compositional data to be incorporated and later used to update model parameters.

We will also discuss the strengths and limitations of the model, by applying it to a number of example solid and liquid solutions. For the liquid solutions, we discuss the difficulties posed with deciding what to choose as the basic "atomic unit" of mixing. For the more straightforward case of solid solutions, we will apply the model to our own DFT calculations and use it to understand the role of spin state in iron-bearing magnesium silicate perovskite.

[1] D. Saulov, (2006) *Calphad.* [2] D. Saulov et al., (2009) *Journal of Alloys and Compounds.* [3] M. Hillert, (1998) *Cambridge University Press.*