Thermodynamics of minerals: From Bragg-Williams to Connolly-Williams

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The presentation will start with a tribute to the Bragg-Williams theory of solid solutions [1], a cornerstone upon which modern non-Bragg-Williams approaches are built. The main ideas of the Cluster Variation, Monte Carlo and Direct Configurational Averaging methods will be reviewed and interlinked. The unifying idea of the Cluster Expansion [2] will be presented as the most efficient way of incorporating quantum mechanical calculations into solid solution modeling. The Double Defect Method, DDM, [3] will be introduced as Occam's razor, resolving dichotomy of efficiency and accuracy of the cluster expansion procedure. DDM-based models of several geochemically and petrologically important solid solution will be discussed.

[1] Bragg, W.L. & Williams E.J. (1934) *Proc. Roy. Soc. London*, **145A**, 699–730. [2] Connolly, J.W.D. & Williams, A.R. (1983) *Phys. Rev. B*, **27**, 5169–5172. [3] Vinograd, V.L. Sluiter, M.H.F. & Winkler, B (2009) *Phys. Rev. B*, **79**, 104201–1-9.

Sr isotope constraints on natural oxy-anionic contaminants in a basin-fill aquifer (Arizona, USA)

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The natural occurrence of oxy-anionic contaminants (e.g. As, B, V, Se, Cr) in the oxic basin-fill aquifers of the Basin and Range region imposes major constraints on water utilization in the southwestern USA. Here we investigate trace metal and Sr isotope distribution in the Willcox Basin (WB), a Tertiary-Quaternary basin-fill aquifer in Arizona, in order to trace the origin of solutes and relationships to lithology. Two trends distinguish sediment sources: (1) Sr from Proterozoic granitic rocks (>0.78; [1]) mixes with a gypsum-carbonate (GC) complex at Willcox Playa (~0.710; [2]); and (2) Sr from Tertiary silicic volcanic rocks (<0.716) contaminated by Paleozoic and Mesozoic sedimentary rocks (<0.709; [3]) mixes with GC.

Waters of trend 1 contain low TDS and $^{87}Sr/^{86}Sr$ from 0.721-0.733 indicating weathering of old K-feldspar up to ~10 km from the mountain front. These highly radiogenic values may be expected throughout the Basin and Range where >1 Ga crystalline rocks supply sediment to basin-fill aquifers.

Waters of trend 2 ($^{87}Sr/^{86}Sr$ 0.710-0.715) contain elevated As, V, Se, Sb, Mo, and B relative to trend 1, and in particular As, Se, and B concentrations are associated with $^{87}Sr/^{86}Sr$. This implies that these trace elements are directly related to volcanic-source sediment and are somewhat conservative in the oxic conditions of WB (e.g. [4]) and the observed pH range (6.7-9.3). Significant U - also an anion under oxic conditions - occurs in both trends 1 and 2 (median 3.7 μg L^{-1}). Very low Ra activities in the basin-fill aquifer (median ^{226}Ra 1.2 mBq L^{-1}, median ^{228}Ra 3.2 mBq L^{-1}) result in low inferred $^{226}Ra/^{238}U$ activity ratios (median 0.06). These conditions of U>>Ra could be explained by oxic conditions throughout the aquifer favoring U solubility and Ra adsorption. High $^{228}Ra/^{226}Ra$ (median 3.7) may further imply that U has been transported towards the center of WB, leaving depleted ^{226}Ra relative to ^{228}Ra at the sampled wells.

[1] Erickson (1981) *Ariz. Geol. Soc. Digest* **13**, 185–194. [2] Naiman *et al.* (2000) *Geochim. Cosmochim. Acta* **64**, 3099–3109. [3] Bryan (1987) *GSA Abstr. Progr.* **19**(6) 362. [4] Johannesson & Tang (2009) *J. Hydrol.* **378**, 13–28.