Isotopic signatures of H_2 and CH_4 at the Cedars: Implications for temperatures and mechanisms of serpentinization at the site

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The Cedars site is an exposed peridotite body in northern California undergoing active serpentinization. Alkaline spring waters (pH >11) with high concentrations of dissolved H_2 and CH_4 discharge at the surface in several locations. Two sets of water samples were collected during high- and low-flow periods for gas concentration and isotopic measurements to assess mechanisms of formation and whether the isotopic compositions of the gases can be used to determine serpentinization temperatures. Multiple samples were taken from each of 3 springs complexes listed in order of increasing elevation: Grotto Pool (GP), Barnes Springs (BS) and Mineral Falls (MF). Gas concentrations within each complex were similar, but gas ratios varied between complexes with the ratio of CH_4 to H_2 ranging from <0.4 at GP to 0.5 to 1.0 at BS, to >2.0 at MF. The variation in δD for all H_2 samples analyzed (n=14) was small (-735 to -756‰), with no differences between complexes. Using the average δD of water (-40‰), and the relationship outlined by Horita [1] for equilibration of water and H_2 gas using a platinum catalyst, gives calculated formation temperatures averaging 24°C. These temperatures imply H_2 formation or equilibration temperatures at near-surface conditions. Significant H_2 production at low temperatures is consistent with H_2 generated in abiotic laboratory experiments with peridotite from Cedars at <100°C. Average $\delta^{13}C$ values of CH_4 vary from -56‰ at GP to -62‰ at BS to -66‰ at MP are similar to data from the same locations recently published by Morrill *et al* [2] and correlate with the observed changes in the ratios of dissolved CH_4 to dissolved H_2 noted above. The isotope compositions of the CH_4 do not fall in the range of typical values for abiotic CH_4 and no generation of CH_4 was observed in the Cedars peridotite experiments, suggesting that the CH_4 is not abiogenic. Although the biological mechanism is not clear at this time, it is worth exploring the role of biological processes in the trend of increasing CH_4/H_2 and decreasing $\delta^{13}C$ from the lower to higher elevation sites.

[1] Horita (1988) *Chem. Geo.* **72**, 89-94 [2] Morrill *et al* (2013) *Geochim Cosmochim Acta* **109**, 222-240