Ti substitution in zircon

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A recently proposed geothermometer (Watson *et al.*, 2006) assumes that the Ti content of zircon is buffered in equilibrium with rutile. However, Ti may substitute into either the Si or Zr site of zircon, and as a result, the concentration of Ti in zircon will change with pressure and with SiO_2 activity as well as temperature. Understanding how Ti partitions between the two sites is therefore crucial to developing this new geothermometer. Based on ionic radius arguments and recent experiments, it was suggested that substitution of Ti for Si dominates (Harrison *et al.*, 2005; Ferry and Watson, 2006).

Gaining a more quantitative understanding of the energetics of Ti substitution in zircon requires the use computational methods. Therefore, quantum mechanical calculations (CASTEP, Dmol, Crystal) were used as a basis for Monte-Carlo calculations to derive the enthalpy and free energy of mixing for the binary $ZrSiO_4$ – $ZrTiO_4$ (assuming that all compositions have the zircon structure) at various temperatures.

Similar calculations are being carried out for the binary $ZrSiO_4$ – $TiSiO_4$, again assuming a zircon structure. Preliminary quantum mechanical calculations suggest that substitution of Ti into the Zr site requires a similar amount of energy as substitution into the Si site for low Ti content (x=0.0625 in $Zr(Si_{1-x}Ti_x)O_4$ compared with $(Zr_{1-x}Ti_x)SiO_4$). Excess volume is also calculated for both solid solutions in order to estimate the effect of increasing pressure.

References

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Understanding carbon isotope records from wetland plants: Implications for paleohydrology

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In contrast to terrestrial plants, carbon isotopic results from wetland plants, such as pond cypress, have a positive relationship with rainfall amount. One important plant in the greater Everglades ecosystems is sawgrass (*Cladium jamaicense*), which comprises an important part of the regional ecosystem. To calibrate and understand the isotopic changes that may potentially be related to changes in water level, which corresponds to hydroperiod in a temporal manner, mesocosm experiments were used to grow these plants at different water levels. 24 mesocosms were randomly assigned 4 different water treatments to simulate changes in hydroperiod and water depth, similar to the typical Everglades wet season and dry season cycle. Our initial results from this work show a strong correlation between variations in water depth and plant carbon isotope values in the shallow water treatments vs. the deeper water treatments (Fig.1). Further analyses are presently underway to compare assimilation with the collected carbon isotopic data. These results confirm the observations from the cypress work, and set the stage for using carbon isotopes from preserved OM and/or biomarkers to reconstruct changes in water level from wetland settings.

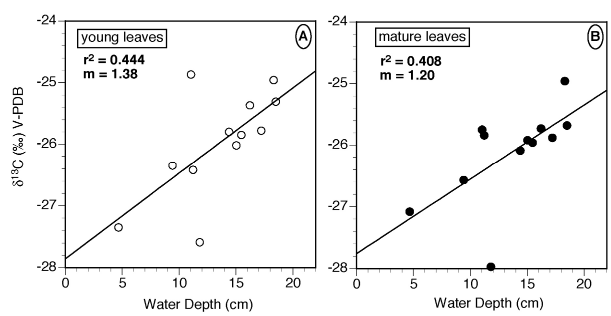

Figure 1: Carbon isotope values compared to water depth in young (A) and mature sawgrass leaves (B).