Ordering in the crystal structure of holtite

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Holtite, [c. $(Ta,\square,Al)Al_6(BO_3)(Si,Sb,As)_3O_{12}(O,OH,\square)_3$], is isostructural with dumortierite and the two minerals share several distinctive structural features such as face-sharing Al-octahedra and both cation and anion vacancies. However, in the crystal structure of holtite SiO_4 tetrahedra are partially replaced by $Sb^{3+}O_3$ triangular pyramids, and Ta replaces Al at the octahedral Al1 site. As a result there are vacancies at the coordinating anion sites (O2 and O7) as well as at the Al1 site. When the Sb sites are occupied the adjacent Si, O2 (for Si1), and O7 (for Si2) positions are vacant. The occupancy of Al1 is equal to or less than that of O2 and O7. Taken together these sites form "tunnels" ‖ **a** in the holtite stucture.

Both Pryce [1] and Hoskins *et al.* [2] reported diffuse layers normal to **a** at spacings of 2*a* and 3*a* in rotation photographs of holtite. Hoskins *et al.* [2] inferred that these layers indicate an ordering effect in any one individual tunnel that it is not strongly correlated with that of adjacent tunnels. The fact that such an ordering exists in individual tunnels suggests that a complete replacement of SiO_4 rings by SbO_3 rings takes place at ordered intervals, which are probably related to the order of the vacancies at the Al1 site [2].

We have refined the crystal structures of two low-Sb and two high-Sb holtite samples from the three known localities. Three of the structures refined to R1 values of 2-3%; the fourth, which exhibits pseudo-reticular twinning**,** refined to R1 = 4.8%. Our results are consistent with a specific model based on the proposal by Hoskins *et al.* [2] that Si and Sb are ordered in a given tunnel, but that there is little correlation from one tunnel to another, so that the crystal as a whole is disordered. This is analogous to disordered stacking of sheets, each of which is ordered, in a layer silicate.

[1] Pryce (1971) *Mineral. Mag.* **38**, 21-25. [2] Hoskins *et al.* (1989) *Mineral. Mag.* **53**, 457-463.

Salinity influence on planktonic foraminiferal Mg/Ca: A case study from the Red Sea

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We present new data from the Red Sea, which is characterized by a large salinity gradient and small temperature changes, in order to explore the influence of large changes in salinity on Mg/Ca. We analysed the planktonic foraminifer *Globigerinoides ruber* from a series of core tops and plankton tows. Analyses were performed on bulk samples by ICP-OES. Core top Mg/Ca ratios range between 4.64 and 22.36 mmol/mol without any correlation to temperature. Correlation with salinity, however, is highly significant (r^2 = 0.68). When expected Mg/Ca ratios are subtracted from the analysed values the correlation coefficient between Δ(Mg/Ca) and salinity further increases (r^2 = 0.74). In contrast, plankton tow Mg/Ca ratios only vary between 4.49 and 4.97 mmol/mol, showing less extreme Mg/Ca ratios than the specimens from the core tops. When the Mg/Ca ratios are corrected for temperature influence, Δ(Mg/Ca) shows a correlation with salinity (r^2 = 0.95). In addition, we used LA-ICP-MS, SEM analysis, and pteropod preservation index to verify the discrepancy between plankton tow material and the core top samples, i.e. whether diagenetic alteration has caused the anomalously high bulk Mg/Ca ratios in the core tops. Results do not indicate the presence of coatings on the core top samples, but rather show homogeneous Mg/Ca ratios throughout the test walls with highest values always present in the oldest chambers. The correlation between core top Mg/Ca and salinity points to an artificial dependency in which differences in salinity possibly triggered diagenetic changes.