Equilibrium experiments and theoretical studies in the MgO-SiO2-H2O system at high pressures:
Clariﬁcation of stabilities and thermodynamic properties of phase A, clinohumite and chondrodite
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The stabilities of clinohumite, chondrodite and phase A were investigated in phase equilibrium experiments using a rocking multi-anvil apparatus at pressures of 7.5-12.5 GPa and 800-1350 °C. The rocking technique, i.e. regular inversion of the experimental apparatus including the capsule, results in nearly homogeneous run products. This overcomes the problem of experimentally producing more phases than can be in equilibrium and thus allows unequivocal determination of stability fields.

Seven reactions were bracketed by equilibrium experiments (every starting material consisted of crystalline phases both, products and reactants).

Our results show that phase A, clinohumite and chondrodite have wider P-T stability fields when compared to the previous studies. More over, above 10 GPa, clinohumite has a lower temperature stability compared to chondrodite. These results contradict works by Wunder, (1994) and Kawamoto, (2004).

Thermal expansivities for clinohumite and chondrodite and the $C_p$ function of chondrodite were predicted from the Debye model. Thermal expansivities correspond to 2.64 · 10⁻⁸ and 2.71 · 10⁻⁹ K⁻¹, respectively. Standard state entropy and enthalpies for phase A, clinohumite and chondrodite were deduced from the fluid absent reactions by mathematical modelling.

References

Effect of montmorillonite dissolution on U(VI) sorption in bentonite
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Along with the fulﬁlling of other safety functions relevant for the final disposal of radioactive waste, bentonites should also retard the release of radionuclides in case of groundwater inﬂow. This study shows that U(VI) interaction with bentonite depends on its aqueous complexation and is strongly inﬂuenced by the dissolution of montmorillonite.

Results and Discussion
A comparison of the time-dependent changes in Mg and U(VI) supernatant concentrations as a result of clay-solution contact at circumneutral conditions reveals their strong correlation. SEM-EDS and FEM analyses of the bentonite samples indicate further that U(VI) is adsorbed at montmorillonite edges, which supports the ﬁndings of previous studies (Catalano and Brown, 2005). Time-dependent changes in the solubility of colloidal silica evidence silica release from montmorillonite and its relation to Mg release occurring at montmorillonite edges as well.

Application of the periodic bond chains (PBC) theory (Hartman and Perdock, 1955) to the observed data and taking into account the mechanism of alkali feldspar dissolution (Oelkers et al., 1994) allows to suggest the following mechanism of the non-stoichiometric montmorillonite dissolution as related to U(VI) adsorption on its edges: (1) surface complexation of U(VI) with Mg edge sites; (2) detachment of Mg; (3) surface complexation of U(VI) with Al, Fe edge sites; (4) diffusion and release of Mg from the outermost but one PBC; (5) hydrolysis of Al-O-Si bonds and release of Al; (6) Si release after dissolution of at most three PBCs. Taking into account the proposed mechanism of orthosilicate dissolution (Casey and Westrich, 1992), we hypothesize that the preferential complexation of dissolved U(VI) with Mg edge sites may be explained by very similar rates of water exchange on $\text{UO}_2(\text{H}_2\text{O})_5^{2+}$ and Mg($\text{H}_2\text{O})_6^{2+}$.

Conclusions
The study proposes a mechanism of montmorillonite dissolution as related to U(VI) adsorption, which provides molecular scale information about the involved processes.

References