Thermal-Mechanical Data of Argillite and Crystalline Disposal Systems: A First-Principles Approach

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Introduction, Objectives and Approach

- **Thermal-mechanical data for natural system (NS) minerals and engineered barrier systems (EBS) materials** are critical to assess their stability and behavior in geologic disposal environments for safety assessments.
- **Thermodynamic Data Gaps and Research Needs:** NS minerals surrounding the waste package (e.g. clays, complex salts, granite…).
- **Objectives:** Using parameter-free first-principles methods to:
  - Calculate missing thermodynamic data needed for geochemical & SNF degradation models, as a **fast and systematic way to predict materials properties and to complement experiments**.
  - Provide an **independent assessment** of existing experimental thermodynamic data and resolve contradictions in existing calorimetric data.
  - Validate our computational approach using high-quality calorimetric data.
- **Approach**
  - Structural optimization using density functional theory (DFT) [VASP code].
  - Use density functional perturbation theory (DF-PT) to calculate the phonon properties of materials relaxed with DFT and derive their thermal properties.

Computational Methods

Structure optimization with DFT

- Crystal Structures
  - *Ionic positions*
  - *Lattice Parameters*
- Molar Volumes
- Mechanical Properties

Phonon calculations with DF-PT

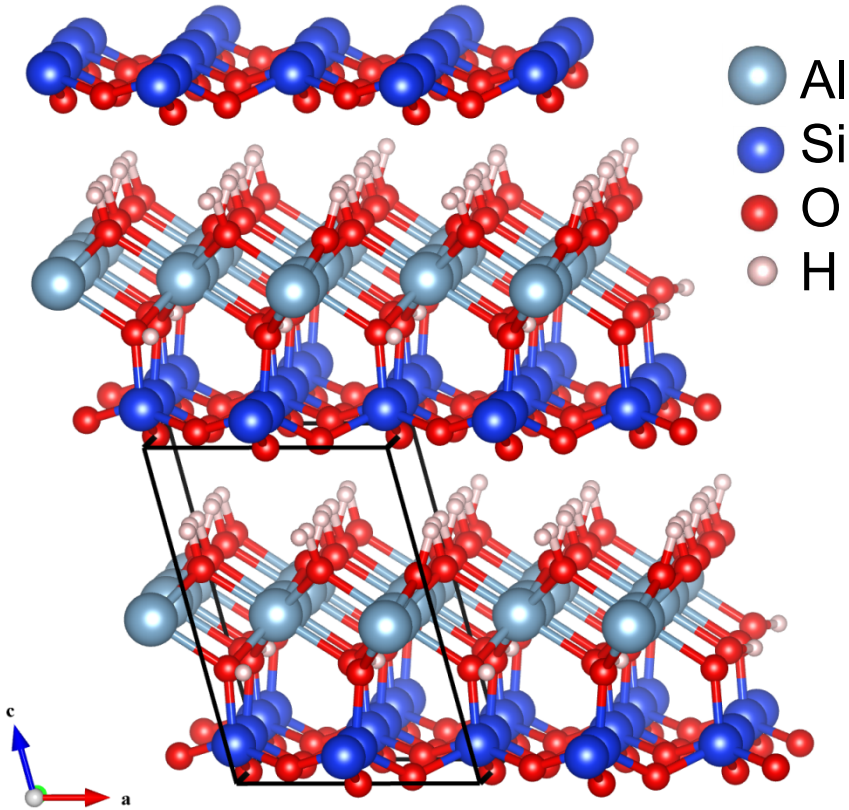
- Forces on atoms
- Phonon frequencies

Thermodynamic Properties

- Helmholtz free energy, C_V, entropy, enthalpy
- Gibbs free energy, C_P

Geochemical and Used Fuel Degradation Models

Clays: Structure & Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)



→ **Important to use DFT corrected for dispersion interaction for layered systems such as clays.**

- **Expt.: *V* = 328.708 Å^3**

  a = 5.153 Å, *b* = 8.942 Å, *c* = 7.391 Å
  α = 91.93°, β = 105.05°, γ = 89.80°.

- **Standard DFT: *V* = 340.11 Å^3**

  a = 5.21 Å, *b* = 9.05 Å, *c* = 7.48 Å
  α = 91.8°, β = 105.1°, γ = 89.7°.

- **DFT + van der Waals correction (DFT-D2): *V* = 329.03 Å^3**

  a = 5.18 Å, *b* = 8.99 Å, *c* = 7.33 Å
  α = 91.6°, β = 105.1°, γ = 89.8°.

Volume calculated with DFT-D2 overestimates experiment by less than 1%, while standard DFT overestimates expt. by *ca*. 3.5 %.

→ All the following calculations were carried out at the DFT-D2 level.

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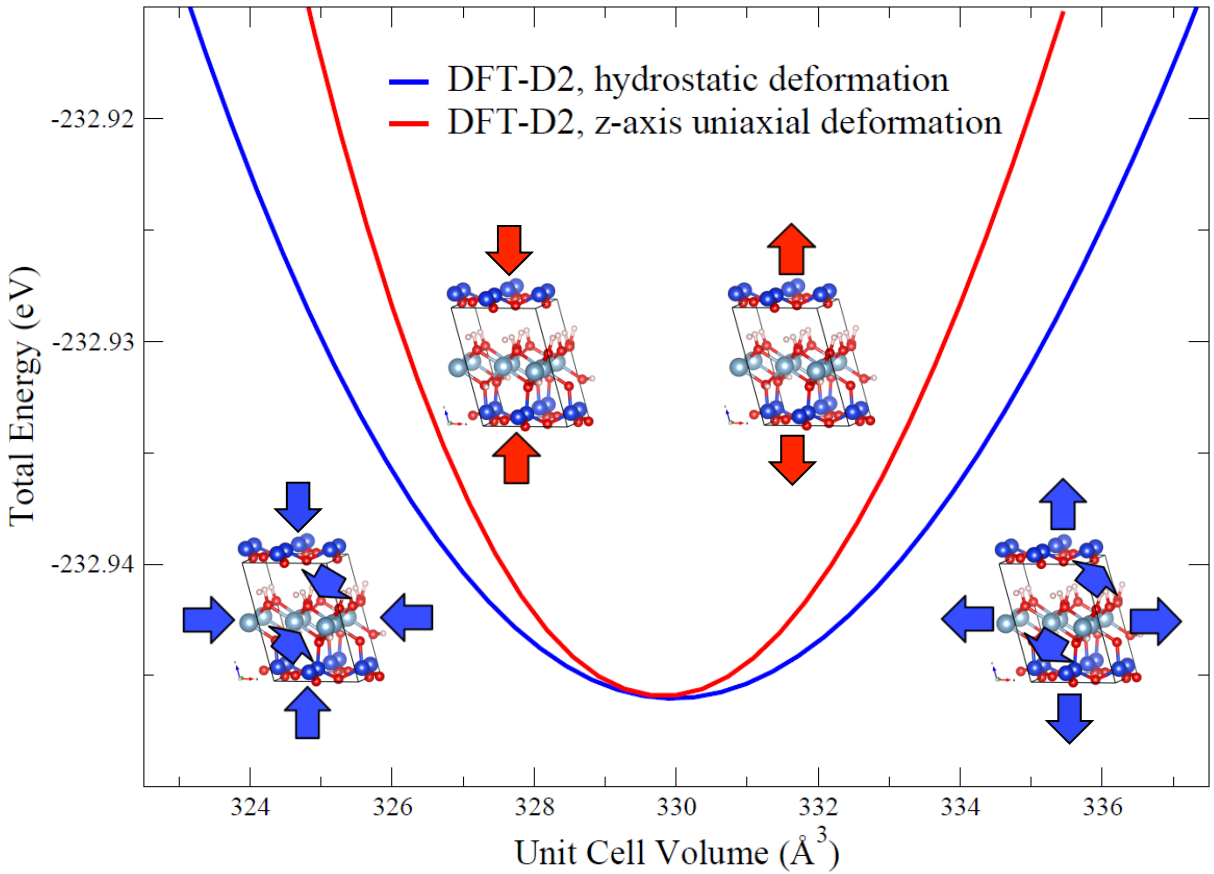


Two types of cell deformation:

- **Hydrostatic deformation**
- **Uniaxial deformation** (along the z-axis normal of the layers)

Bulk modulus:

- **Expt.:** B_0 = 44-56 GPa
- **DFT, hydrostatic:** B_0=54 GPa
- **DFT, uniaxial:** B_0 = 116 GPa

→ Strong impact of the system anisotropy on the mechanical-elastic properties of the clays.

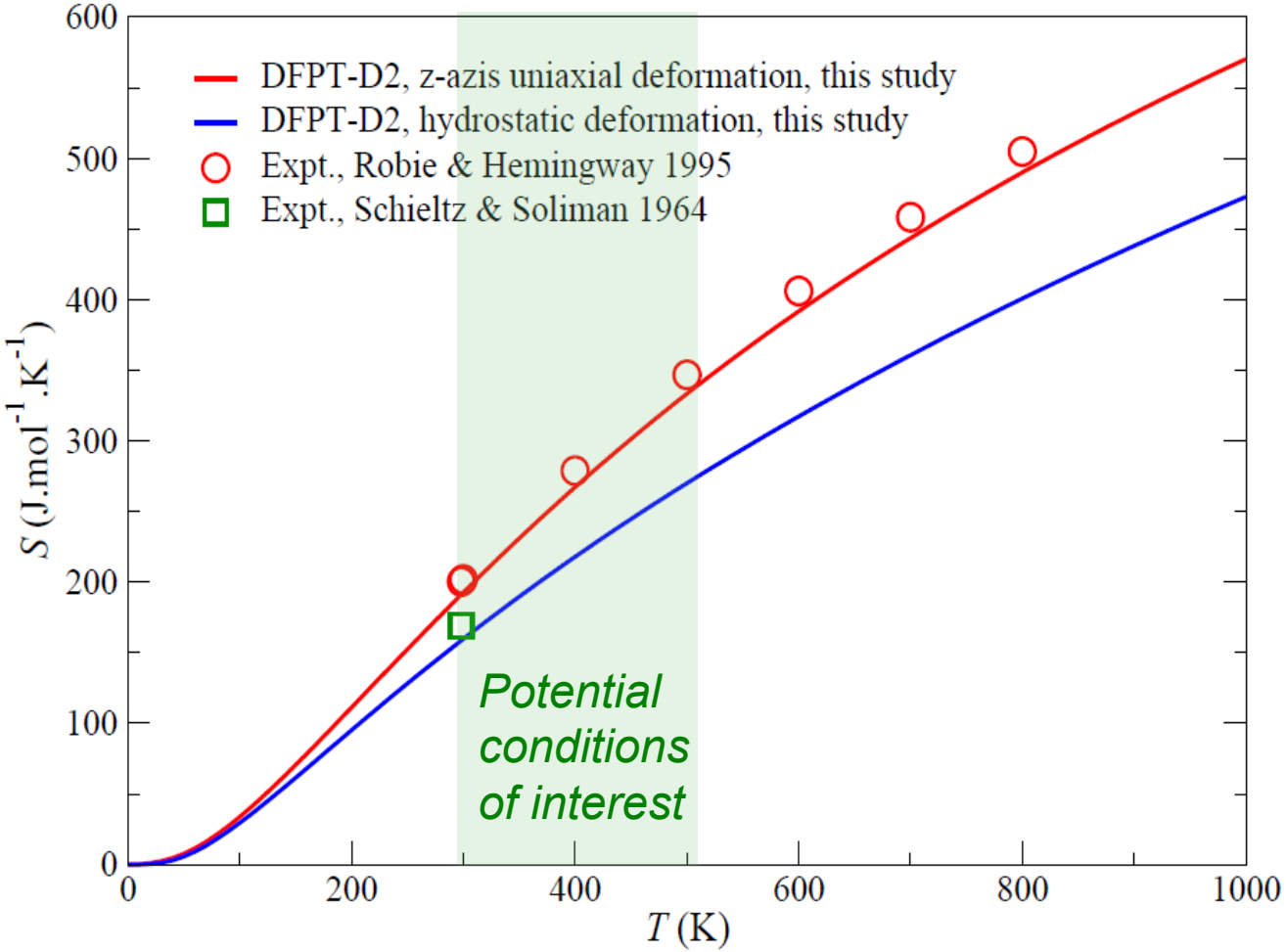
Birch-Murnaghan 3rd-order equation of state:

$$P(V) = \frac{3B_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}\left(B_0' - 4\right)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\}.$$

P: pressure; V_0: ref. volume; *V:* deformed volume.

$$B_0 = -V\left(\frac{\partial P}{\partial V}\right)_{P=0} \quad B_0' = \left(\frac{\partial B}{\partial P}\right)_{P=0}$$

Clays: Structure & Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)



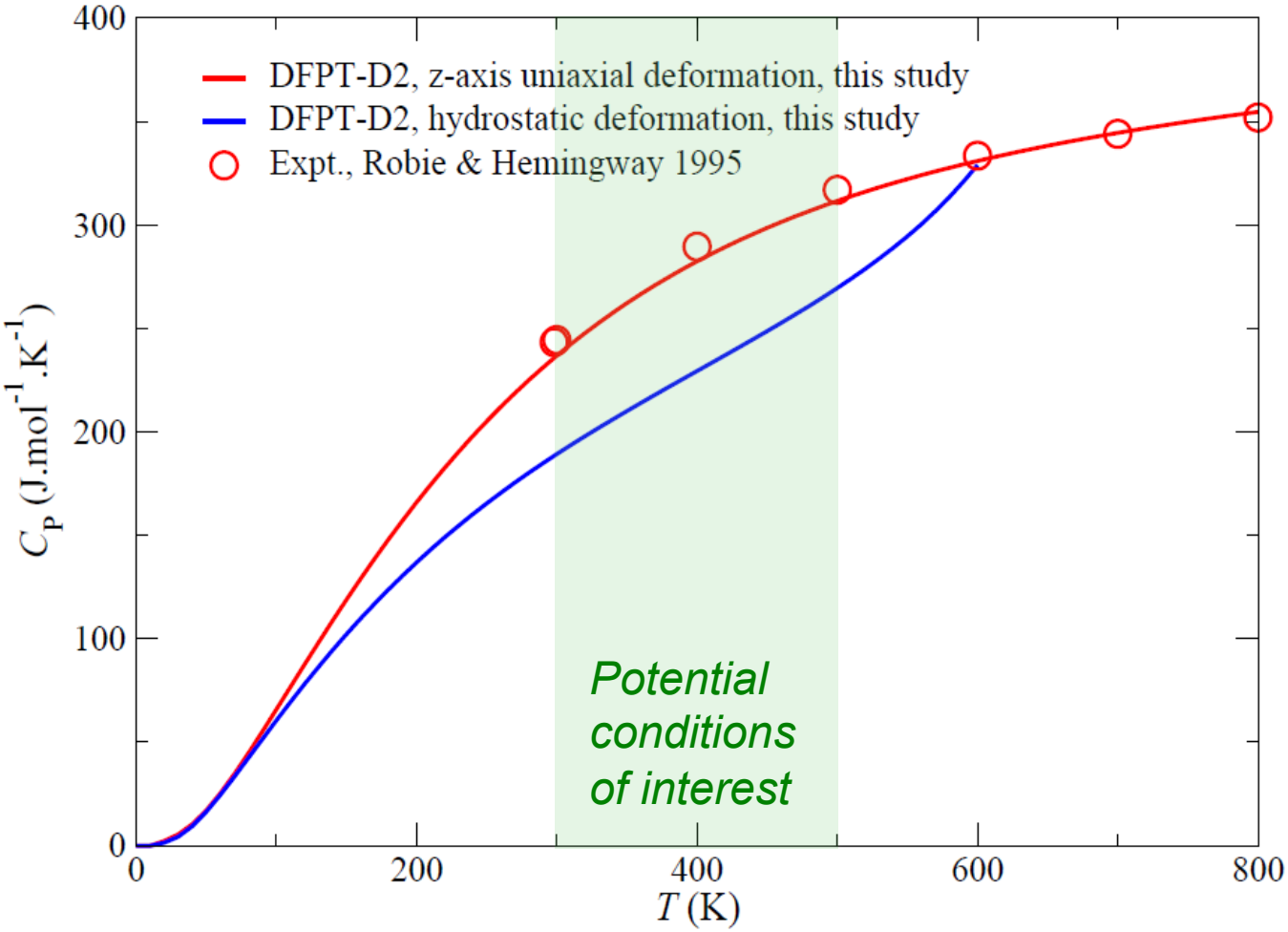
Isochoric calculations:

- Calculated entropy using **uniaxial deformation** of the unit cell is in excellent agreement with experiment.
- Entropy computed using **hydrostatic deformation** always underestimates data derived from calorimetry.

→ Uniaxial deformation of the cell maximizes the entropy compared to hydrostatic deformation.

→ Thermodynamic driving force for the formation of layered structures.

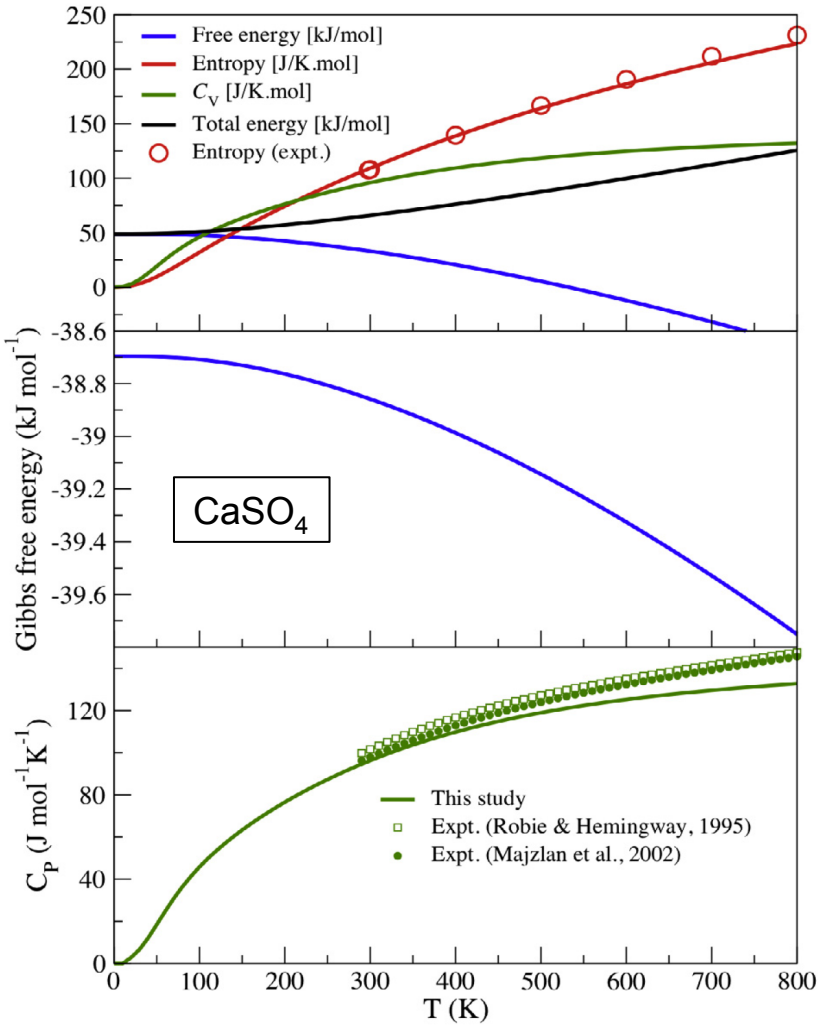
Clays: Structure & Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)

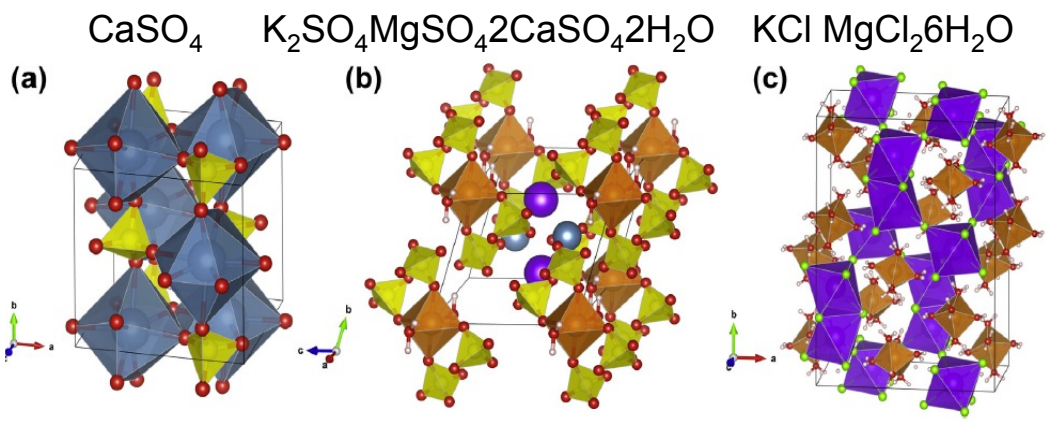


Isobaric calculations:

- Calculations carried out within the quasi harmonic approximation (QHA), at a fixed pressure of 1 bar.
- Computed isobaric heat capacity using uniaxial deformation of the cell reproduces calorimetric data
- C_p calculated with hydrostatic deformation underestimates calorimetric data for temperatures < 600 K.

R&D Highlight on Crystalline Salts: Anhydrite, Polyhalite and Carnallite

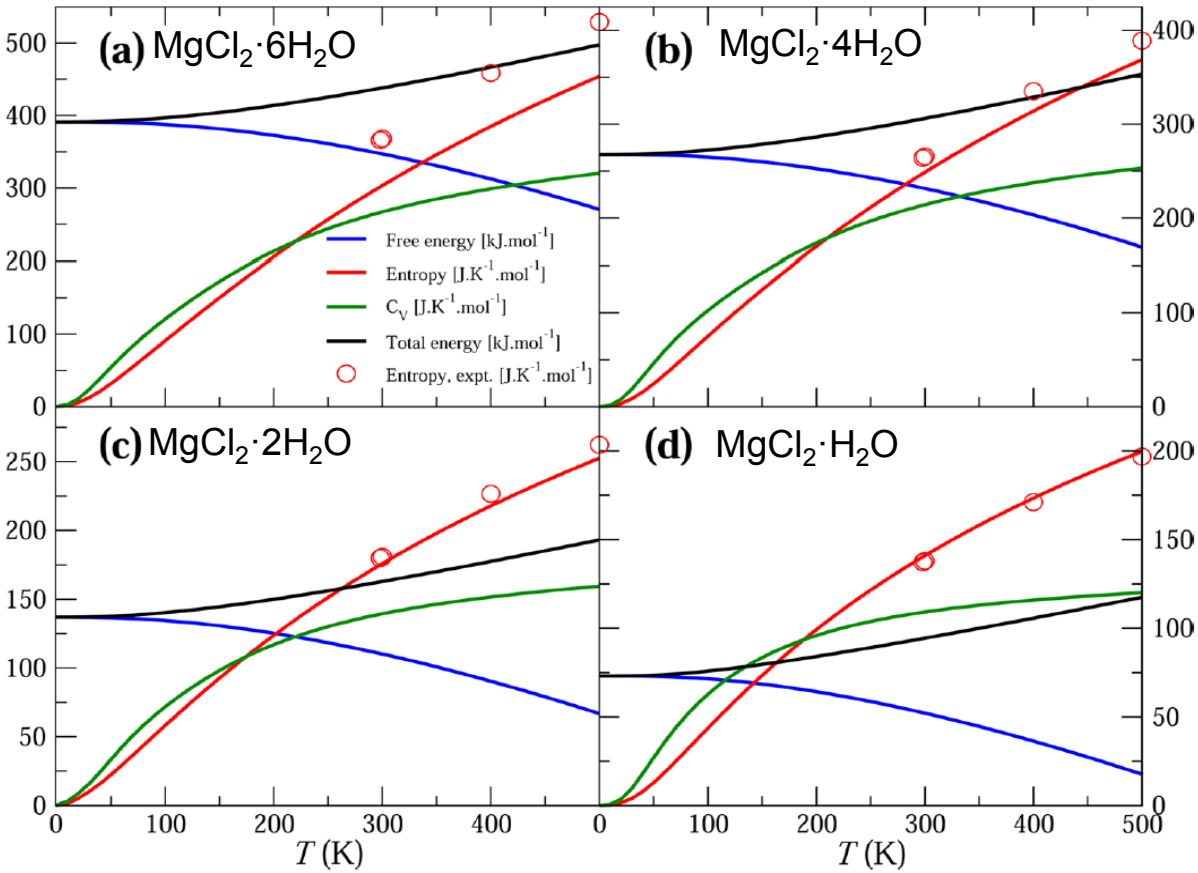


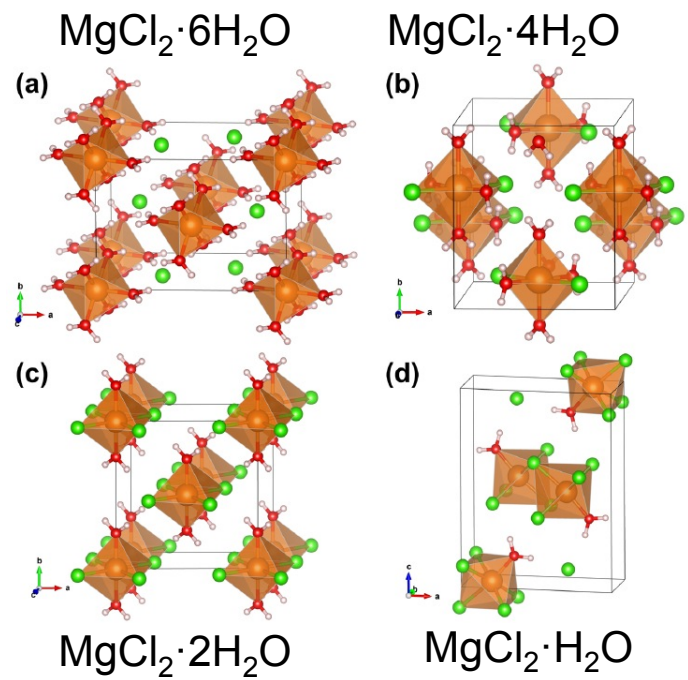


Paper selected as Cover Page:

Weck P.F., Kim E., Jove-Colon C.F., Sassani D.C., *"First-Principles Study of Anhydrite, Polyhalite and Carnallite", Chemical Physics Letters* ***594****, 1-5 (2014)*

R&D Highlight on Crystalline Salts: Bischofite and its Dehydrated Phases





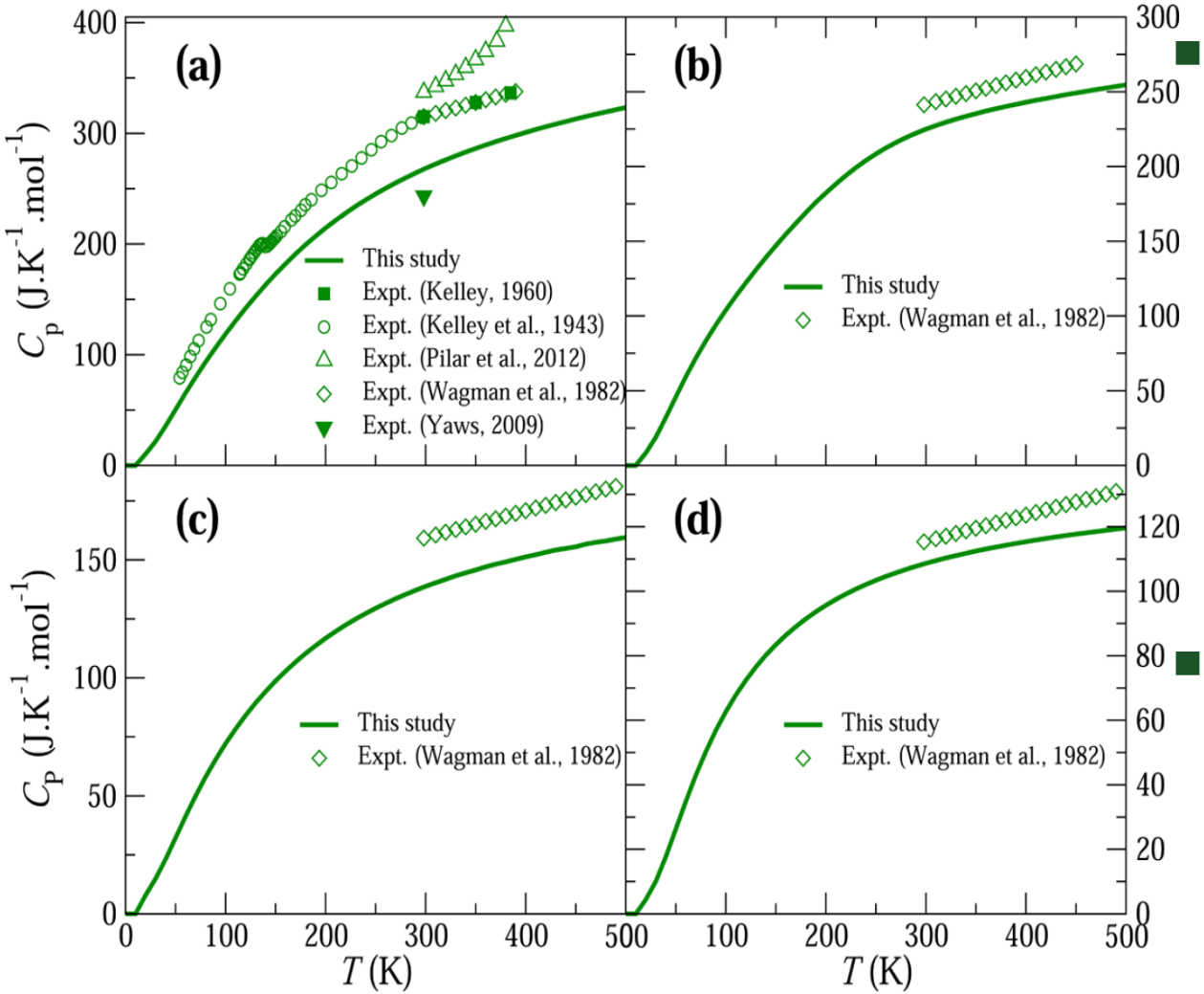
$$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O + 2H_2O$$

$$MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O + 2H_2O$$

$$MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O + H_2O$$

(Experimental data for the entropy: FactSage FACTPS database.)

R&D Highlight on Crystalline Salts: Bischofite and its Dehydrated Phases



- **Thermal properties:**
  - Isochoric and isobaric properties were calculated for bischofite and its dehydrated phases.
  - Good agreement between computed molar latent heat Q_P = 60.8 kJ mol^{-1} for the $MgCl_2 6H_2O$ to $MgCl_2 4H_2O$ transformation and expt. (Q_P = 68.2 kJ mol^{-1}).
- **FY14/15 outlook:**

  Extend structural and thermal-mechanical calculations within the framework of DFT/DFPT to other NS minerals (clays, salts, granite…) and EBS materials.