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Used Fuel Disposition Campaign

Thermal-Mechanical Data for Argillite Disposal Systems: Beyond Standard Density Functional Theory

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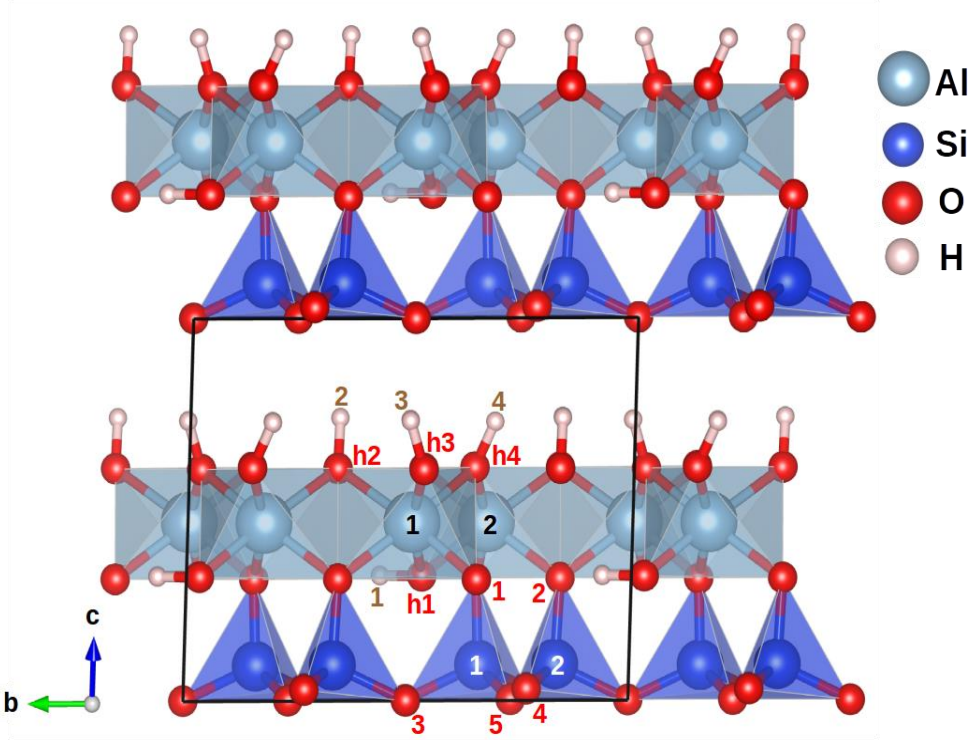
Introduction, Objectives and Approach

- **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.
- **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.

Structure of Kaolinite ($Al_2Si_2O_5(OH)_4$)



Layered crystal structure of kaolinite, $Al_2Si_2O_5(OH)_4$, relaxed with DFT-D2. The unit cell is indicated by solid black lines.

- **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 agrees with experiment within ca. 1% (while standard DFT overestimates expt. by *ca*. 3.5 %).

Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)

Thermal evolution of the bulk modulus computed for *single-crystal kaolinite* with:

1. Birch-Murnaghan 3rd-order (BM3) equation of state (EOS):

$$P(V) = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\left\{1 + \frac{3}{4}(K_0' - 4)\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]\right\},$$

where P is the pressure, V_0 is the reference volume, V is the deformed volume, and

$$K_0(T) = -V\left(\frac{\partial P}{\partial V}\right)_{P=0} \text{ and } \quad K_0'(T) = \left(\frac{\partial K}{\partial P}\right)_{P=0}.$$

2. Universal Vinet EOS:

$$P(V) = 3K_0\frac{(1-x)}{x^2}\exp\left[\frac{3}{2}(K_0' - 1)(1-x)\right],$$

$$\text{where } \quad x = \left(\frac{V}{V_0}\right)^{\frac{1}{3}}.$$

Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)

Elastic properties and bulk modulus computed for *polycrystalline kaolinite*:

Elastic constants (C_{ij}) calculated with DFPT as the second derivatives of the energy with respect to the strain:

$$C_{ij} = \frac{1}{V}\left(\frac{\partial^2 U}{\partial \varepsilon_i \partial \varepsilon_j}\right) \rightarrow$$ elastic compliances (S_{ij}) obtained by $S = C^{-1}$

with volume *V, total energy U of the system, and infinitesimal displacement ε.*

1. Voigt approximation: Fixed strain and average over stress → *upper limit*

Bulk modulus: $K_V = \frac{C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})}{9}$

Shear modulus: $G_V = \frac{C_{11}+C_{22}+C_{33}-C_{12}-C_{13}-C_{23}+3(C_{44}+C_{55}+C_{66})}{15}$

2. Reuss approximation: Fixed stress and average over strain →*lower limit*

Bulk modulus: $K_R = [S_{11}+S_{22}+S_{33}+2(S_{12}+S_{13}+S_{23})]^{-1}$

Shear modulus: $G_R = \frac{15}{4(S_{11}+S_{22}+S_{33}-S_{12}-S_{13}-S_{23})+3(S_{44}+S_{55}+S_{66})}$

3. Hill approximation: Average of Voigt and Reuss values

Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)

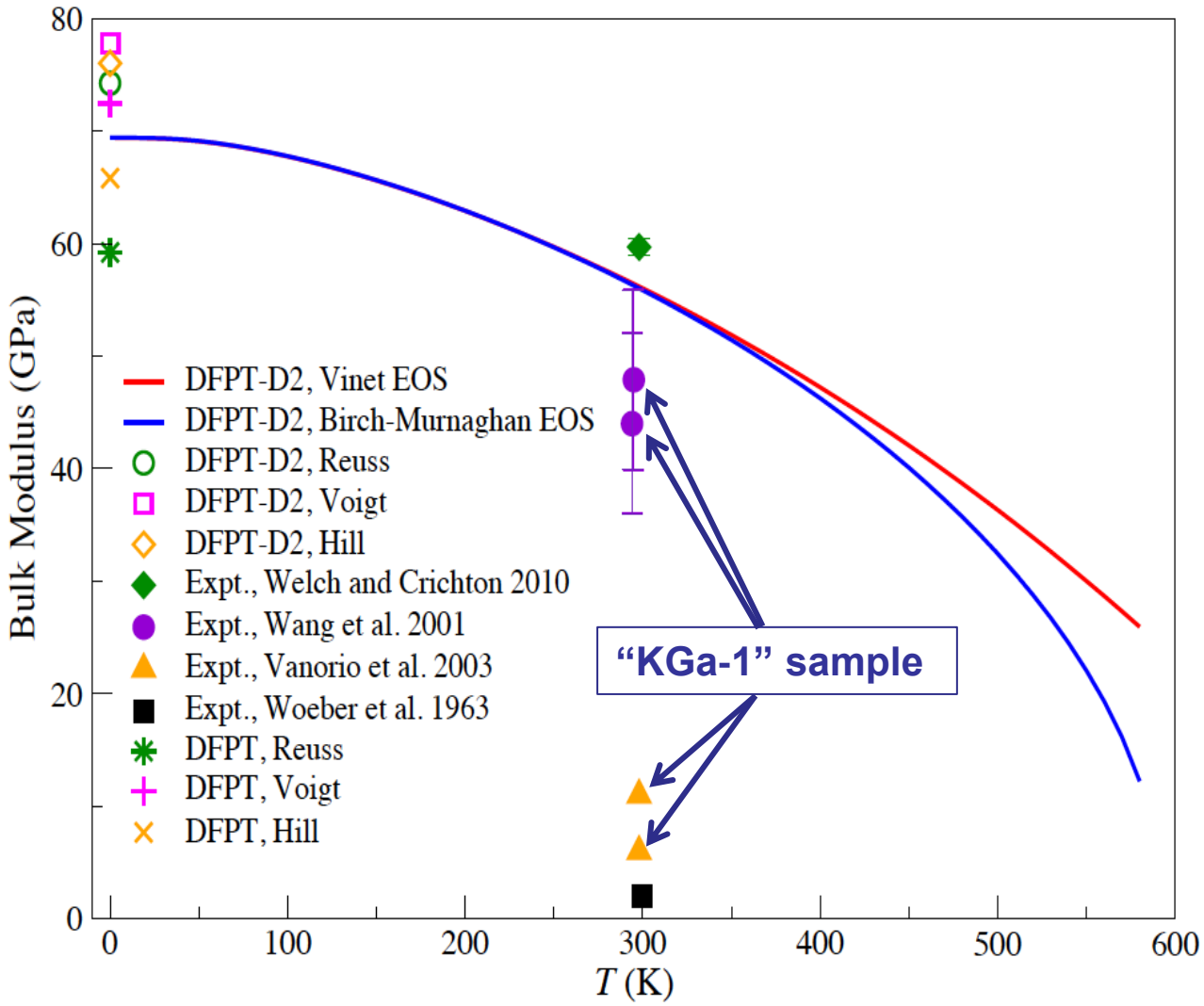
C_{ij}	DFT	DFT-D2	Experiments
C_{11}	187.20	175.16	171.51[a] 48.1[b] 79.3[b] 121.1[b] 126.4[c]
C_{22}	180.56	168.65	
C_{33}	88.02	133.99	52.62[a] 45.2[b] 72.5[b] 112.5[b] 57.8[c]
C_{44}	9.63	10.07	14.76[a] 16.7[b] 25.6[b] 41.1[b] 31.6[c]
C_{55}	12.36	12.78	
C_{66}	62.10	62.30	66.31[a] 16.9[b] 26.3[b] 41.3[b] 53.6[c]
C_{12}	66.42	54.10	
C_{13}	15.63	28.58	27.11[a] 12.9[b] 24.1[b] 34.8[b] 8.5[c]
C_{14}	-0.74	-1.90	
C_{15}	1.18	-0.79	
C_{16}	-6.14	-5.79	
C_{23}	16.00	28.46	
C_{24}	-0.30	-2.70	
C_{25}	-0.04	-1.42	
C_{26}	0.58	0.96	
C_{34}	-0.96	-3.57	
C_{35}	-0.56	-2.44	
C_{36}	0.37	0.71	
C_{45}	-0.45	-0.84	
C_{46}	-1.20	-1.78	
C_{56}	-0.02	-0.13	

Elastic constants of kaolinite:

- Large variability of experimental data due to different samples crystallinity, water and impurity content, measurement techniques,…
- First-principles calculations can help to assess the accuracy of some data sets and predict missing data.
- Overall good agreement between predicted and measured elastic constants.

[a] Katahara, 1996.
[b] Lonardelli *et al*., 2007.
[c] Wenk *et al*., 2008.

Thermal-Mechanical Properties of Kaolinite ($Al_2Si_2O_5(OH)_4$)



Thermal evolution of the bulk modulus of kaolinite:

- Large variability of experimental bulk modulus data using the high-crystallinity "KGa-1" Georgia kaolinite sample.
- A significant bulk modulus softening is predicted from first-principles in the 0-600K range.
- Differences in EOSs above ~300 K.

Used Fuel Disposition

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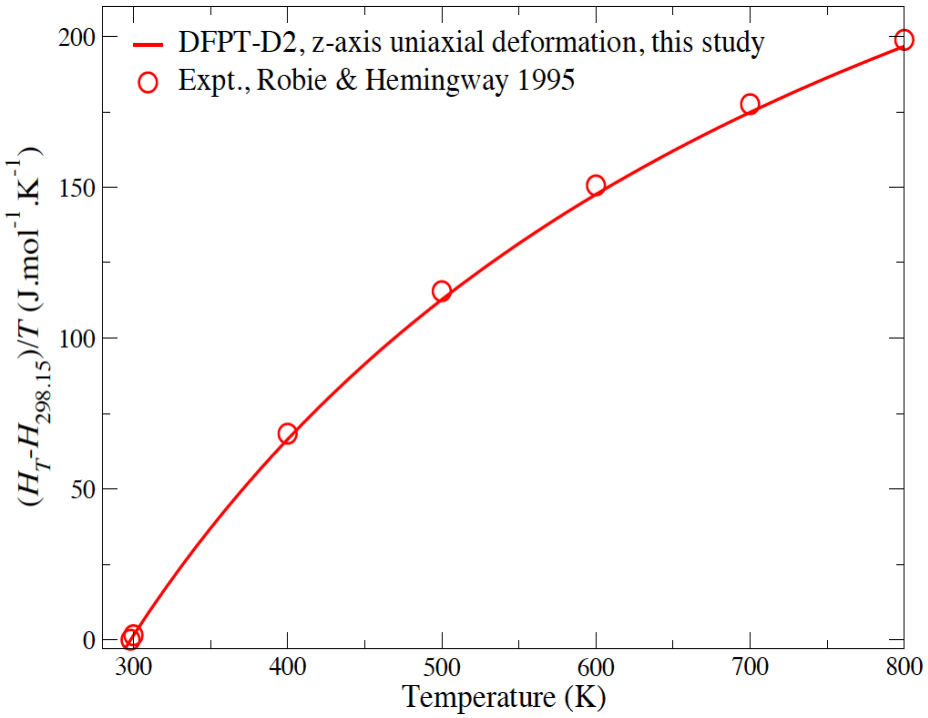
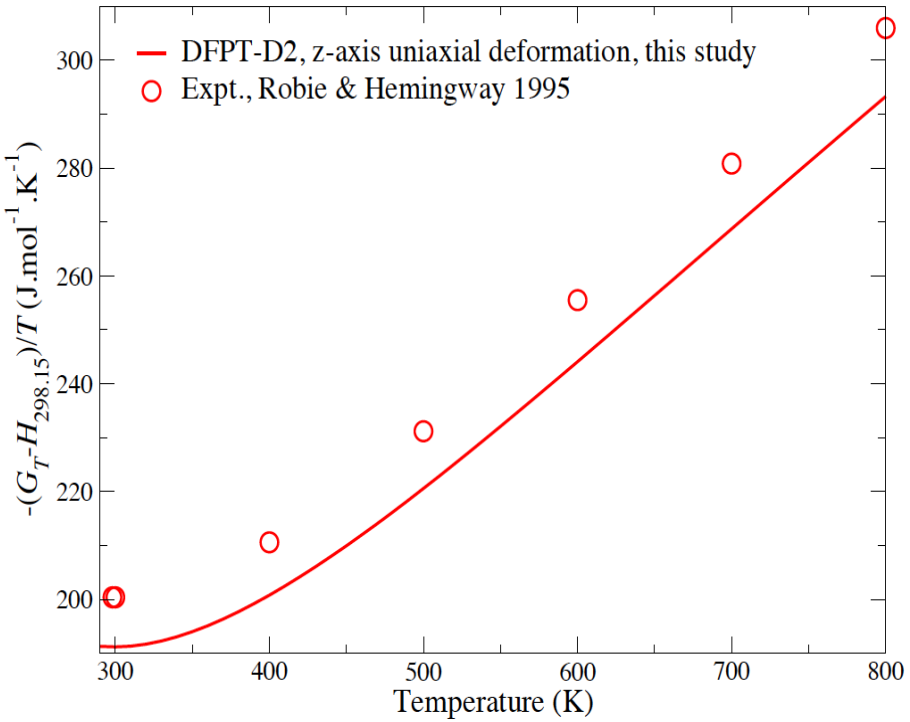




Enthalpy function of kaolinite

$$(H_T - H_{298.15}).T^{-1} = \int_{298.15}^{T} C_P dT$$

Differences of 2.0–2.5% in the 298–600 K range, and only 1% at 800 K.

Gibbs energy function of kaolinite

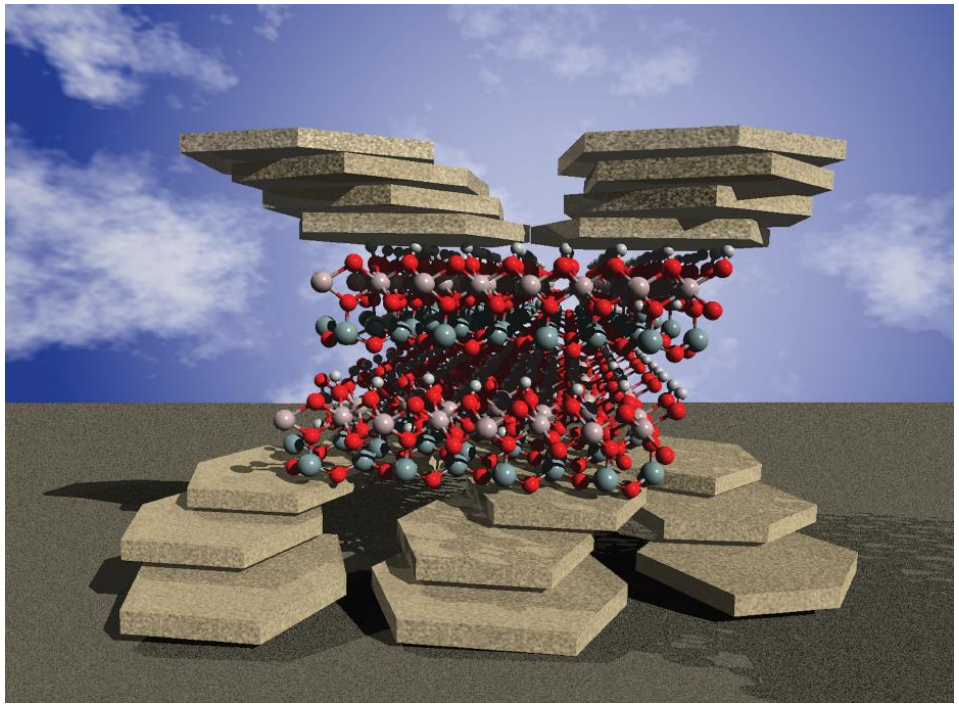
$$-(G_T - H_{298.15}).T^{-1} = S_T - (H_T - H_{298.15}).T^{-1}$$

Differences of 4.1–4.6% in the 298–800 K range.

R&D FY15 Highlight and FY16 Outlook

Paper selected as Cover Page of *Dalton Transactions* (July 2015):

Weck P.F., Kim E., Jove-Colon C.F., *"Relationship Between Crystal Structure and Thermo-Mechanical Properties of Kaolinite Clay: Beyond Standard Density Functional Theory"*, *Dalton Transactions, in press (2015);* DOI: *10.1039/C5DT00590F*



FY16 outlook:

- Testing the present theoretical approach using more complex clays, such as Na/Ca-montmorillonite.
- Extend structural and thermal-mechanical calculations within the framework of DFT/DFPT to other NS minerals (clays, salts, granite…) and EBS materials.