Structural Changes and Thermal Behavior of Pb^{2+}-Modified Zeolites

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Introduction

Zeolites are interesting minerals used in various applications. They are built by a framework (mainly aluminosilicate tetrahedra) which forms channels and voids where extrafrmaework (EF) cations and H_2O are hosted (Bish and Ming, 2001).

Zeolites are characterized by the cation-exchange property. The modification of the EF content induces structural changes that have a direct influence on their properties and thermal stability.

Heavy metal exchanged zeolites are of interest in two ways: i) because of environmental remediation related problems and ii) their use in catalytic processes.

This study aims at the investigation of structural changes and thermal stability of the zeolite stellerite (STI framework type) after Pb^{2+}-exchanged in aqueous solution.

Cation exchange experiment

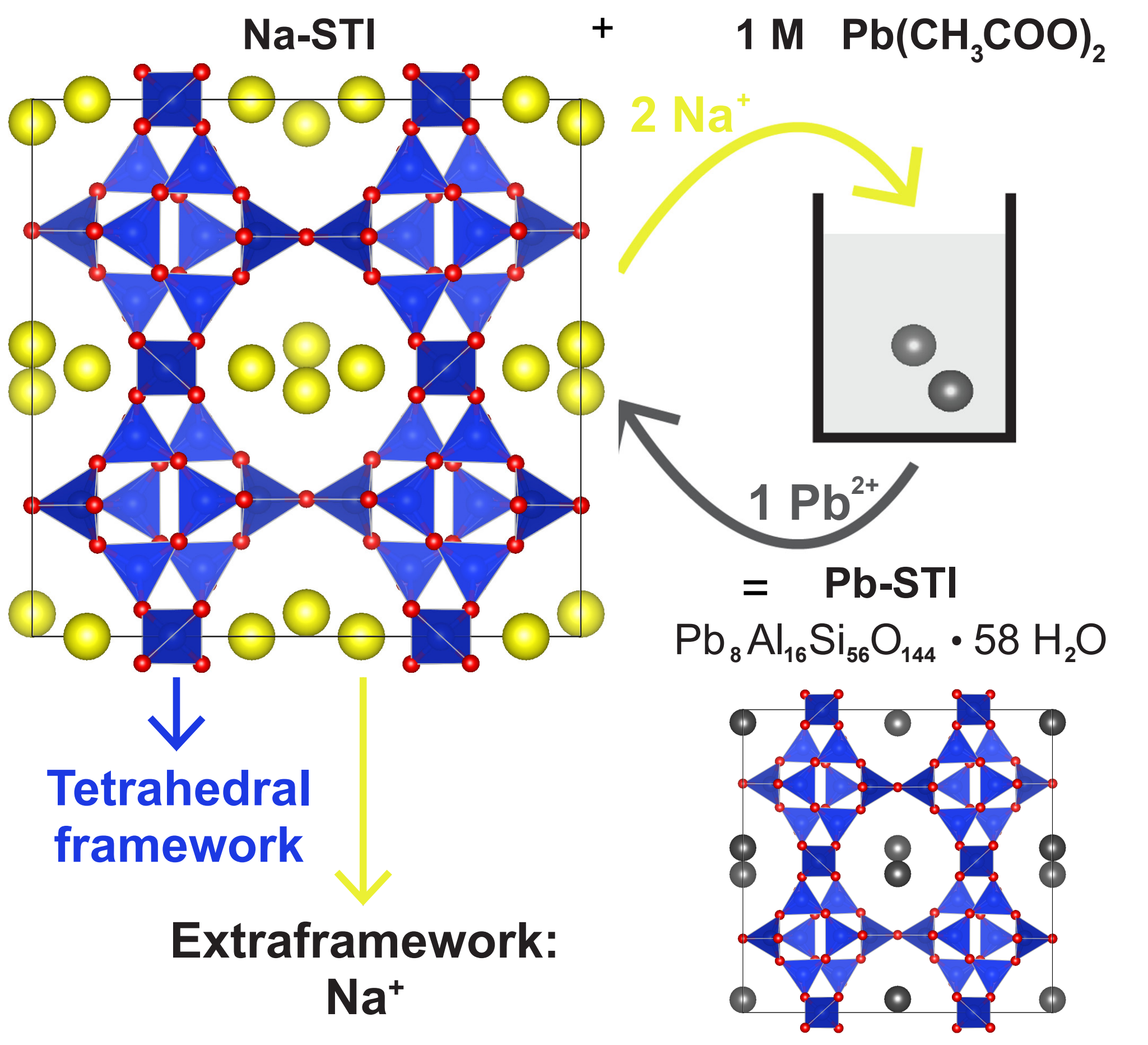


Fig. 1. Schematic representation of the cation exchange experiment. Na-stellerite (Na-STI) was put in contact with a 1 M $Pb(CH_3COO)_2$ solution for 4 weeks at 100 °C.

Analytical methods

Single Crystal X-Ray Diffraction (SC-XRD)
Room Temperature (RT) – 450 °C (in situ)

Molecular Dynamics Simulations (MD)
Simulation of real time motion of atoms
CP2K (Kühne et al., 2020), DFT, NPT

Electron Microprobe (EPMA)
15 kV, 2 nA

Thermogravimetric Analysis (TGA)
RT – 500 °C, 1 °C/minute

Infrared Spectroscopy (IR)
RT and ex situ 430 °C

Vibrational Density of State (VDOS)
TRAVIS (Brehm and Kirchner, 2011)

Results I. Chemical composition

$$Pb_{13}Al_{17}Si_{55}O_{144} \cdot 11\ OH^- \cdot 10\ H_2O$$

(Chemical composition normalized to 72 (Si+Al))

The measured chemical composition differs from the ideal chemical composition: 13 instead of 8 Pb^{2+} p.f.u. In this case, more Pb^{2+} than that needed to charge balance the framework is present. Additional Pb^{2+} can be charge-balanced by hydroxyl groups.

→ **Pb-STI is more than 50 % overexchanged.**

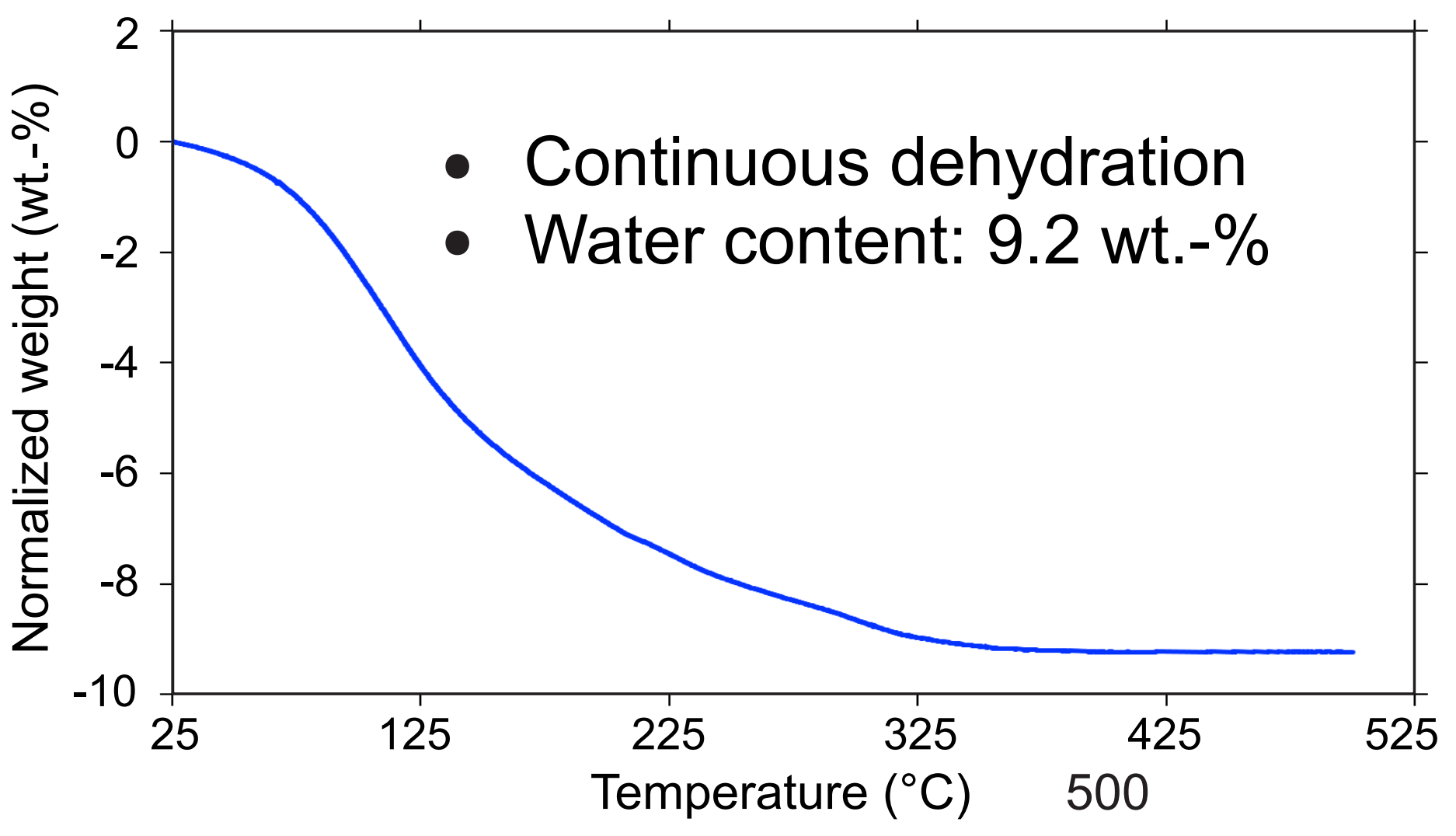


Fig. 2. Normalized weight ([weight – weight(RT)] / weight(RT) * 100) of Pb-STI as a function of temperature, measured by TGA.

II. Structural changes

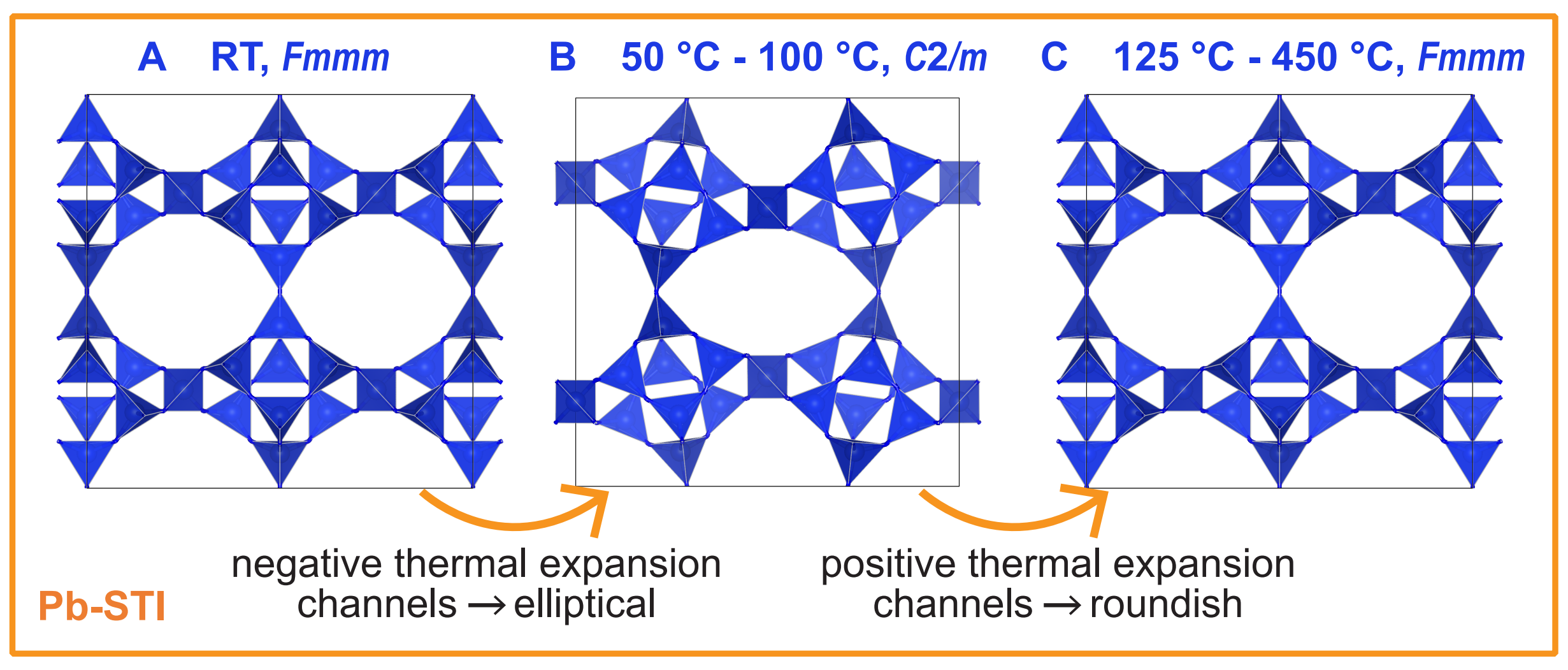


Fig. 3. Structural changes upon thermal treatment of Pb-STI: Crystal structures of framework at different temperatures, determined by SC-XRD.

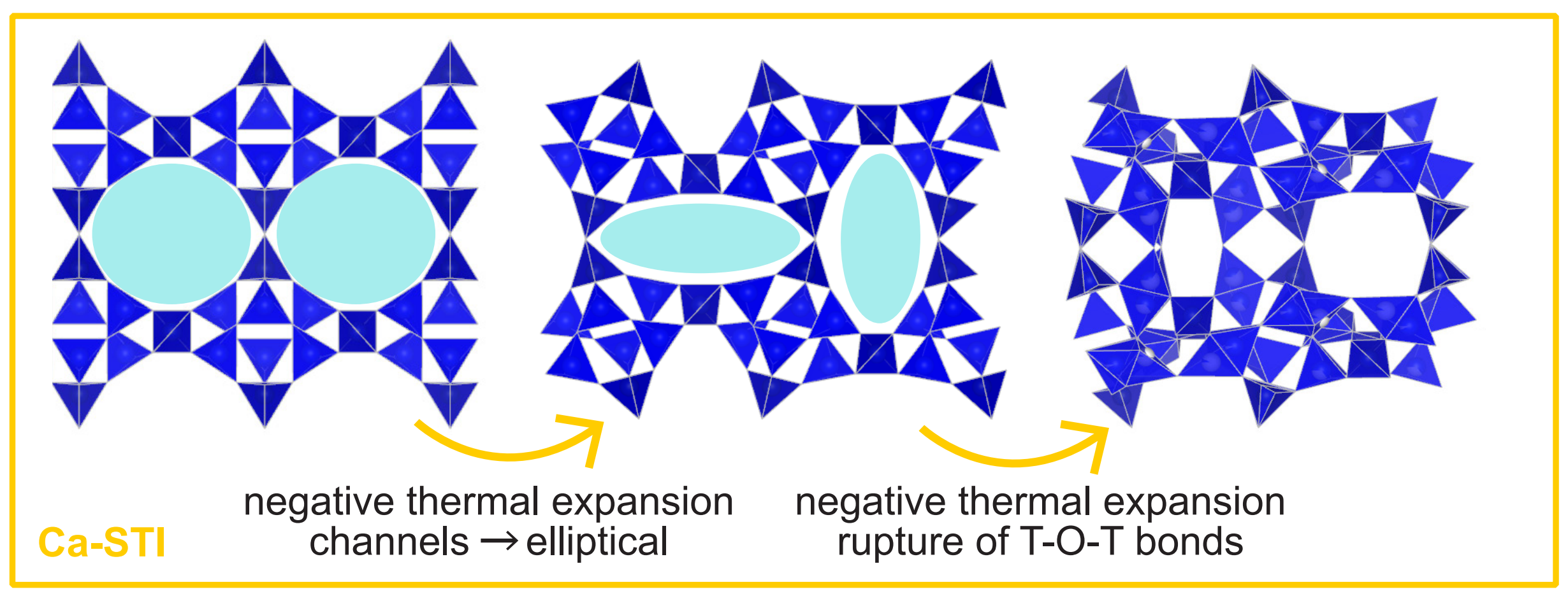


Fig. 4. The "normal" thermal behavior of STI zeolites due to H_2O loss: Crystal structures of Ca-STI at RT, 100 °C and 425 °C. Light blue areas indicate the amount of water which is left inside the channels (Cametti et al., 2017).

→ **Pb-STI has an anomalous thermal behavior.**

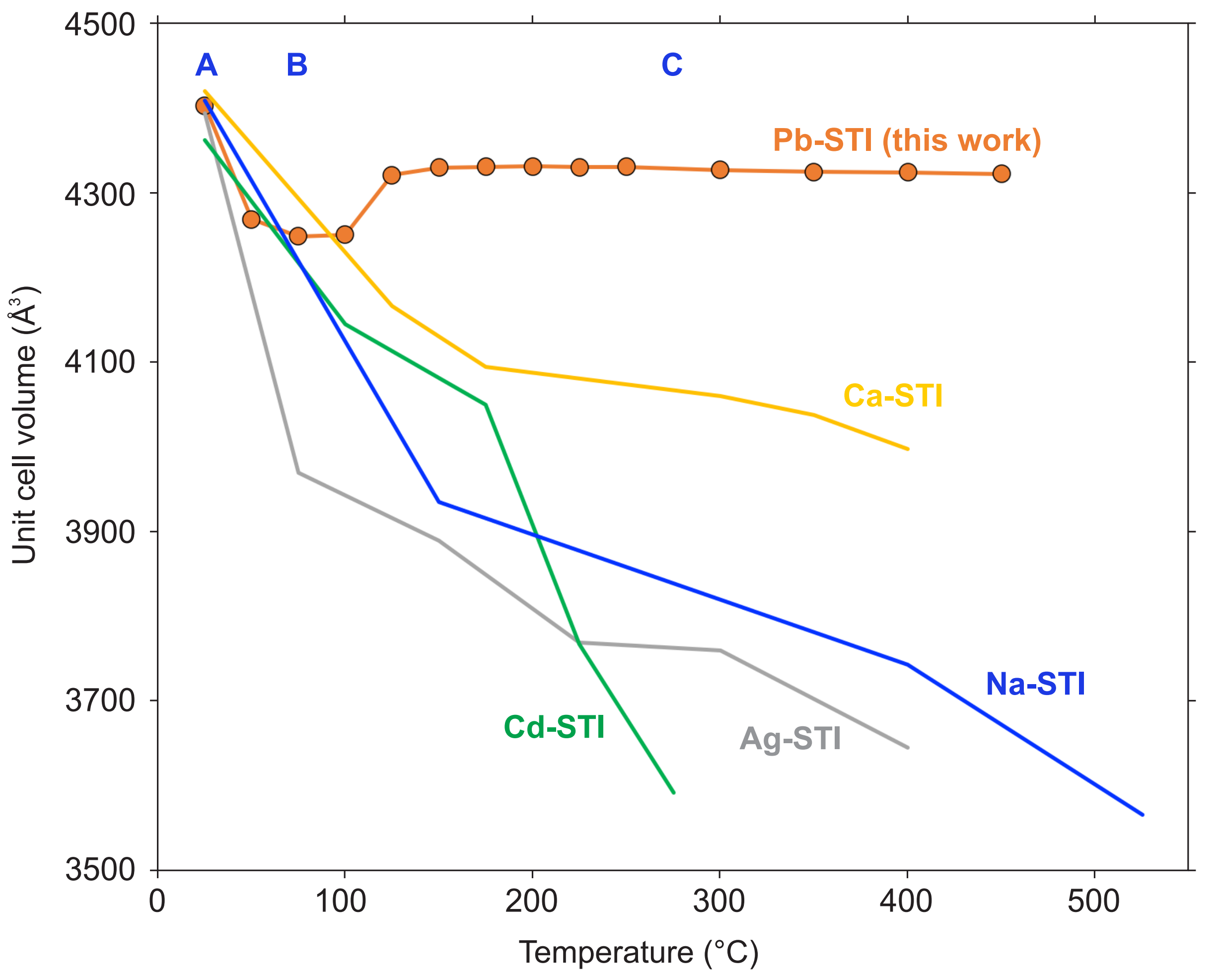


Fig. 5. Unit cell volume of different STI zeolites as a function of temperature (Cametti et al., 2017; Cametti et al., 2019).

Due to highly disordered EF content, Pb^{2+} and H_2O positions can not be distinguished by SC-XRD and complementary techniques are required.

III. Presence of hydroxyl groups

According to the calculated VDOS curves, hydrogen belonging to hydroxyls vibrate only at ~3600 cm^{-1}. This is helpful for the interpretation of the experimental IR measurements.

The only remaining peak after ex situ thermal treatment belongs to hydroxyl groups.

→ **Pb-STI is completely dehydrated at HT.**

→ **Presence of hydroxyl groups supports Pb-overexchange.**

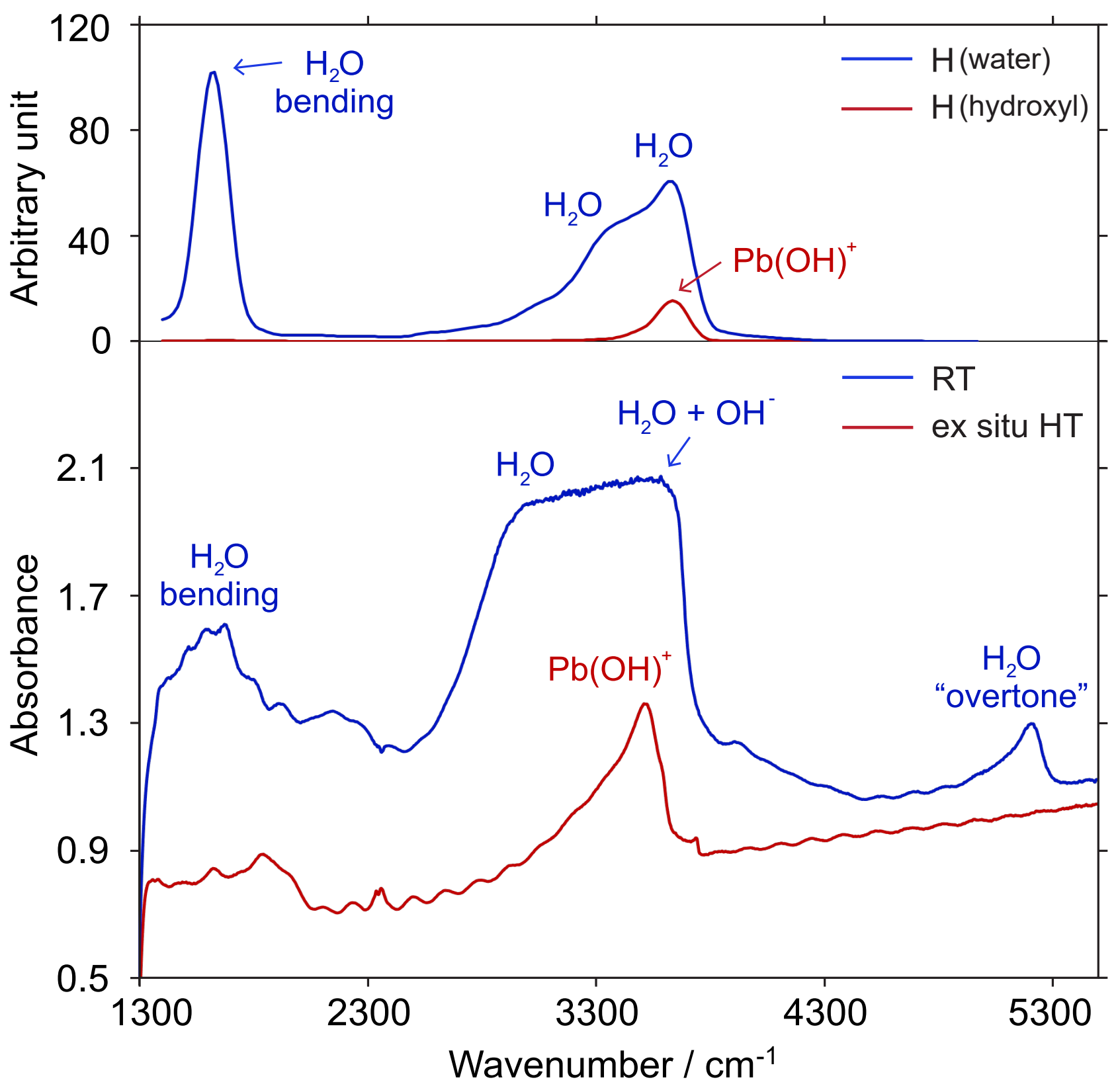
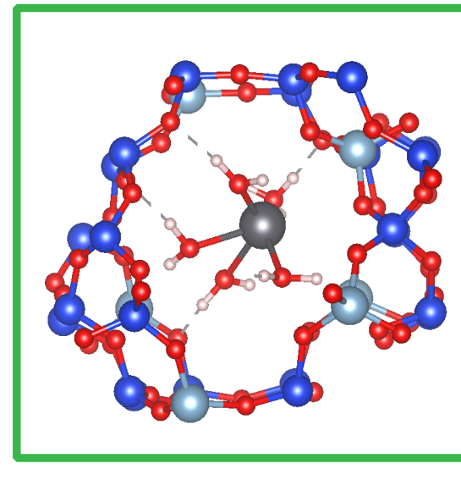


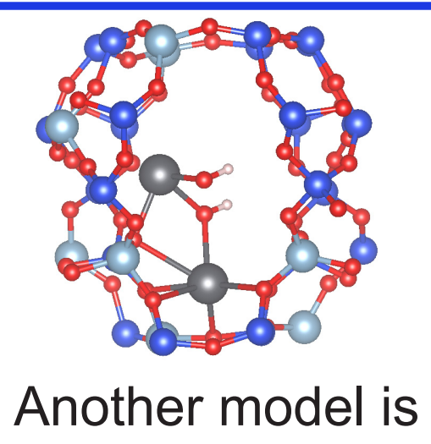
Fig. 6. Top: VDOS curves of 50 % Pb-overexchanged Pb-STI with 2.8 H_2O per Pb at RT. **Bottom:** IR spectra of Pb-STI showing H_2O/OH absorptions.

IV. MD simulations

Different structural models in terms of H_2O-, Pb-content and temperature are tested with MD simulations, in order to find or exclude possible reasons for the anomalous thermal behavior of Pb-STI. Some of these models are reported in figure 8.



No overexchange
Continuous dehydration
→ contraction
Not in agreement with experiment.



50% overexchange
Better in agreement with experiment, but completely dehydrated Pb-STI is too contracted.
Another model is currently testing a possible oxidation of Pb^{2+} to Pb^{4+} at elevated temperatures.

Fig. 7. Fragments of two models that are used for MD simulations. **Top:** No overexchange, 5 H_2O per Pb. **Bottom:** 50 % overexchange, no H_2O.

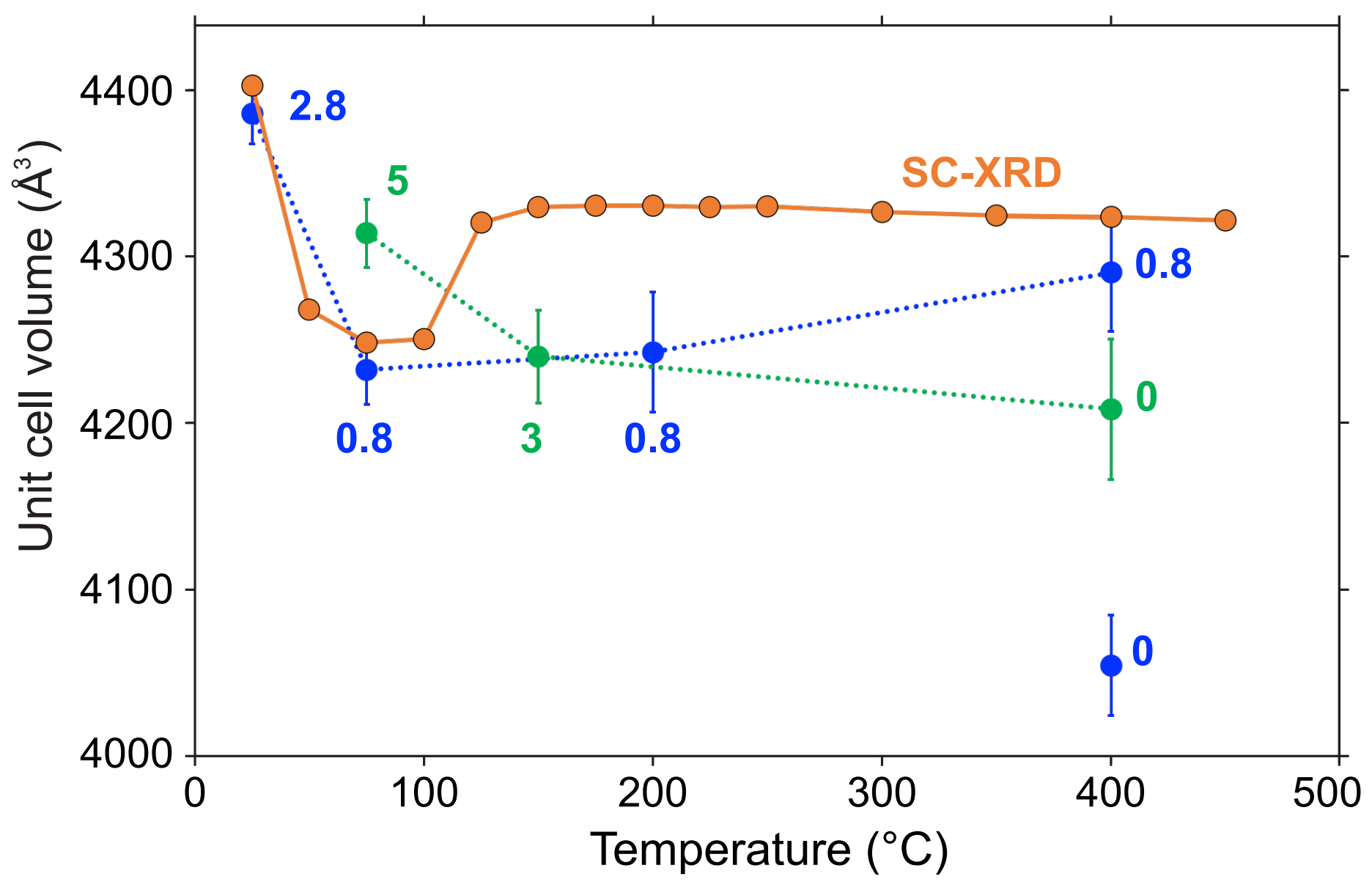


Fig. 8. Unit cell volume of different MD models as a function of temperature with experimental data for comparison. Numbers indicate number of water molecules per Pb for each model.

Conclusion

- Pb-STI shows anomalous behavior upon heating compared to other STI zeolites
- Pb^{2+} incorporation into stellerite leads to increased thermal stability
- Chemical and spectroscopy analysis suggest a Pb-overexchange
- Further investigations are in progress to test eventual oxidation of Pb^{2+} to Pb^{4+}

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