MS27-2-6 Interplay between hydrogen-bonding proton dynamics and Fe valence fluctuation in Fe$_3$(PO$_4$)$_2$(OH)$_2$ barbosalite at high pressure
#MS27-2-6

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Abstract
Pressure dependence of mixed-valence barbosalite Fe^{2+}Fe^{3+}$_2$(PO4)2(OH)2 is investigated based on a combination of single crystal X-ray diffraction, DFT calculations, infrared and Mössbauer spectroscopy to determine how the change in hydrogen bonding, i.e. O-H…O, may influence Fe2+→(OH)-→Fe3+ intervalence electron transfer and vice-versa.
Recently, the original P21/n space group of barbosalite was questioned as n-glide plane reflection conditions (h0l:h+l=2n) were found to be violated based on TEM and single crystal X-ray diffraction. A doubled unit-cell barbosalite structure in the P21 space group, i.e. along the c axis, was proposed[1]. However, subsequent analysis reveals that such reflections thought to be attributable to the doubled unit-cell, are in fact due to a non-merohedral twinning with a 90° rotation angle. The barbosalite structure is clearly still centrosymmetric with the P21/n space-group as either suggested by the cumulative probability distribution curves and the use of a polar twinning law in the P21 space group solution. Moreover, contrary to what was originally proposed, the presence of an additional non-stoichiometric iron statistically connects the face sharing FeO6 octahedra trimers, i.e. Fe2+-Fe3+-Fe2+, to form infinite chains along <110> as observed in the lipscombite-like structure[2]. Based on DFT calculations, hydrogen atoms are located in the octahedral volume of this additional non-stoichiometric atom iron site and forms a hydrogen bond O–H⋯O between the (OH)- common vertex of three octahedra and one of the oxygens of a PO4 group, i.e. as part of Fe-O–H⋯O-P structural sequences. This means that the FeO6 octahedral trimers are either connected by a hydrogen bond or by this non stoichiometric iron site.
Pressure triggers proton delocalization involving a P21/n-Cc phase transition in a 2a×2b×c supercell at ~5 GPa in hydrogen bonds of the Fe-O-H…O-P structural segments. Hydrogen bond reinforcement and anticipated proton dynamics, discerned by IR spectroscopy and symmetrization of lattice parameters, impact on the crystal field at proximate Fe cations. This triggers dynamical minority-spin electron exchange along Fe2+®L®Fe3+ pathways (ligand L = O or (OH)- of shared octahedral faces), discerned by 57Fe Mössbauer spectroscopy at 10-30 GPa. The pressure response of these mixed-valence hydroxy phosphates exemplify the interplay between proton (THz) and electron (MHz) dynamics on two disparate time scales in the same condensed phase. This is of widespread relevance to charge dynamics in hydrogen bonded systems (e.g., biomolecular complexes and planetary interiors).

References
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Barbosalite structure in (P21/n)
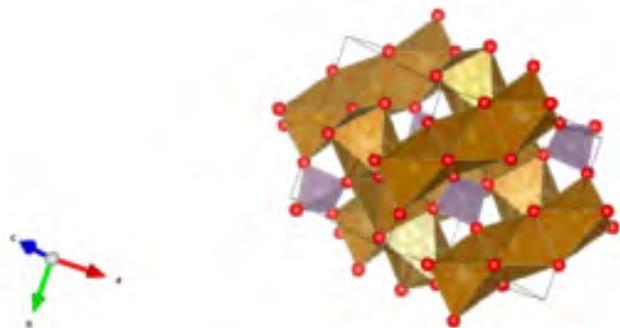
HP-structure of barbosalite at 9.9 GPa (Cc)