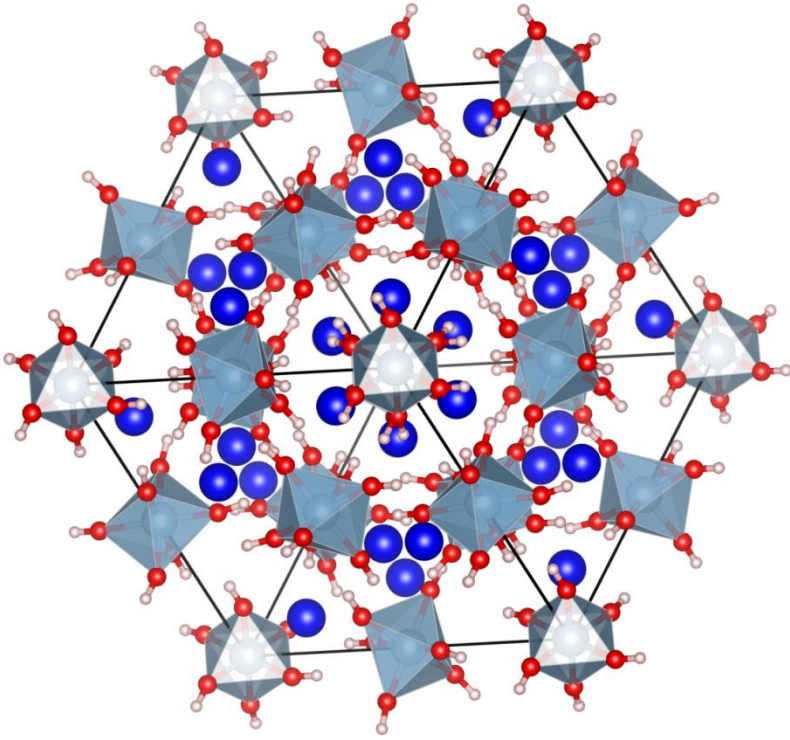


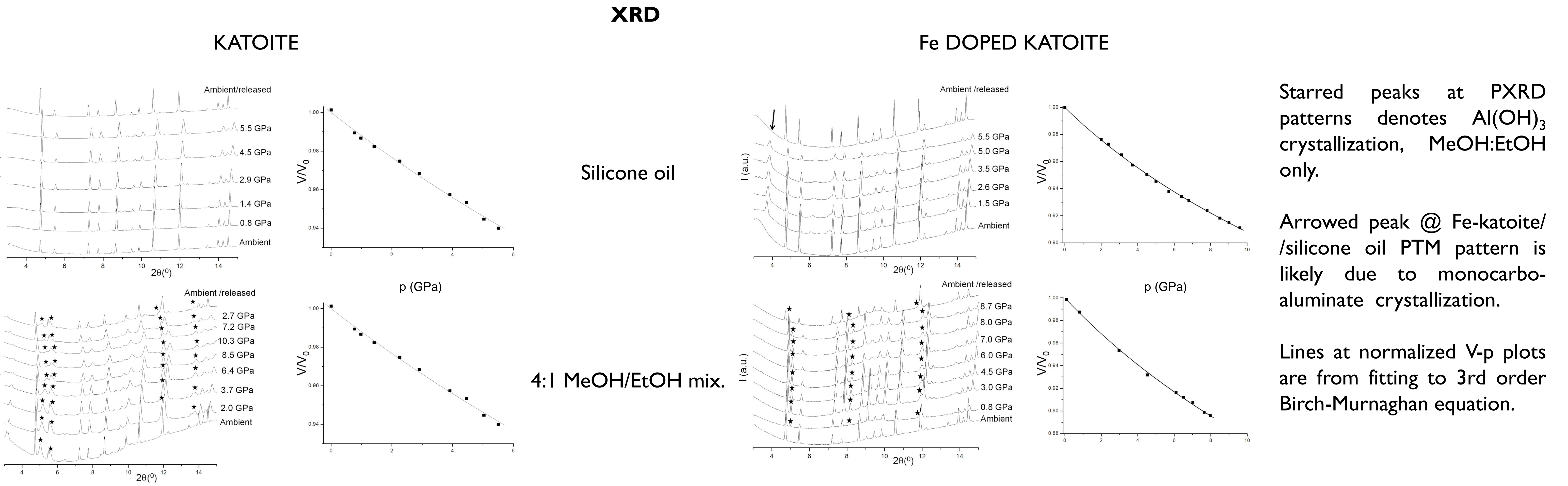
THE SYNCHROTRON POWDER XRD & PERIODIC DFT STUDIES ON THE PRESSURE BEHAVIOR OF KATOITE

P. Rejmak,¹ A. Cuesta,² A. Ayuela,³ A.G. De la Torre,⁴ I. Santacruz,⁴ L.F. Carrasco,⁵ C. Popescu,¹ M.A.G. Aranda^{1,4}
¹Institute of Physics PAS, Warszawa, Poland ²ALBA synchrotron, Barcelona, Spain
³Centro de Física de Materiales CFM-MPC CSIC-UPV/EHU, Donostia-San Sebastián, Spain
⁴Departamento de Química Inorgánica, Universidad de Málaga, Málaga, Spain

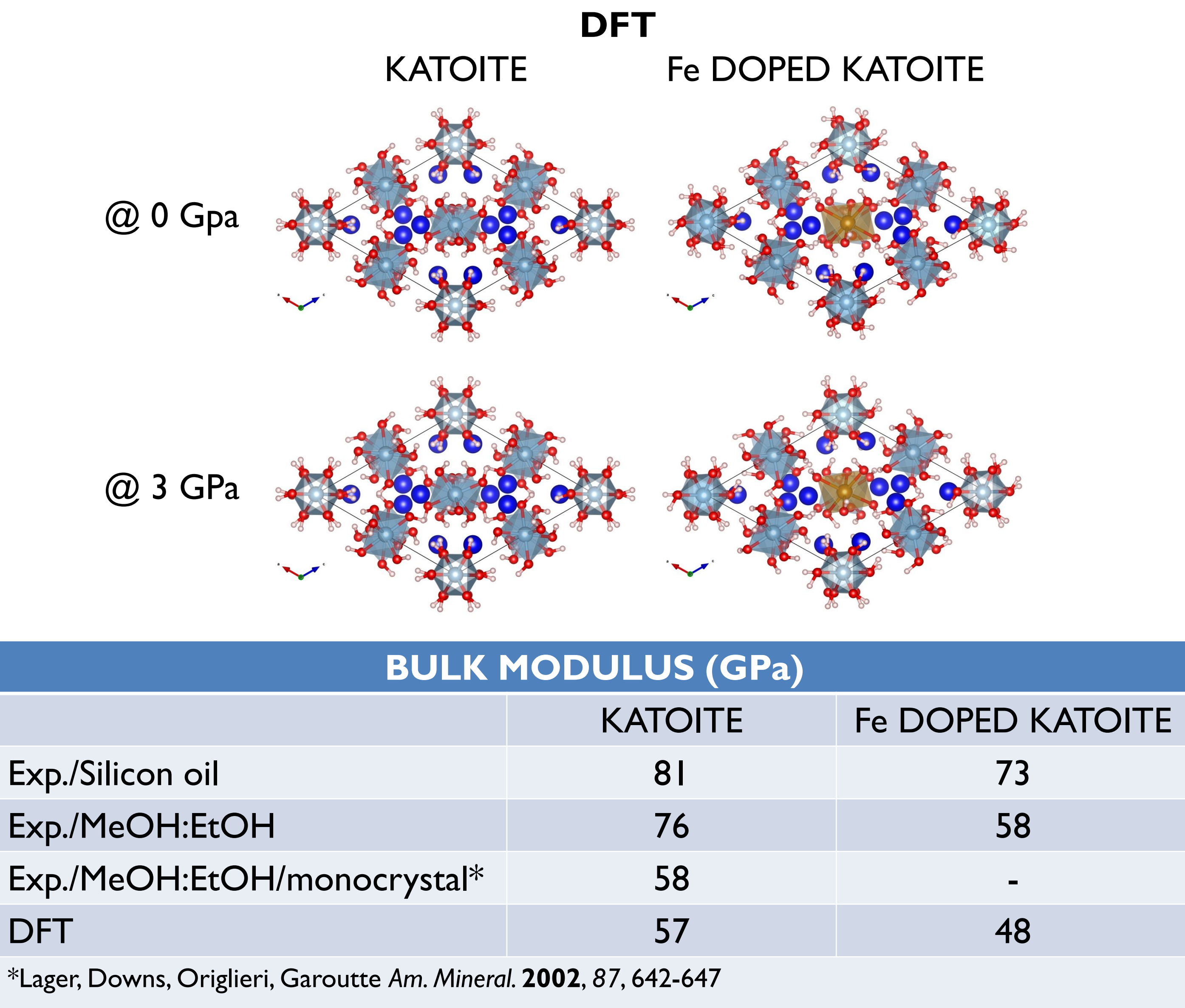


SCOPE
Katoite $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, $x=1.5-3$ is a garnet mineral, crystallizing in cubic system ($la3d$). It is considered as one of the main water reservoir in the Earth's mantle. Si free ($x=3$) katoite is the only thermodynamically stable calcium hydroxyaluminate in the hydrated Portland cements, where Al^{3+} may be partially substituted by Fe^{3+} ions. The understanding of katoite pressure behavior is an important issue for geoscience and civil engineering. This work presents the experimental & computational results for pure Al katoite along with the first such data for Fe doped one.

METHODS
Synthesis Pure Al katoite $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ & Fe doped one $\text{Ca}_3\text{Al}_{1.7}\text{Fe}_{0.3}(\text{OH})_{12}$ were obtained from a few days hydration of $\text{Ca}_3\text{Al}_2\text{O}_6$ & $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$, respectively.
Measurements High pressure synchrotron X-ray diffraction patterns were collected in transmission geometry for powder samples at MSPD beamline of ALBA synchrotron. The samples were grounded with pressure transmitting medium (PTM) an loaded into diamond anvil cells. Two types of PTM were used: (1) silicon oil, up to 5.5 Gpa, (2) 4:1 MeOH/EtOH mixture, up to 10 Gpa. Bulk modulus obtained from pressure-volume curves.
Calculations Periodic density functional theory (DFT) calculations with SIESTA code, using PBE functional. Primitive cell (half of the bcc) were used, gamma point only in k-space. Both atomic positions & cell units were optimized. Then calculations performed for several compressed & expanded structures to get bulk modulus from energy-volume curve fitting to 3rd order Birch-Murnaghan equation of state.



DFT				
	KATOITE		Fe DOPED KATOITE	
Mean A-B distances (R_{A-B} , in Å) & coordination numbers (N_{A-B})				
	0.0 GPa	3.0 GPa	0.0 GPa	3.0 GPa
$R_{Ca-O} // N_{Ca-O}$	2.48//8	2.45//8	2.50//7.83	2.46//7.75
R_{Al-O}	1.94	1.93	1.94	1.93
$R_{O(Al)-H}$	0.98	0.98	0.99	0.99
$R_{H(OAl) \cdots O} // N_{H \cdots O}$	2.44//1	2.40//1	2.16//1.25	2.16//1.5
R_{Fe-O}	-	-	2.10	2.09
$R_{O(Fe)-H}$	-	-	0.99	0.99
$R_{H(OFe) \cdots O} // N_{H \cdots O}$	-	-	2.06//1	2.18//1.5
Total charge transfer upon compression (Hirshfeld atomic charges)				
ΔQ_{Ca}	-0.28		-0.29	
ΔQ_O	+0.29		+0.32	
$\Delta Q_{Al} // \Delta Q_{Fe}$	-0.02// -		-0.03//0.00	
$\Delta Q_{H(OAl)} // \Delta Q_{H(OFe)}$	0.00// -		-0.04// -0.03	



BULK MODULUS (GPa)		
	KATOITE	Fe DOPED KATOITE
Exp./Silicon oil	81	73
Exp./MeOH:EtOH	76	58
Exp./MeOH:EtOH/monocrystal*	58	-
DFT	57	48

*Lager, Downs, Origlieri, Garoutte *Am. Mineral.* **2002**, 87, 642-647

CONCLUSIONS
➤ Fe doping increases the compressibility of katoite.
➤ DFT shows that
• compression proceeds via bond shortening rather than polyhedra rotation in both pure Al & Fe doped katoite
• Fe doping strengthens interpolyhedra hydrogen bonds, which in turn weakens Ca-O bonds
• the most compressible are hydrogen & Ca-O bonds, then Fe-O ones, Al-O & H-O bonds barely shrink.
➤ Katoite compressibility strongly depends on the sample crystallinity, presence of admixtures & pressure transmitting medium.

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