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Phase behavior and equations of state of the actinide oxides

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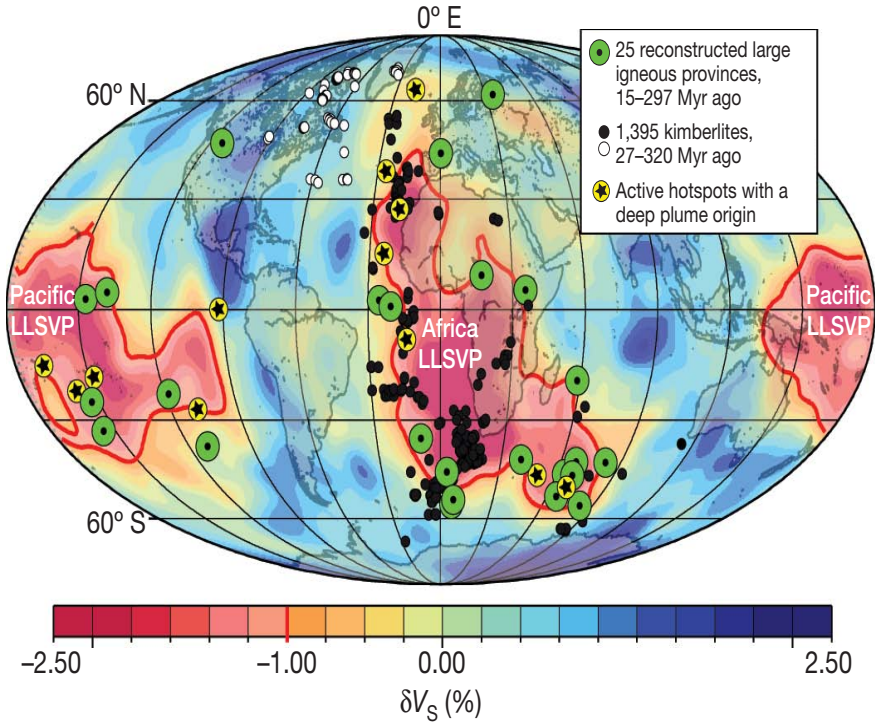
Actinide materials at extreme conditions

Actinide-bearing minerals as tracers for heat generation in the deep Earth

~36 % of heat fluxed at the surface produced by **U** and **Th**

Hosts of these elements in the deep Earth uncertain

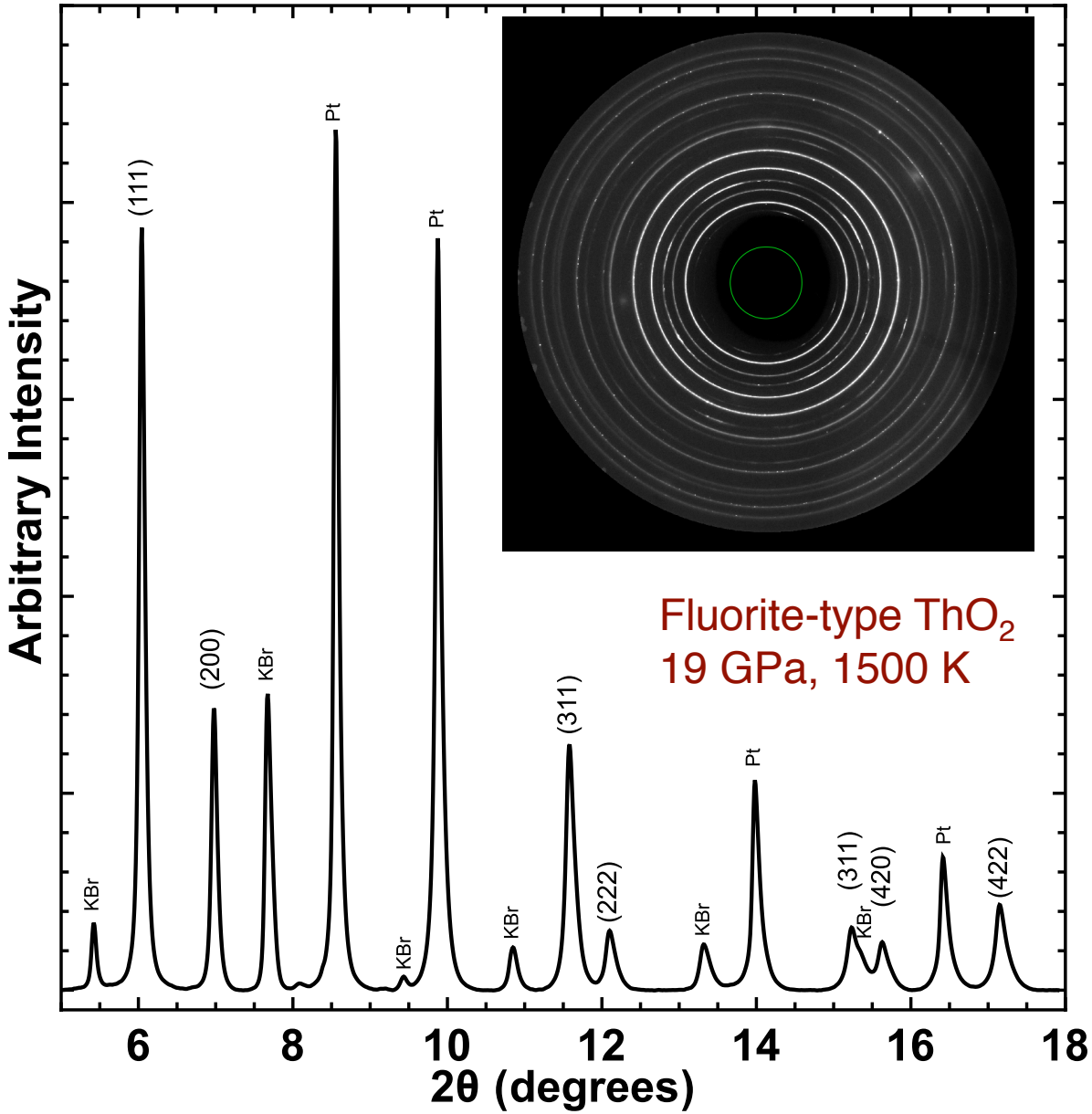


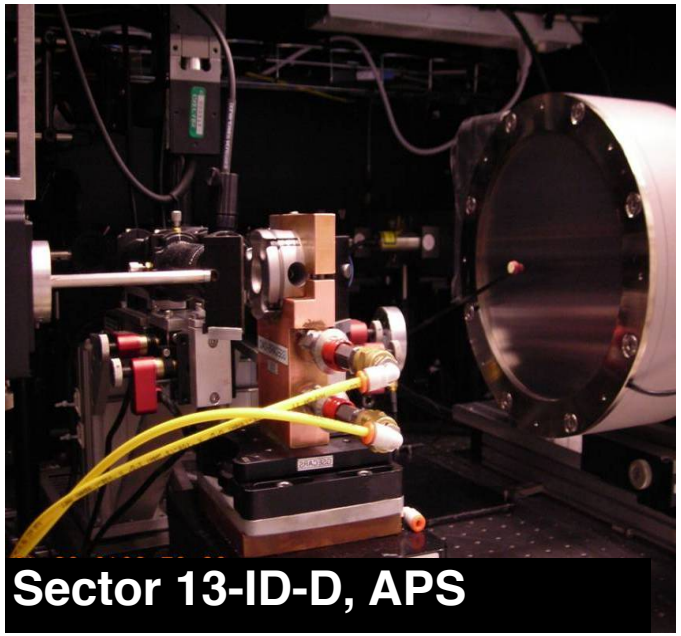
Torsvik et al. *Nature* (2010)

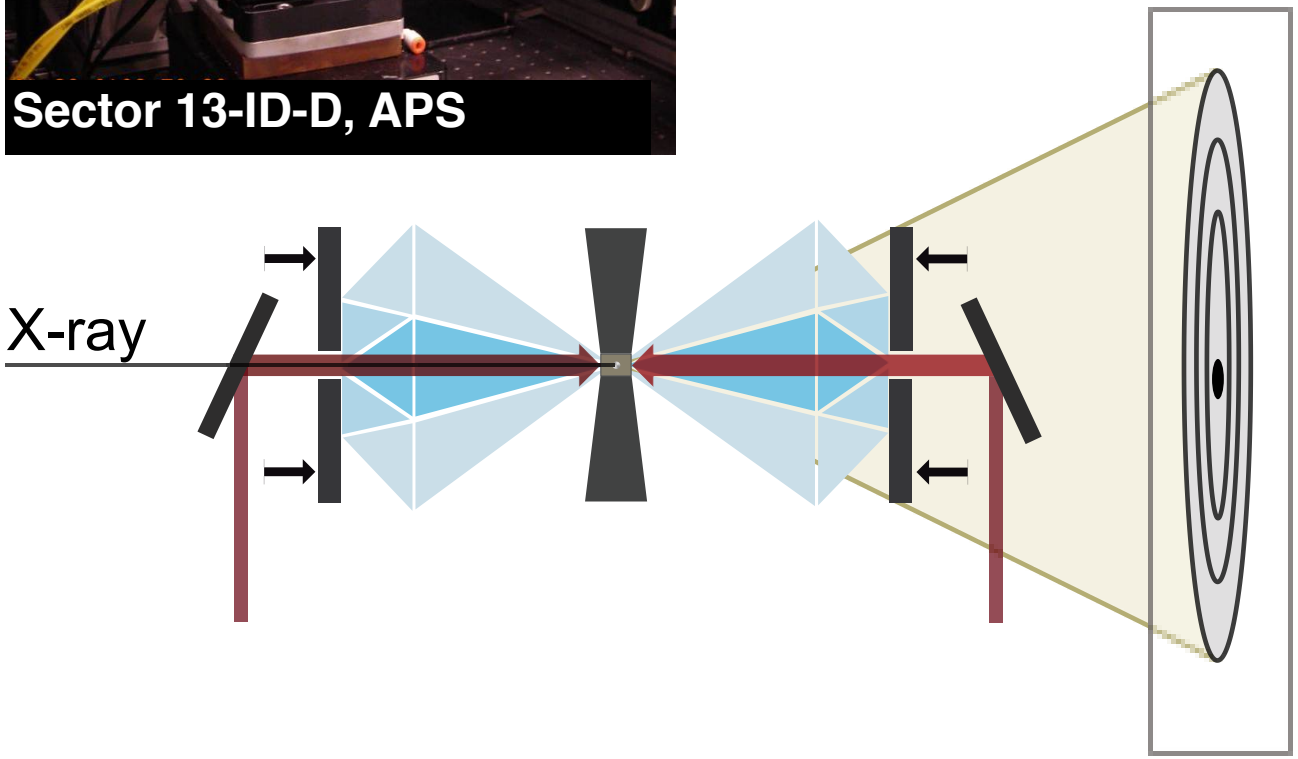
http://www.areva.com/EN/global-offer-386/highperformance-uo2-fuel-assemblies-for-all-reactors.html

Fundamental studies of actinide-bearing materials at extreme conditions for nuclear fuel generation and spent fuel storage

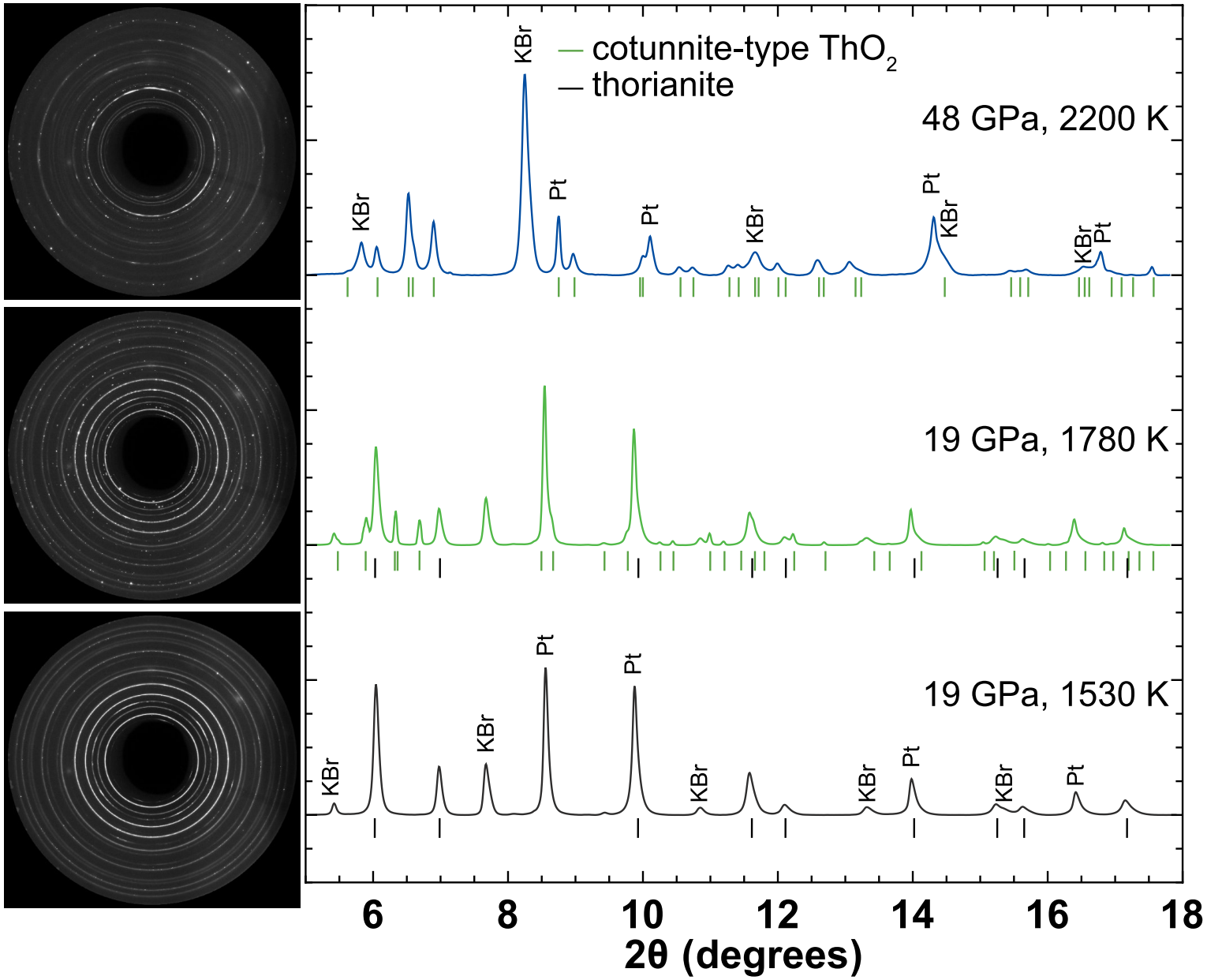
In-situ synchrotron XRD experiments

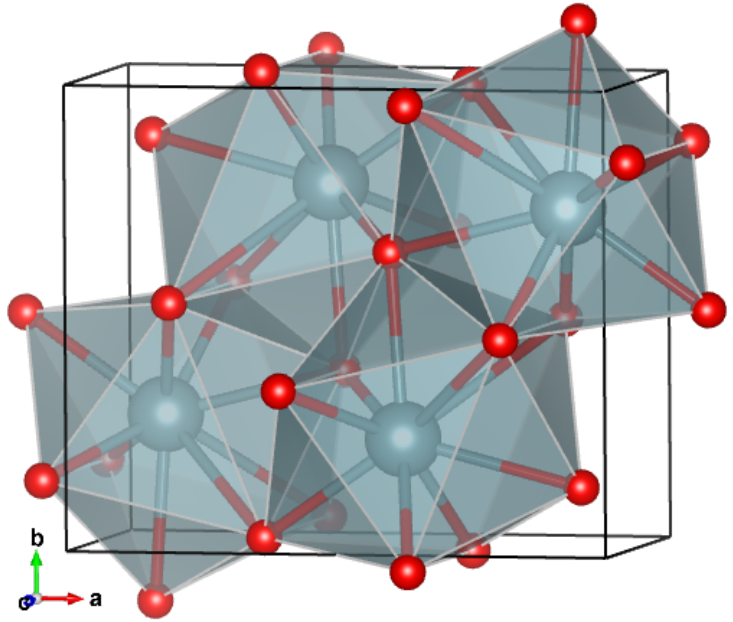


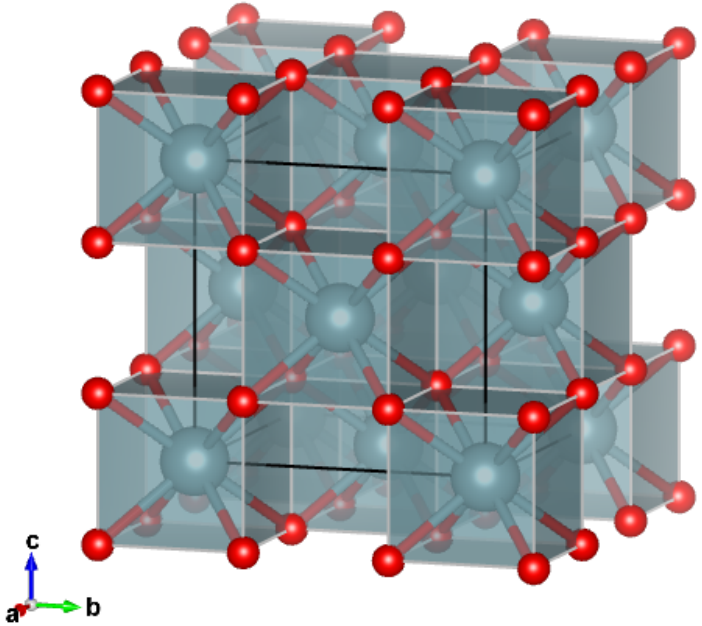




ThO_2 *P-T* phase diagram

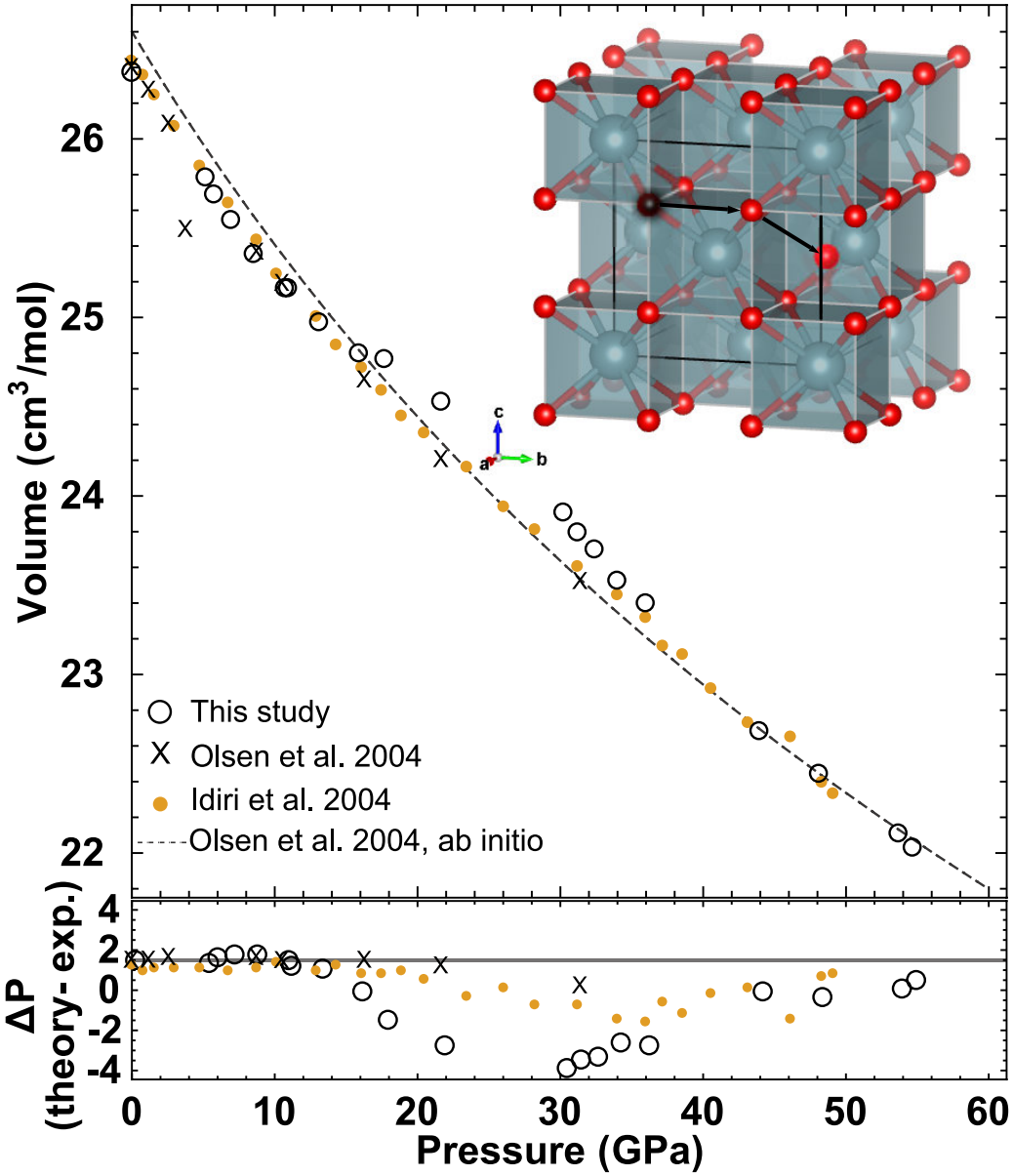


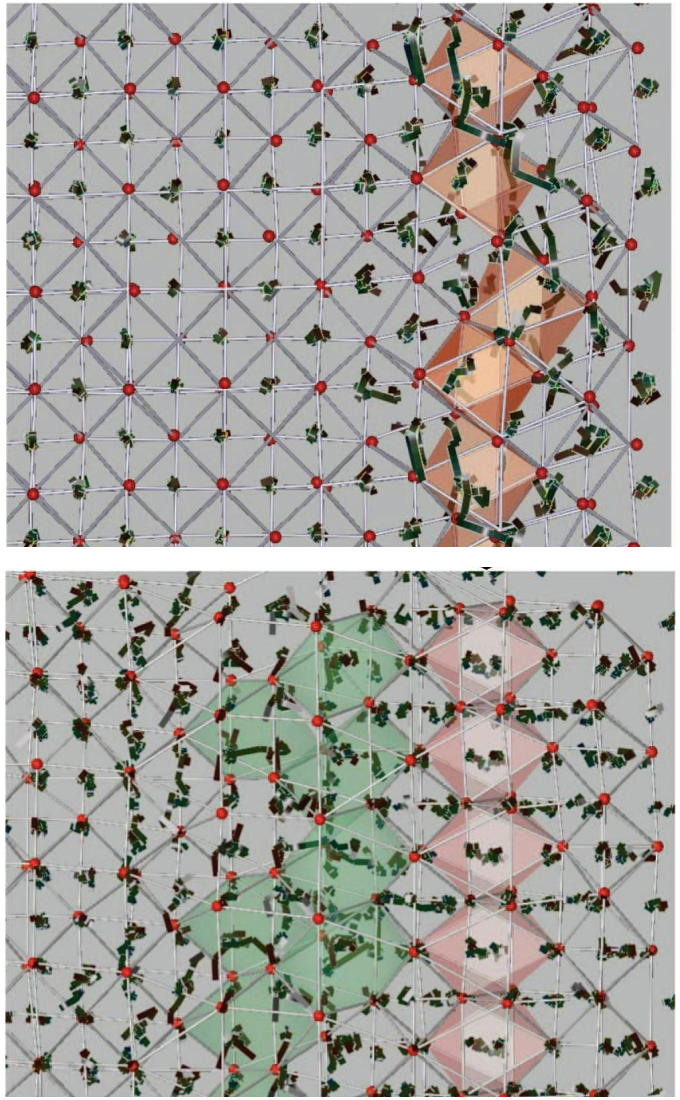




Chidester et al., Revised and Resubmitted, *American Mineralogist*

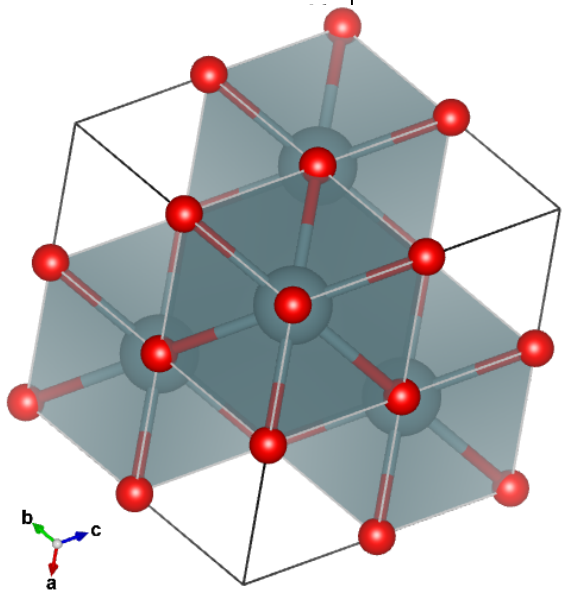
Room-temperature compression behavior

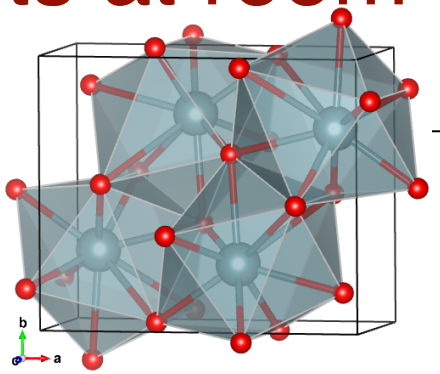


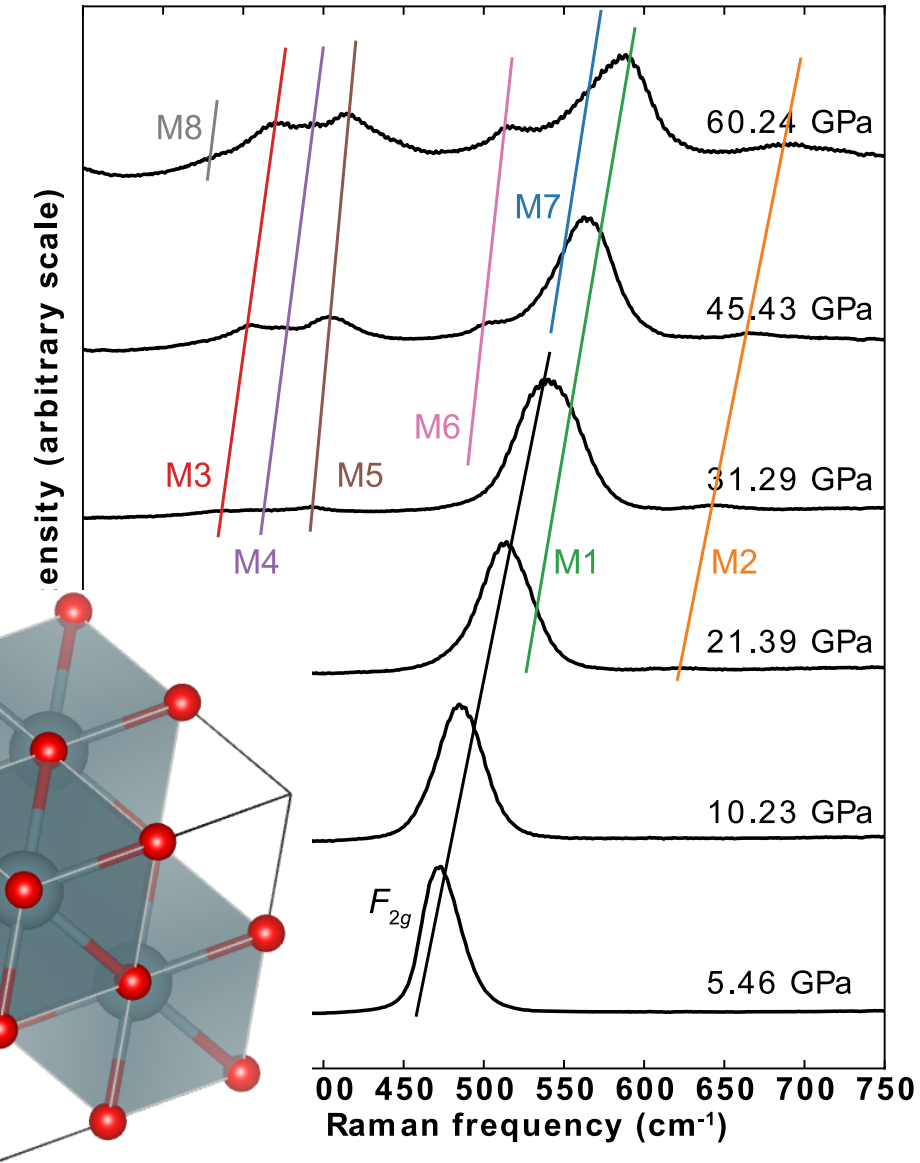


Boulfelfel et al. PRB 2006

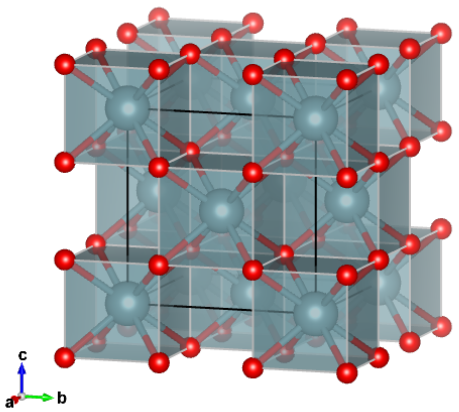
Raman measurements at room temperature

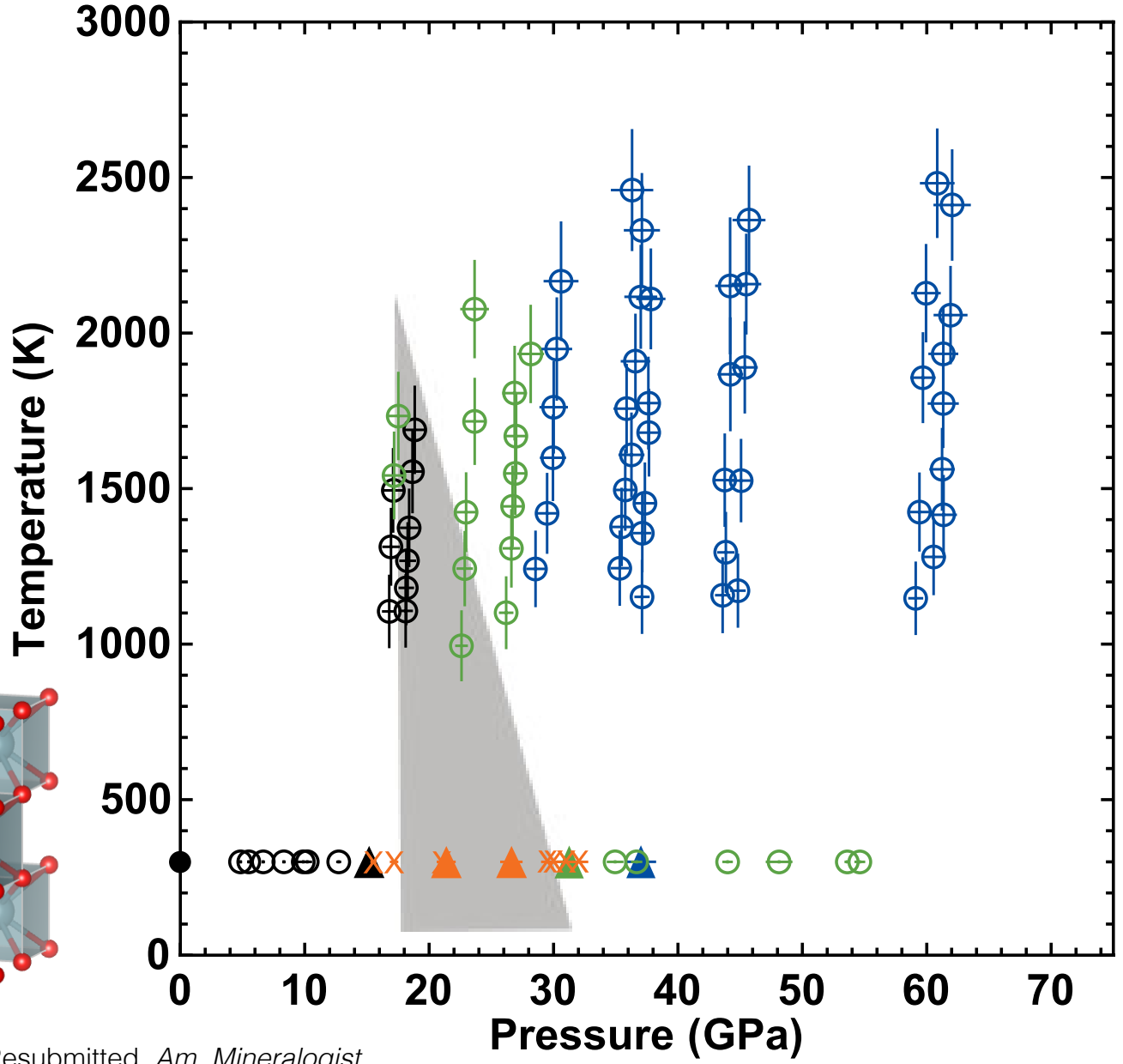


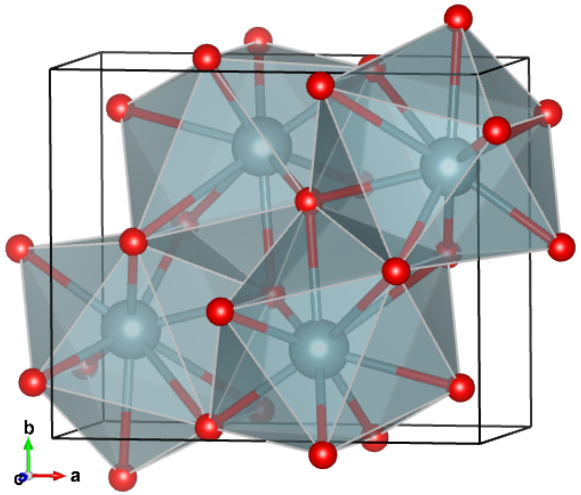




ThO_2 *P-T* phase diagram

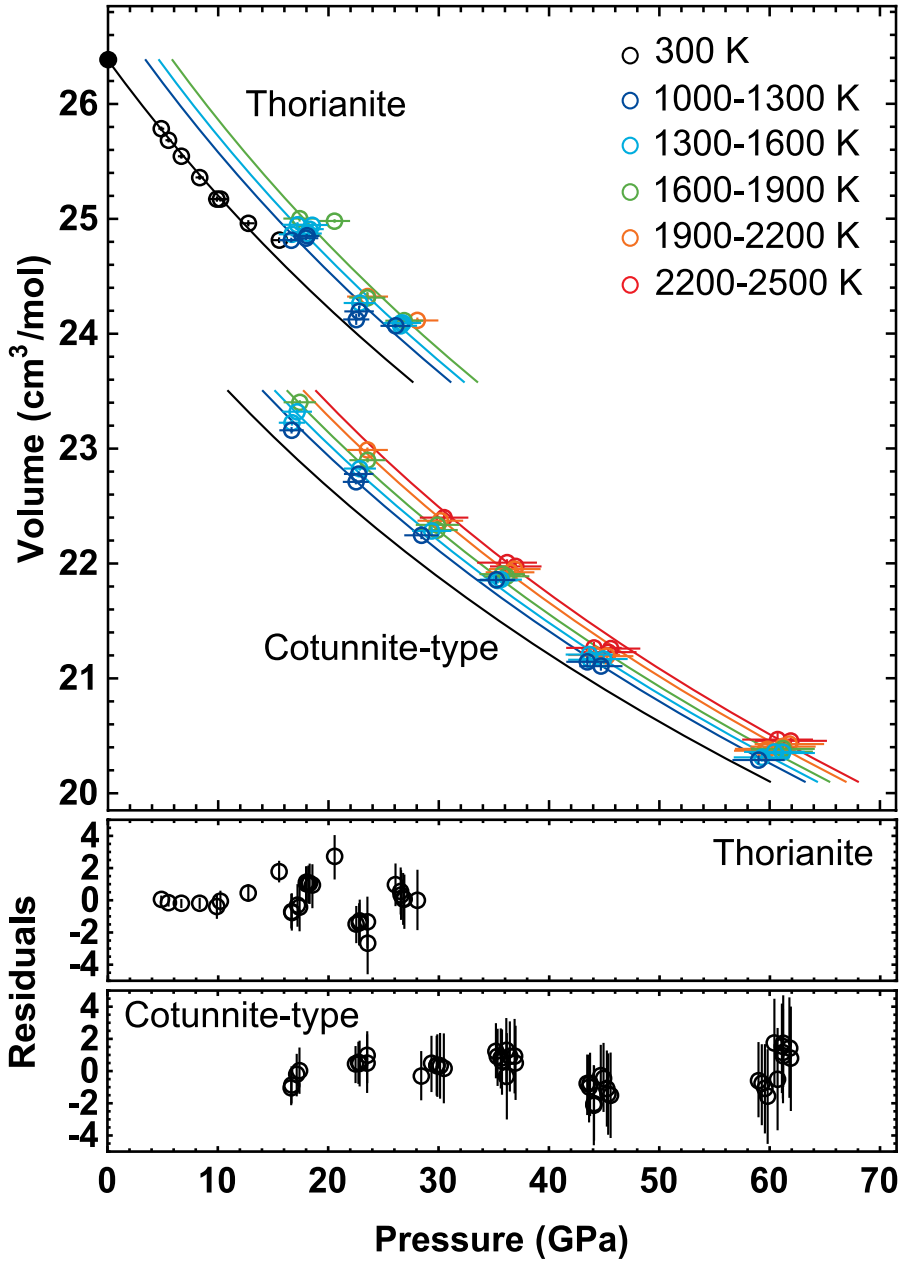






Chidester, Revised and Resubmitted, *Am. Mineralogist*

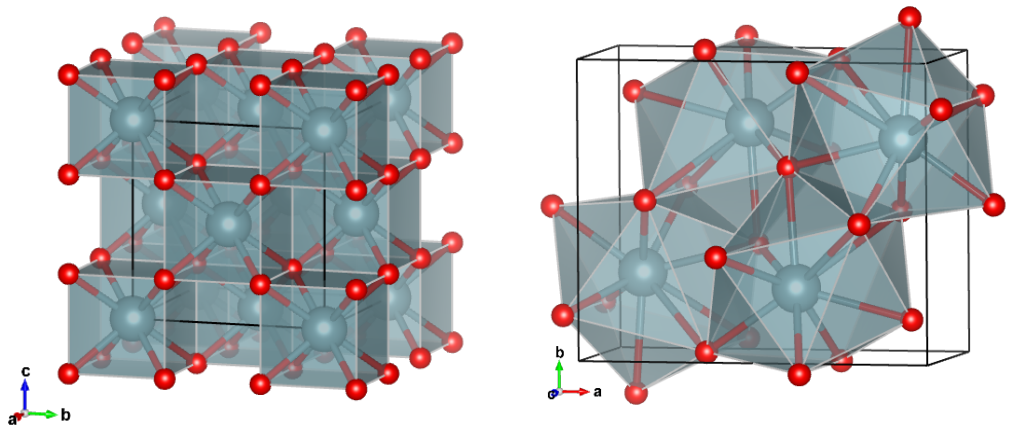
Equations of state of ThO_2 polymorphs



$$P = 3K_0 f(1+2f)^{5/2}(1+{}^3/_2(K_0'-4)f)+\alpha K_T(T-300)$$

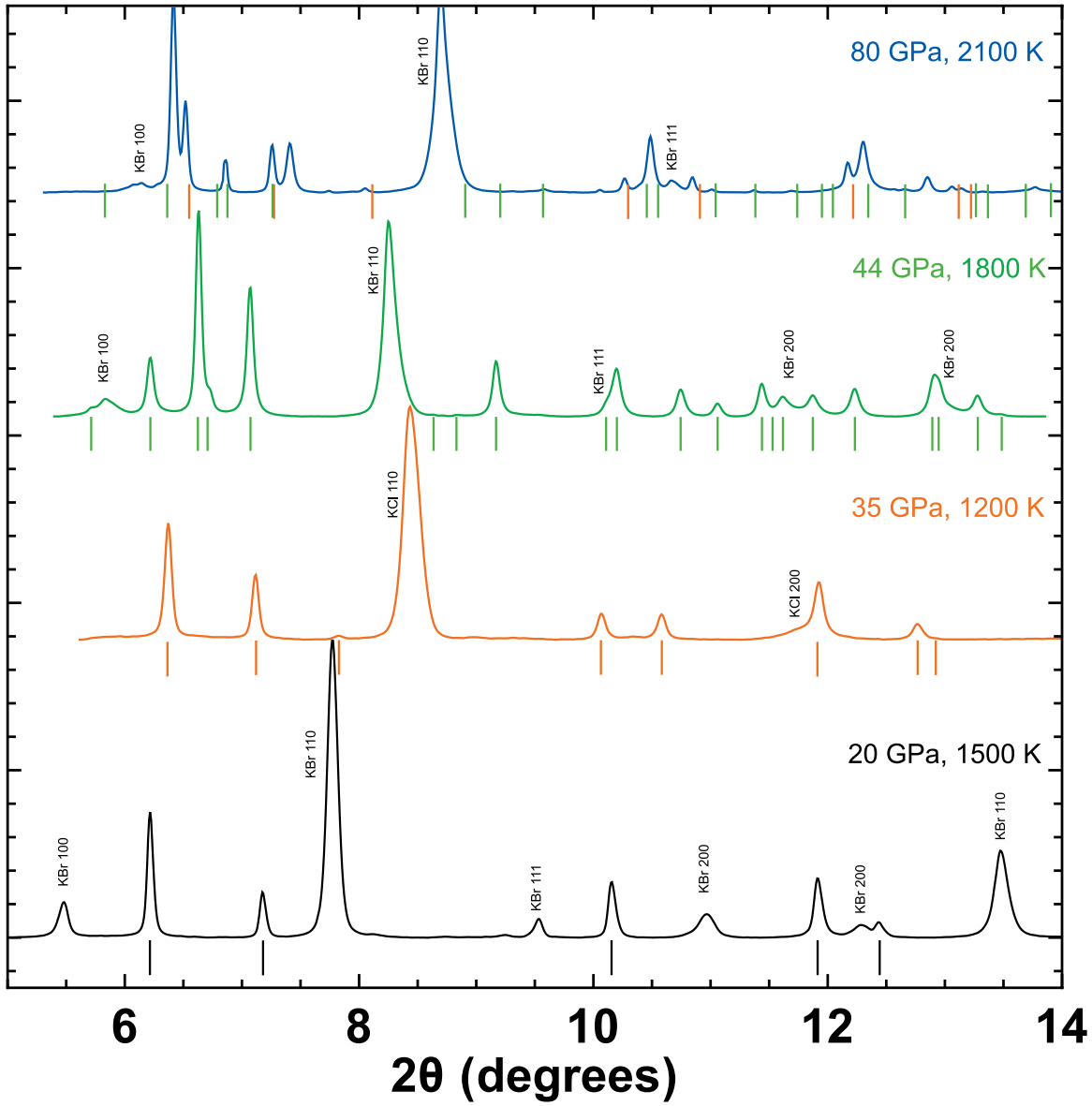
$$f = {}^1/_2((V/V_0)^{-2/3}-1)$$

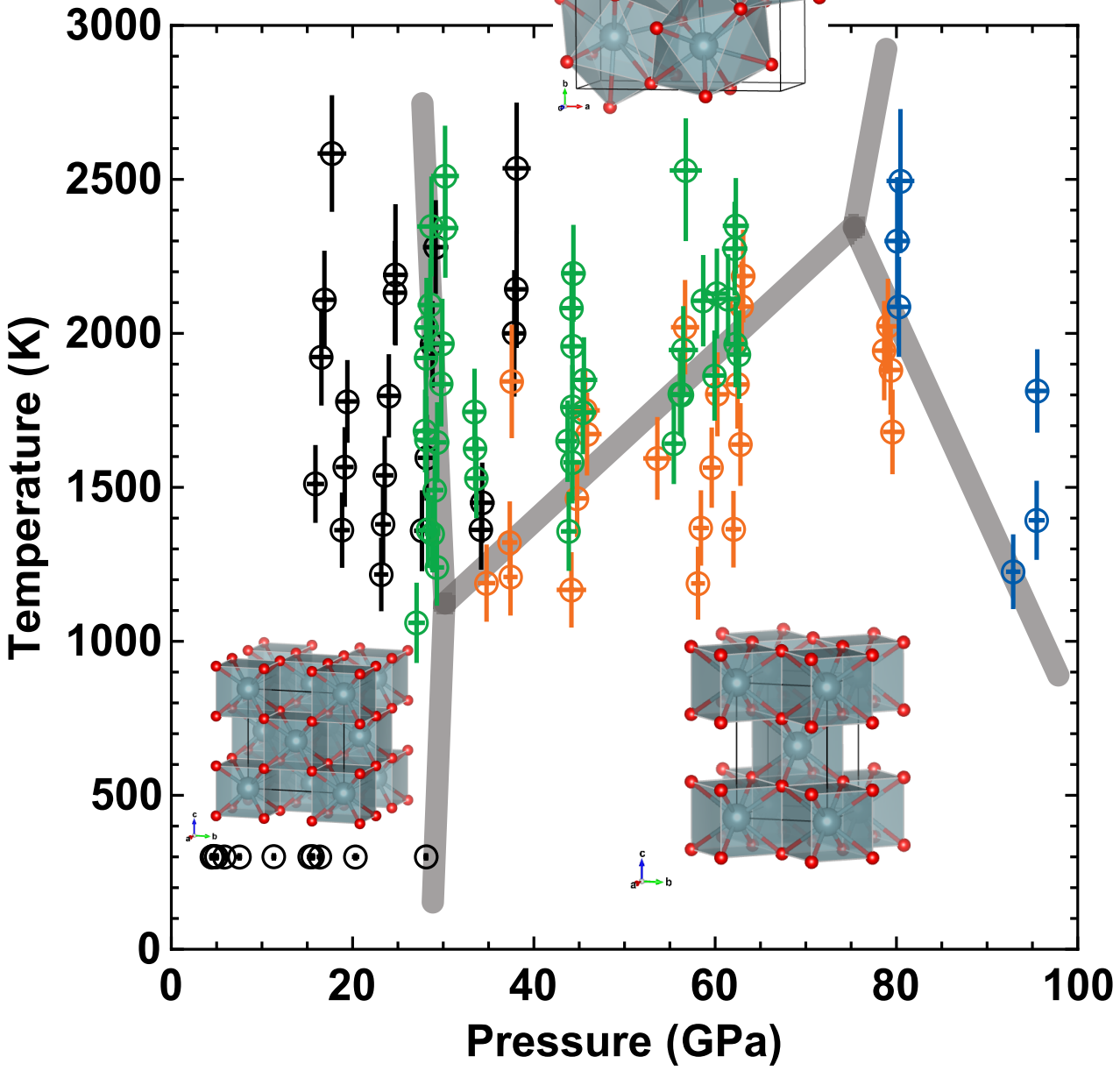
Thorianite			
V_0 (cm^3/mole)	K_0 (GPa)	K_0'	αK_T (GPa/K)
26.379(7)	204(2)	4	0.0035(3)
Cotunnite-type ThO_2			
24.75(6)	190(3)	4	0.0037(4)



Chidester et al., Revised and Resubmitted, *American Mineralogist*

UO_2 *P-T* phase diagram

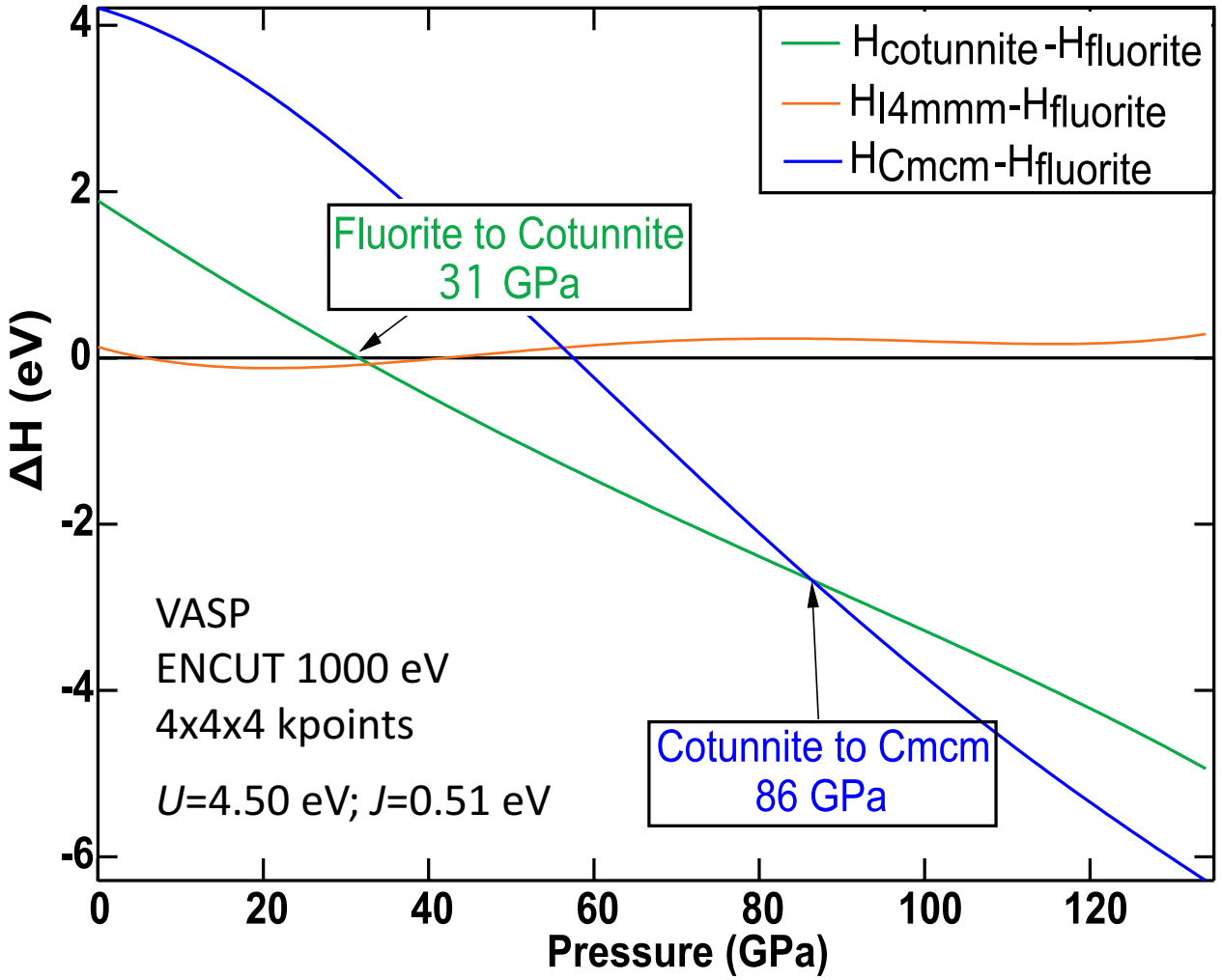


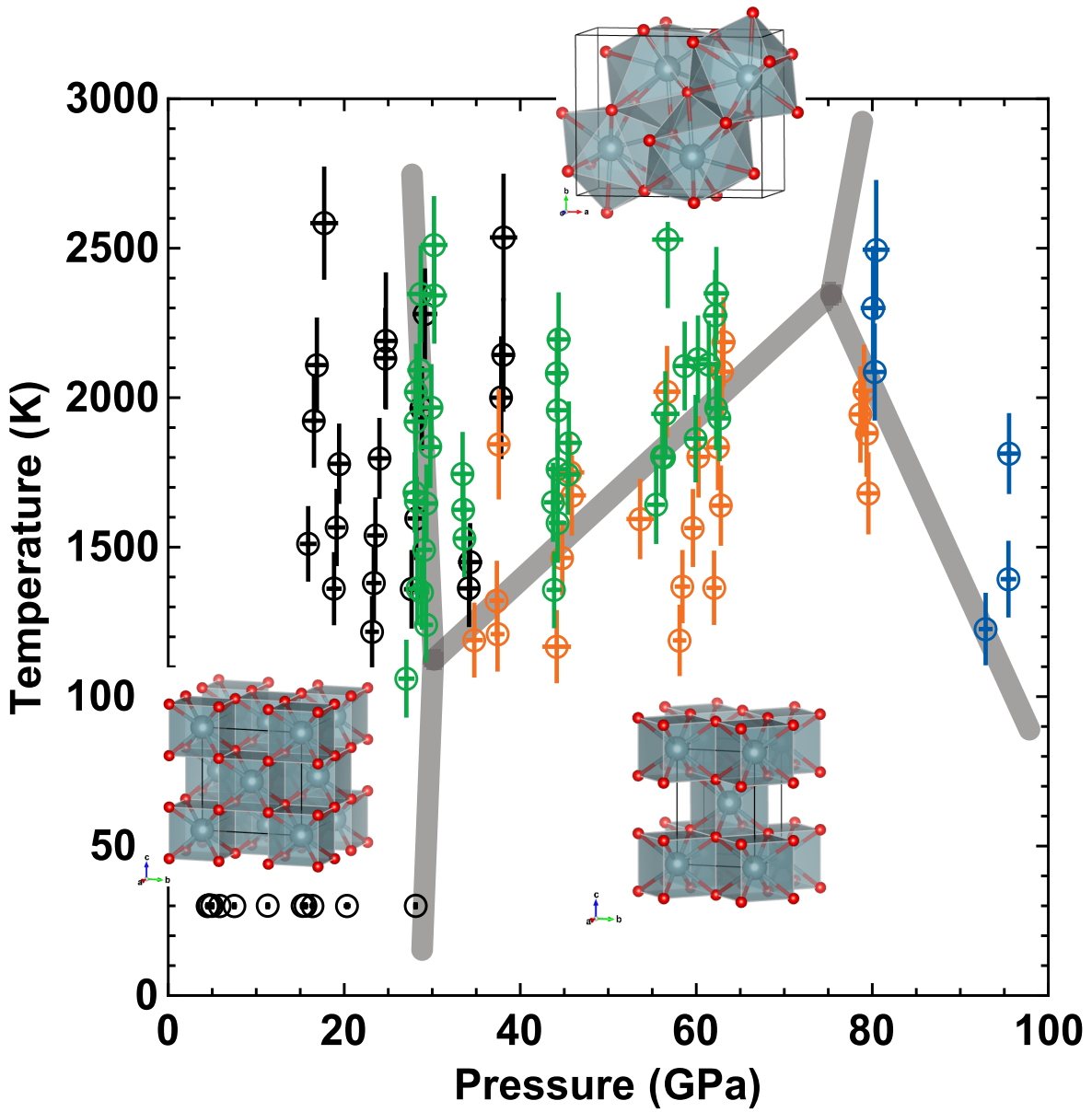


DFT + U Calculations

$$E_{dc} = \frac{U}{2}N(N-1) - \frac{J}{2}\sum_{\sigma}N^{\sigma}(N^{\sigma}-1)$$

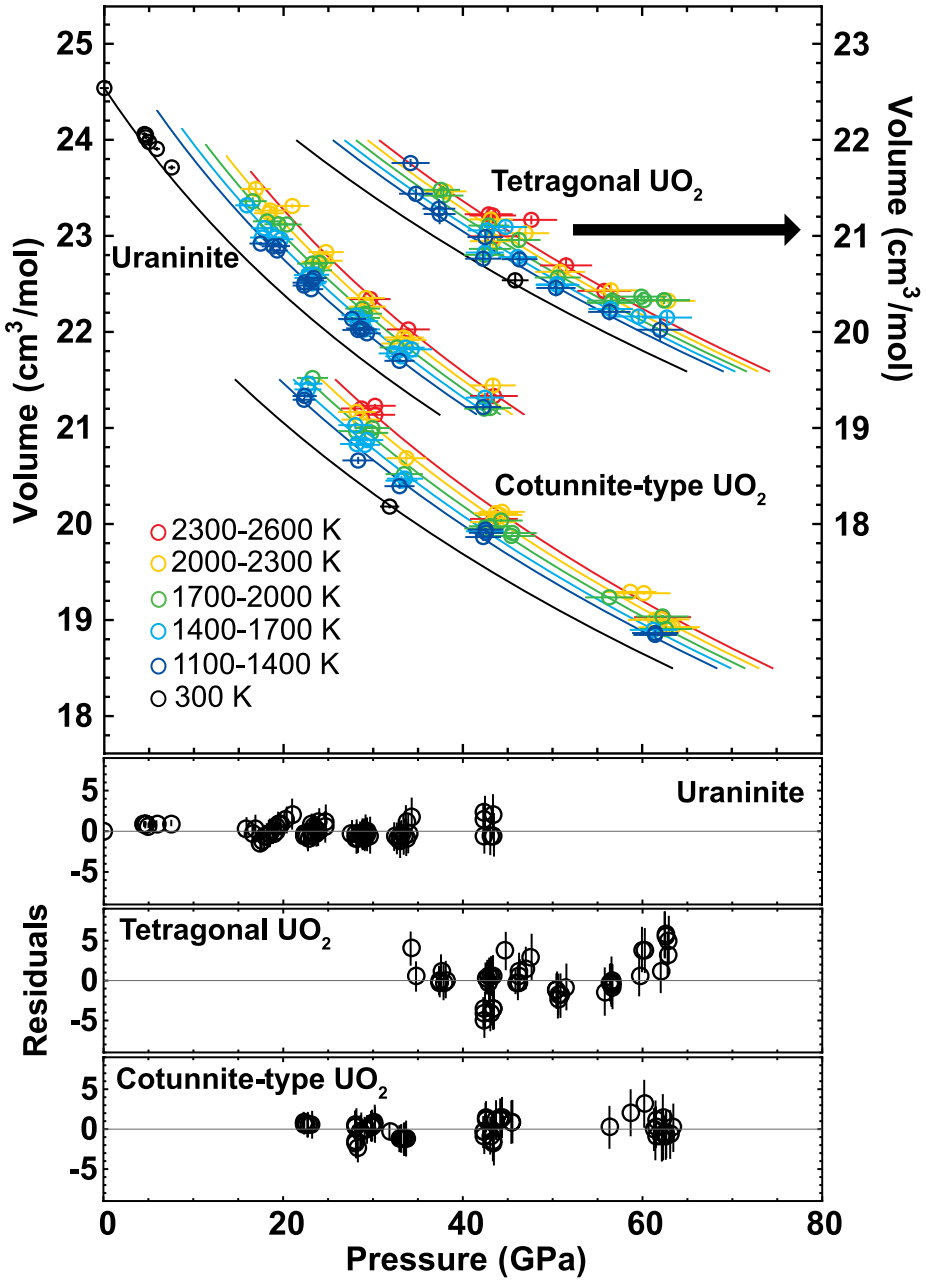
$$E_{DFT+U} = E_{DFT} + E_{Hub} - E_{dc}$$





Perry et al., 2016; Geng et al., 2007; Dudarev et al., 1997

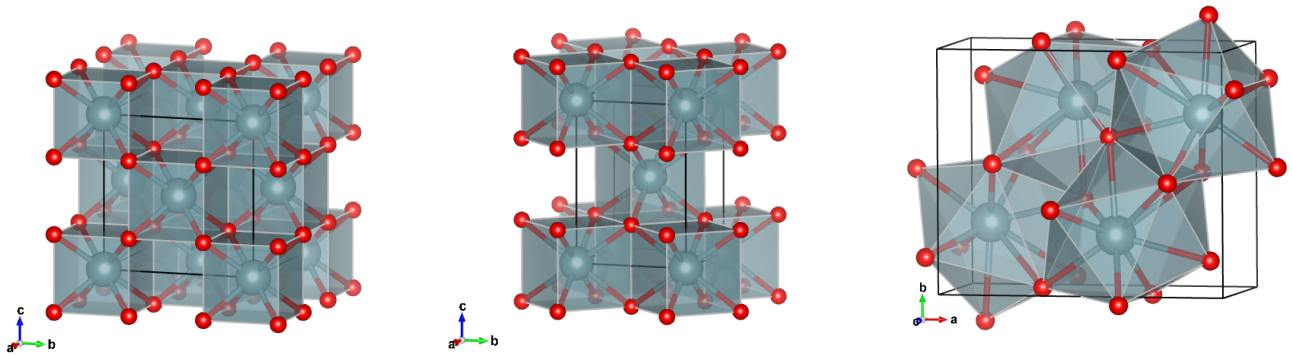
Compressibility of UO_2 polymorphs



$$P = 3K_0 f(1+2f)^{5/2}(1+{}^3/_2(K_0'-4)f)+\alpha K_T(T-300)$$

$$f = {}^1/_2((V/V_0)^{-2/3}-1)$$

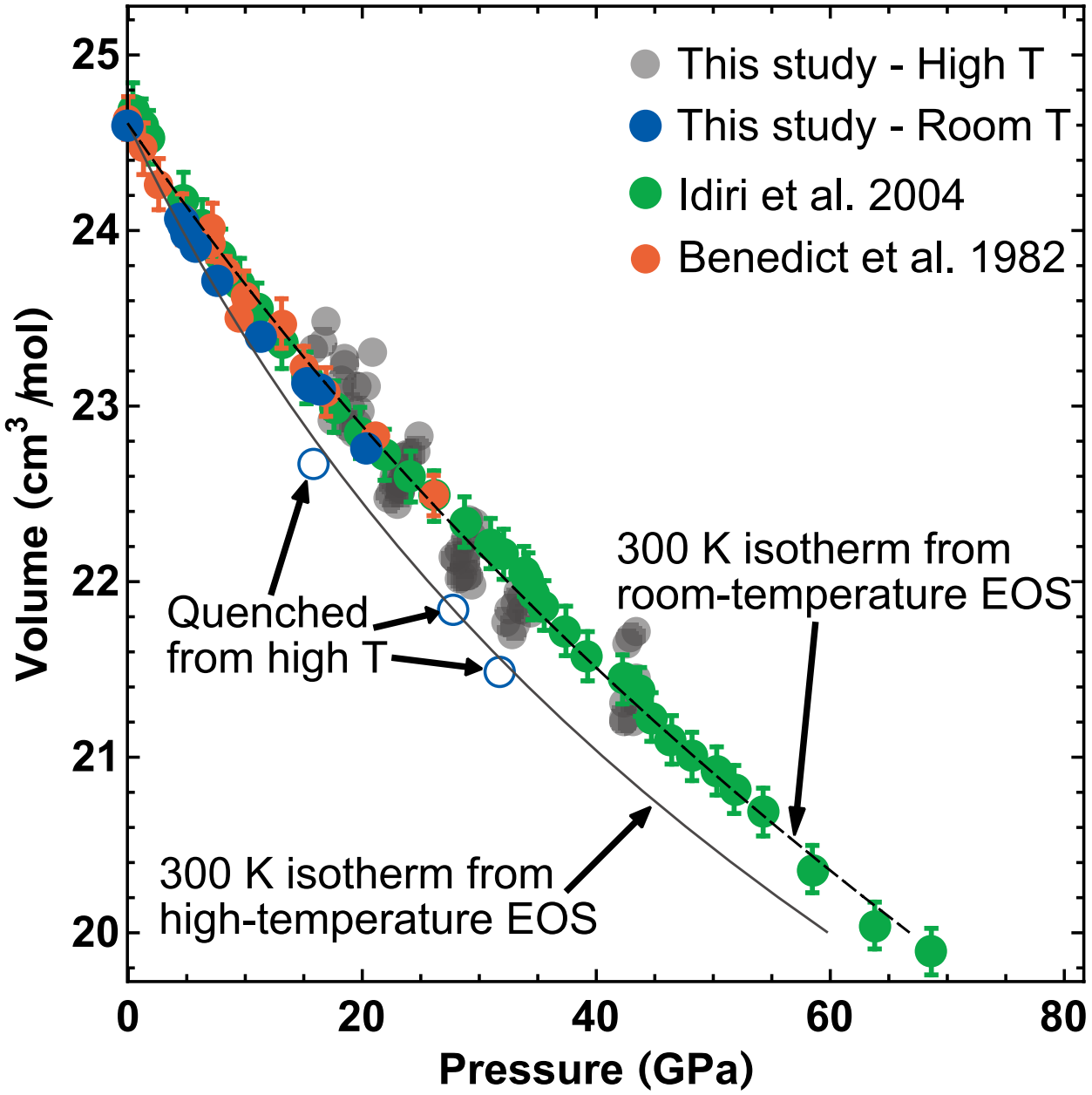
Uraninite			
V_0 (cm³/mole)	K_0 (GPa)	K_0'	αK_T (GPa/K)
24.605(5)	175(7)	4.8(5)	0.0044(2)
Tetragonal UO_2			
23.9(2)	220(20)	**4**	0.0043(7)
Cotunnite-type ThO_2			
23.02(6)	187(4)	**4**	0.0052(3)

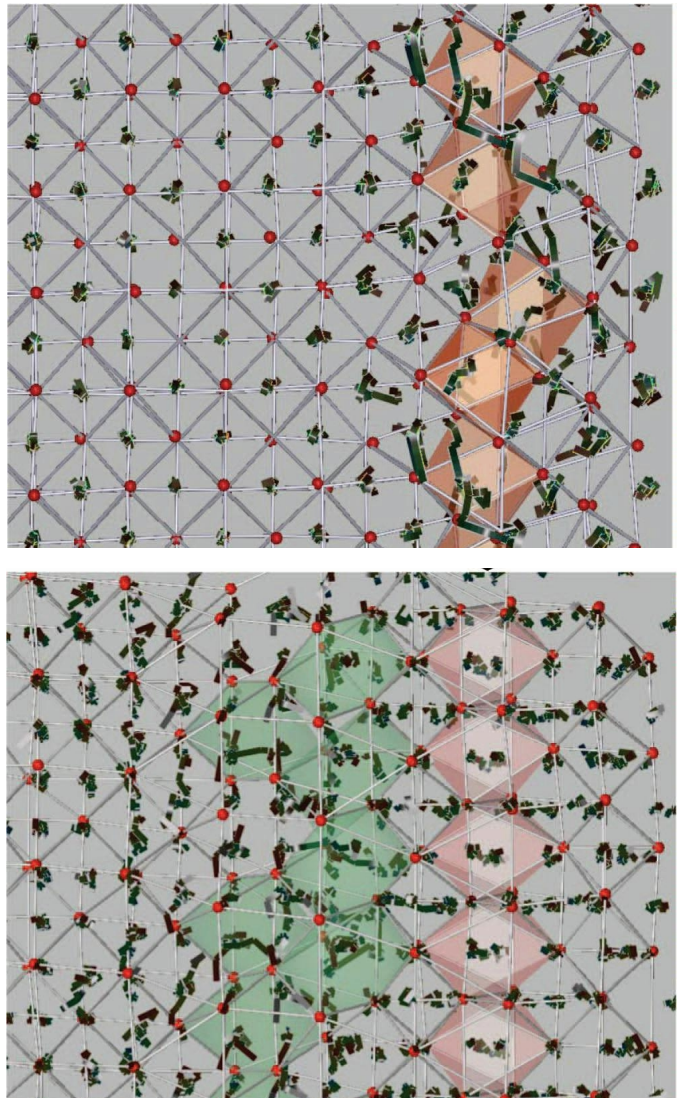


Conclusions for actinide mineralogy

- This study provides thermal parameters for the fluorite phases of these actinide oxides and measurement of the equations of state (i.e. V_0, K_0) for the high pressure-temperature polymorphs of these materials
- Both ThO_2 and UO_2 undergo the fluorite-type to cotunnite-type phase transition at room temperature and moderate pressures
- Both materials exhibit anomalous compression behavior at room temperature in the fluorite phase
- ThO_2 exists in the cotunnite-type structure up to 60 GPa and 2500 K.
- UO_2 takes on a previously unidentified tetragonal structure at high pressures and low temperatures and either undergoes a second transition or decomposes above 80 GPa at high temperatures
- UO_2 and ThO_2 (along with ZrO_2) likely exist as a solid solution in the cotunnite-type phase in the upper-most lower mantle, but the actinides are likely hosted in a different mineral at deeper conditions.

UO_2 room temperature compressibility





Boulfelfel et al. PRB 2006