

A Career in Thermodynamics, Geochemistry, and Materials Science



UCDAVIS
PETER A. ROCK
Thermochemistry
Laboratory

Alexandra Navrotsky
UC Davis

Why I Count Calories for a Living

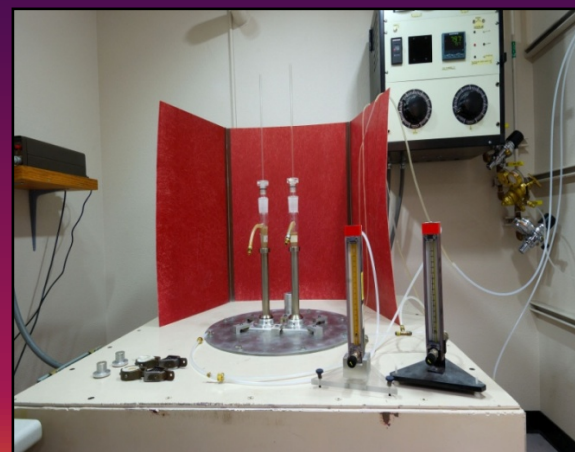
- **They are fascinating**
 - Energetics whisper secrets of the strength of chemical bonds
 - Entropies sing of vibrating atoms, moving electrons, and structural disorder
 - Systematics have predictive power
- **They pay**
 - thermodynamic data are essential to good materials processing
 - Environmental science needs thermodynamics, both for issues of stability and as a starting point for kinetics
 - Mineralogy, petrology, and deep Earth geophysics need thermodynamic data.

Calorimetry Measures

- Heat capacities
- Heats of phase transitions'
- Heats of formation



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Commercial Setaram AlexSYS Calorimeter



From these data one calculates

Enthalpies, entropies, free energies

- **Solubilities**
- Phase diagrams
- **Petrologic and geochemical processes**
- **Materials synthesis and compatibility**

Home Runs

- Spinel cation distributions and thermodynamics: **1967-present**
- Lower mantle mineralogy, negative P-T slopes for perovskite forming reactions : **1985-95**
- Energy landscapes in zeolites , MOFs, and other porous materials: **1992-present**
- Huge shifts in thermodynamics and phase equilibria at the nanoscale: **2008-present**
- Other events and ambience in these time periods

Events and Ambience 1965-80

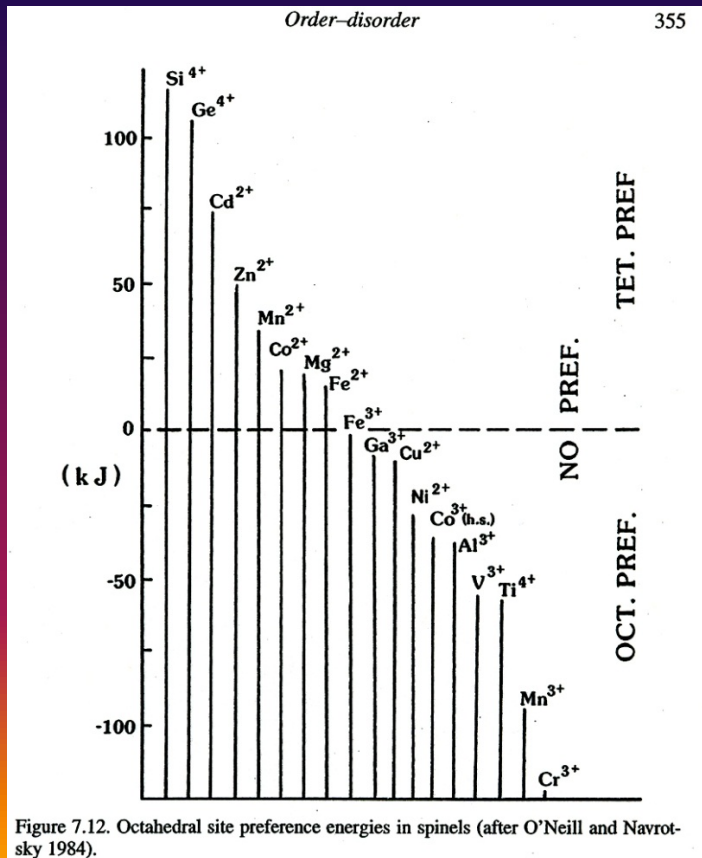
The World

- Emphasis on science and the space race
- Assassinations and riots of 1968
- Oil crisis of 1973
- Major universities simply not hiring women or minorities
- Research funding relatively good

Alex

- Ph.D. U. Chicago 1967
- Postdoc in Germany 1967-68
- Postdoc Penn State 1968-69
- Faculty position ASU 1969-85 a splendid start
- Established research program
 - Spinel
 - Ceramics
 - Minerals
- NSF rotator 1976-77

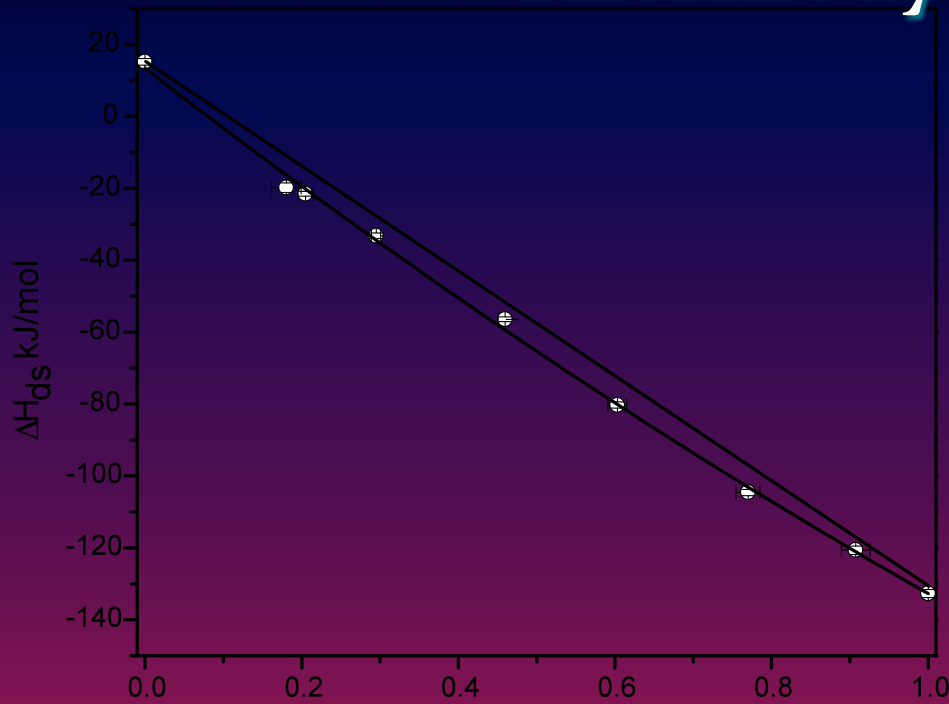
SPINELS 1967



Experimental thermodynamic basis of site preference energies and enthalpies of formation of spinels. Crystal field effects are but a small contribution

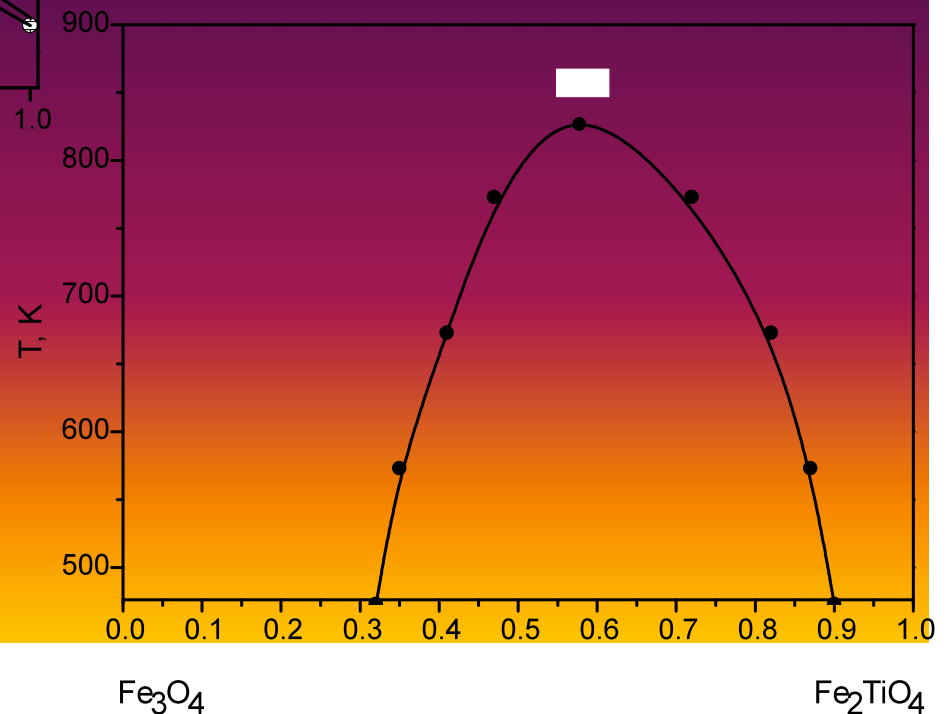
A dream- high pressure silicate spinels

Spinels now: Magnetite–Ulvöspinel Thermodynamics



Drop solution enthalpies of Fe_3O_4 – Fe_2TiO_4 solid solutions in sodium molybdate at 973 K. The straight line connects the two end-members, the curve represents a second degree polynomial fit of the experimental data.

Calculated solvus in the Fe_3O_4 – Fe_2TiO_4 system. The critical temperature is 823 K, the composition $z = 0.58$



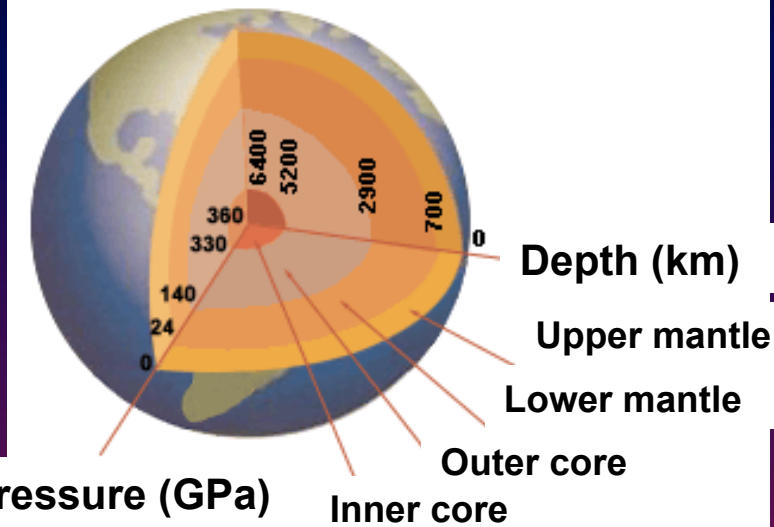
Events and Ambience 1980-95

The World

- Economic and political oscillations
- End of cold war
- Affirmative action programs
- Science funding variable

Alex

- Moved to Princeton 1985
- Research program
 - High pressure phases
 - Melts and glasses
 - Superconductors
 - Started work on zeolites
- Elected National Academy of Sciences 1993



Pressure (GPa)

Inner core

Depth (km)

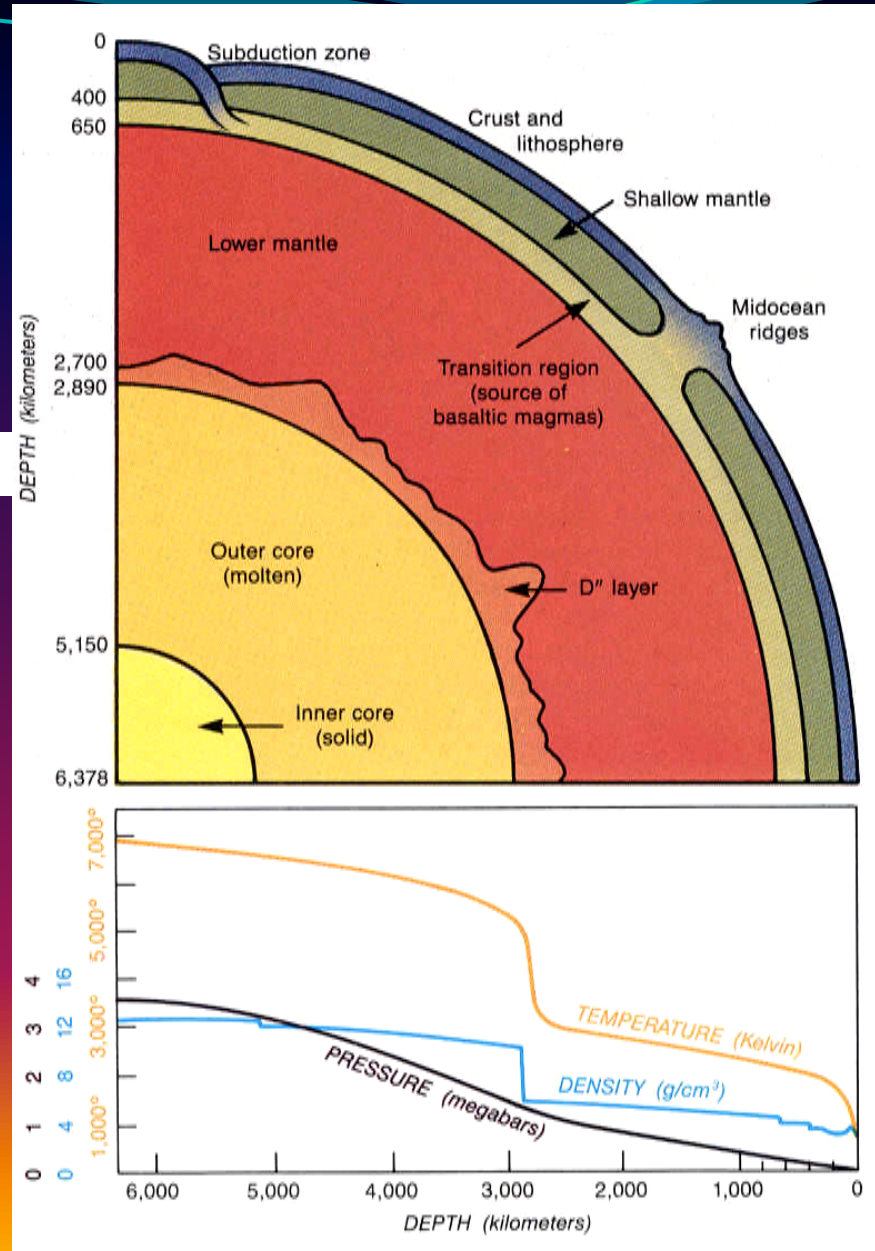
Upper mantle

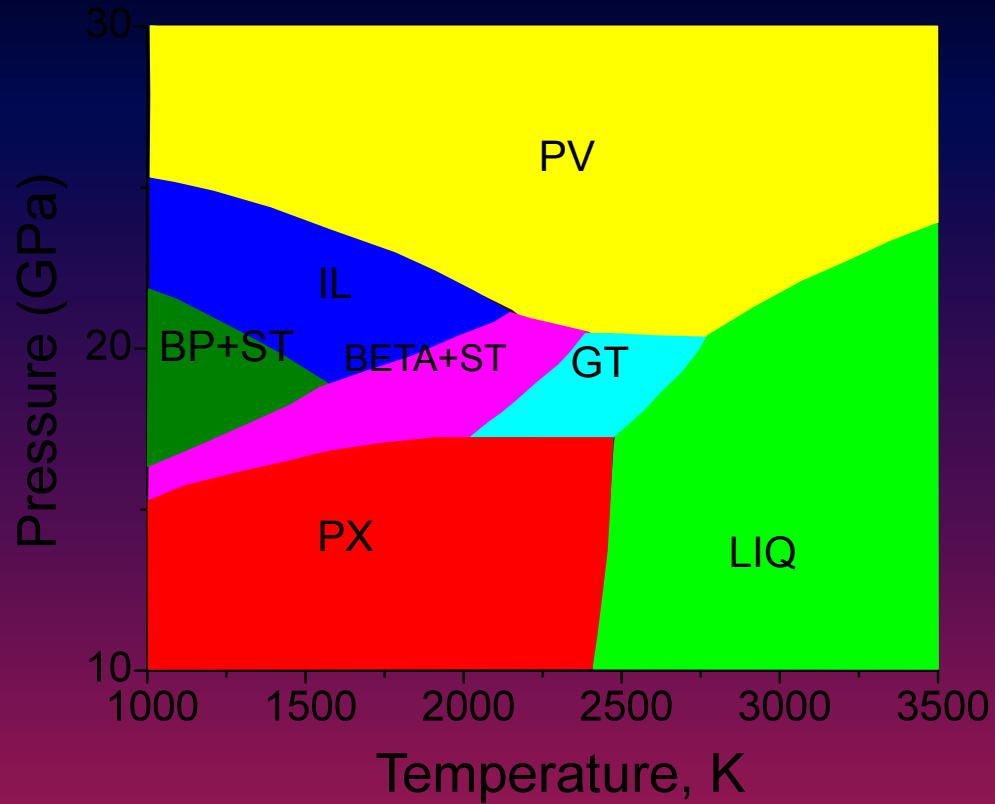
Lower mantle

Outer core

Concentric shells of different phase assemblages with sharp discontinuities between them

- Olivine-spinelloid-spinel at 400 km
- Spinel- perovskite + periclase at 670 km
- Core-mantle boundary





Phase relations in MgSiO₃ composition (PX – pyroxene, BETA -wadsleyite, LIQ –liquid, SP –spinel, ST –stishovite, IL – ilmenite, PV -perovskite (After Fei Saxena, Alexandra Navrotsky, 1990)

Events and Ambience 1995-2005

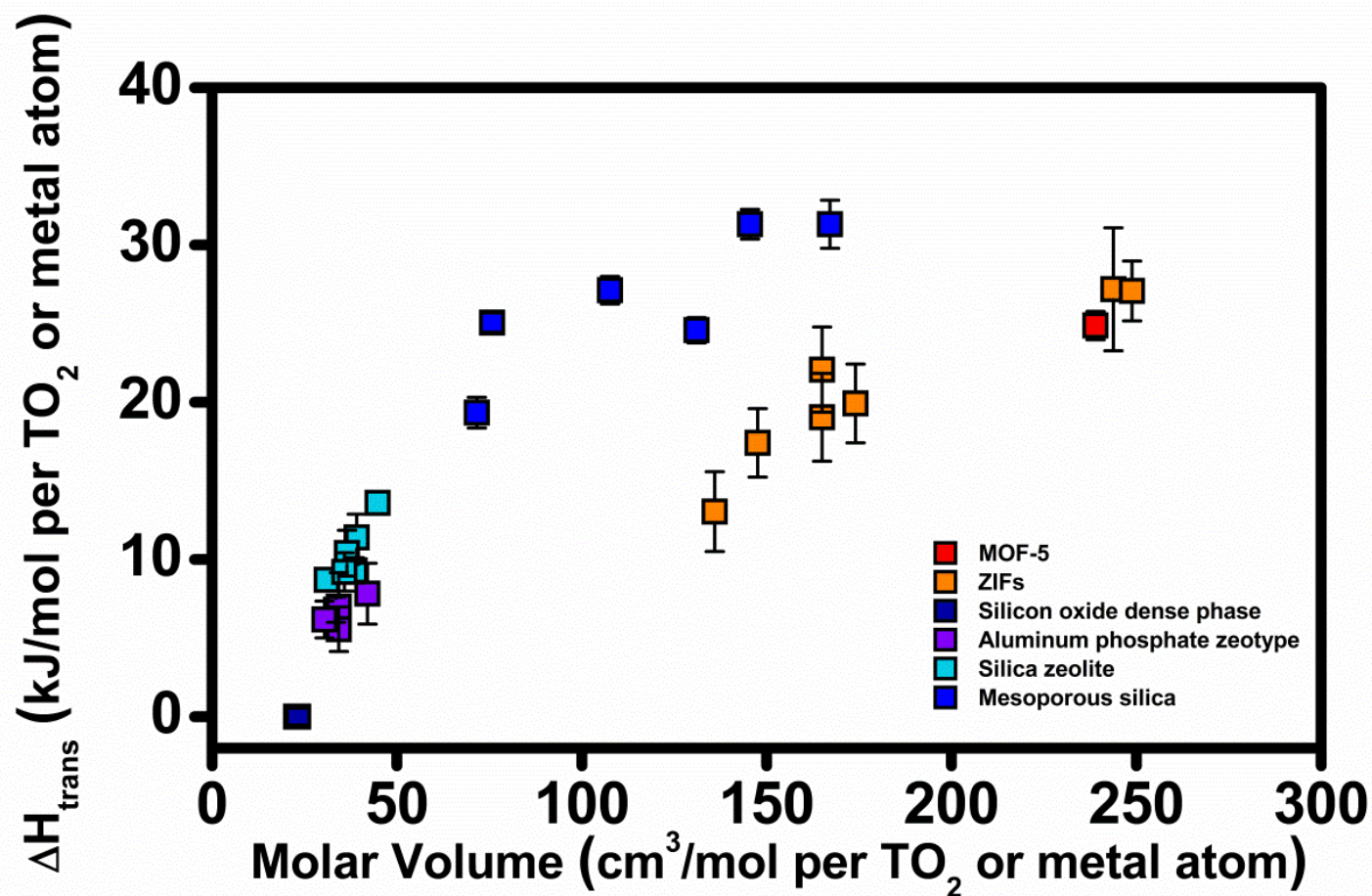
The World

- Economic and political oscillations
- 911 and increasing violence
- Science funding variable - emphasis on nanotechnology
- Increasing diversity

Alex

- Moved to Davis 1997
- Benjamin Franklin Medal 2002
- NEAT
- Research program
 - Zeolites
 - Nitrides
 - Ceramics and functional materials
 - Nanomaterials

Zeolite, Zeotype, and Metal-Organic Framework Energetics



Events and Ambience 2005-2016

The World

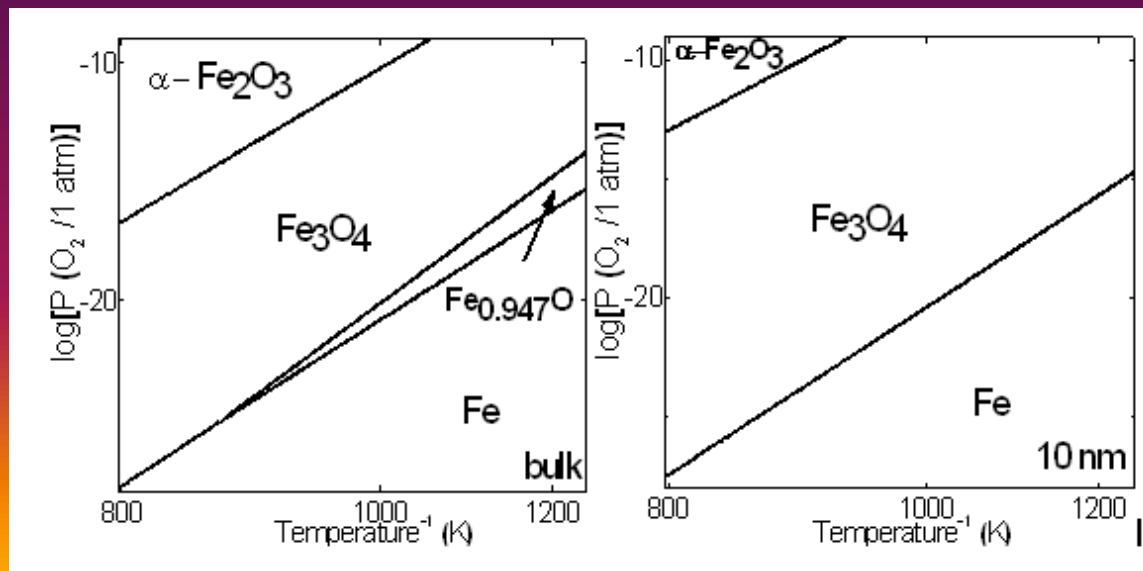
- Economic and political oscillations
- The recession and budget constraints at universities
- Science funding variable
 - Stimulus funding 2008-13
 - Major cutbacks 2012 - ?
 - Emphasis on large projects
- Increasing diversity
- Increased university hiring

Alex

- Roebling Medal 2009
- Interim Dean of Mathematical and Physical Sciences 2013 – present
- Goldschmidt Medal 2016
- Research program
 - Zeolites and MOFs
 - Nanomaterials
 - DOE EFRCs – part of Materials Science of Actinides and 2 others
 - DOE Hub - part of Critical Materials Institute

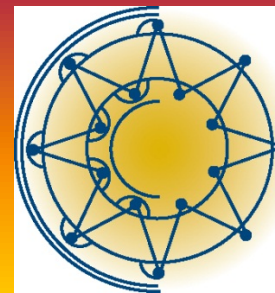
Oxidation-Reduction Equilibria among Transition Metal Oxides Change Dramatically at the Nanoscale Because of Differences in Surface Energies

- Spinel, M_3O_4 have lower surface energies than divalent oxides MO and trivalent oxides M_2O_3 , expanding the spinel stability field.
- For example, for 10 nm iron oxides, wustite FeO has no stability field at all, with iron coexisting with magnetite
- Relevant to materials processing, environmental science, geology, and even biology
- Navrotsky et al. Science 330, 199-201 (2010)



Major Current Projects

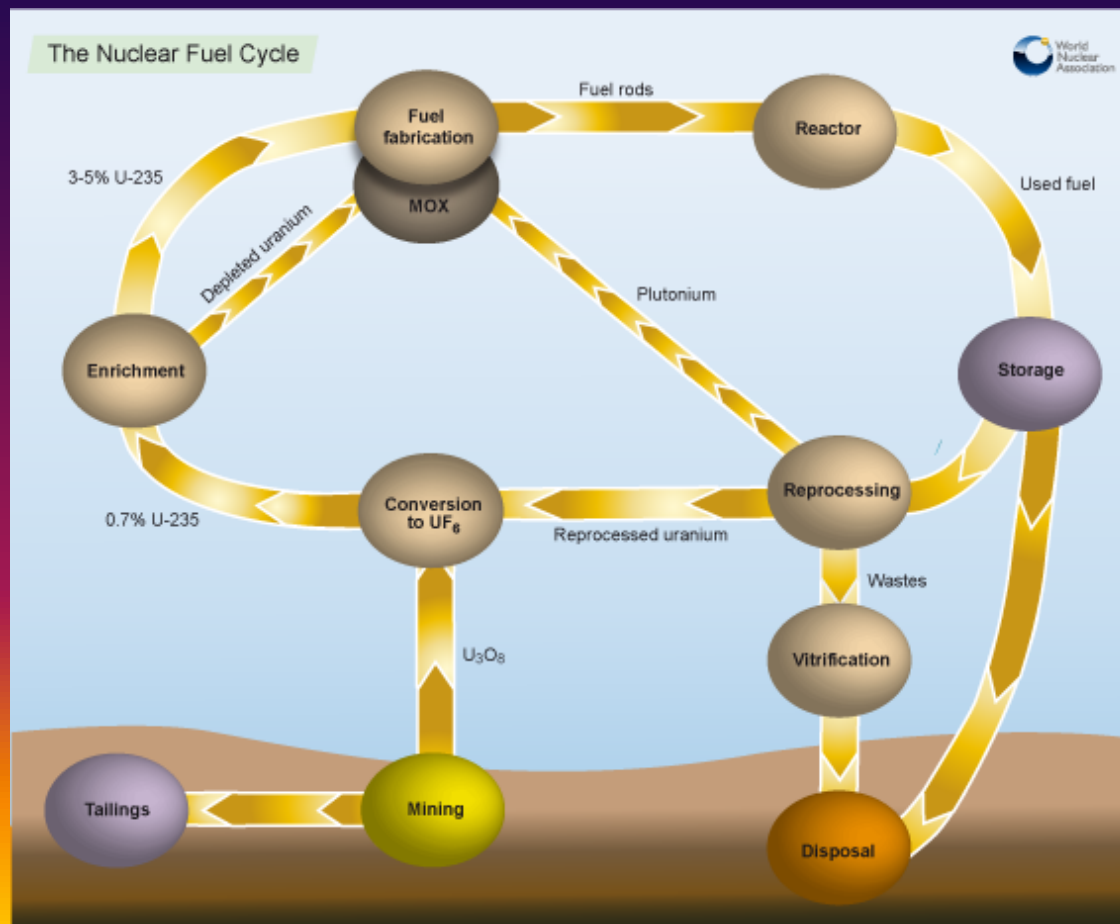
- Actinides
- Lanthanides and critical materials
- Fuel cell and battery materials
- Ultra high T processes
- Nanomaterials
- Open frameworks and confinement



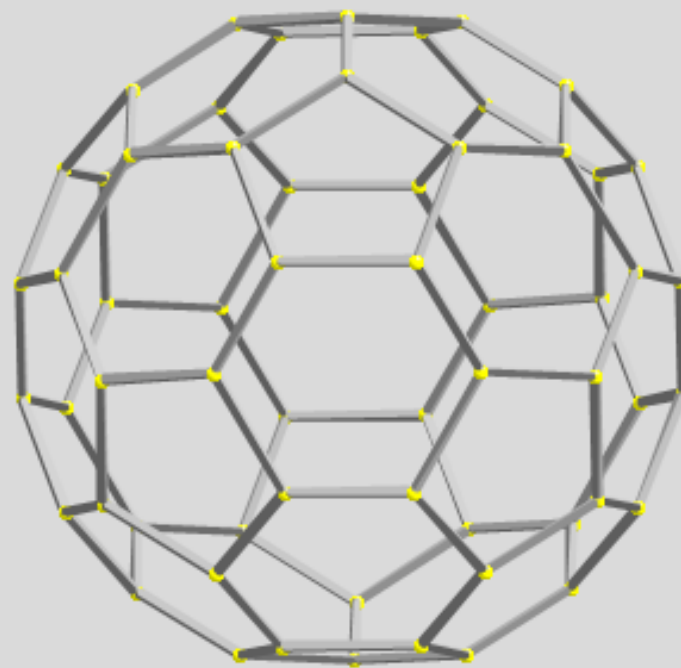
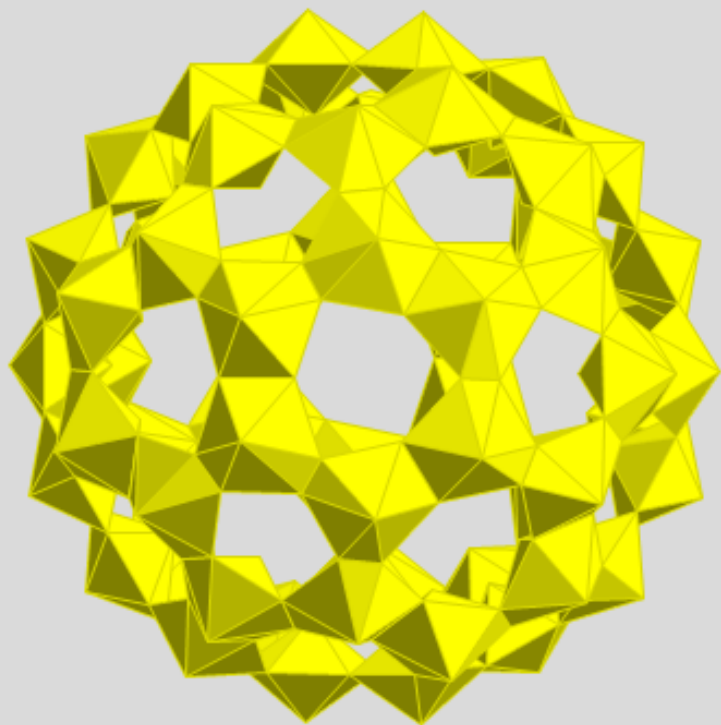
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The Nuclear Fuel Cycle

Energy Frontier Research Center:
Materials Science of Actinides



The Uranium Buckyball – U60

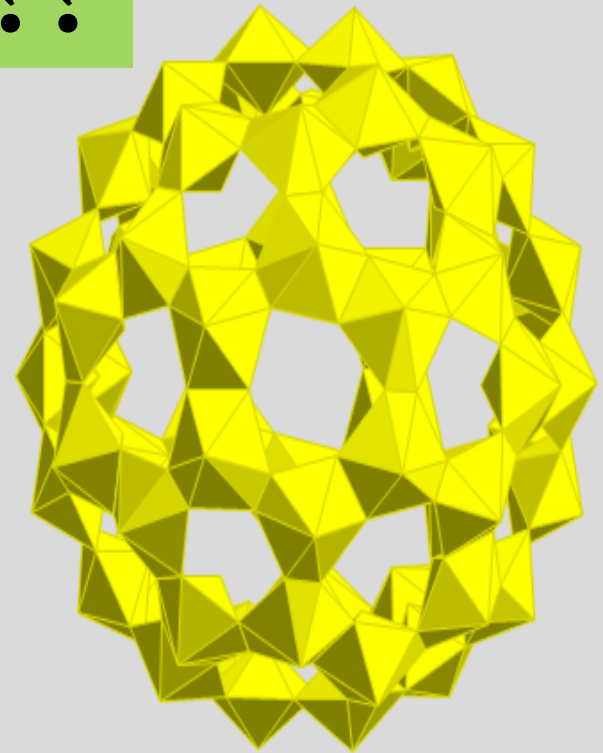


G. Sigmon et al., Angewandte Chemie 2009

Fukushima Nuclear Accident



?????



Other Societally Important Issues

- Critical elements including rare earths
- Drought in the American West, including CA
- Food and sustainability and quality
- Catalysis
 - CO₂ sequestration and reuse
 - Water splitting
- Sensors
 - Environmental
 - Medical diagnostics

Thermodynamics Rules

- Thermodynamics tells what is possible, kinetics how fast it will happen
- New processes and materials
 - More efficient technology
 - Environmental and social impacts
 - New materials and concerns have outrun the database
- **Know, optimize, do not compromise**



Think Big