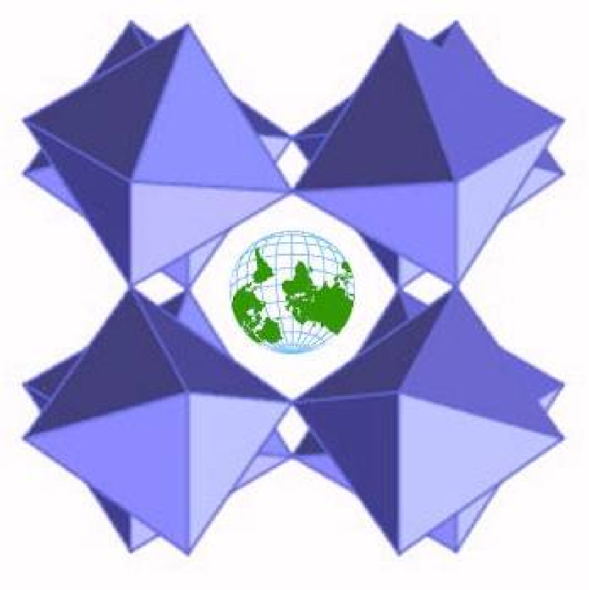
Melts, Glasses, and Amorphous Materials in Earth and Planetary Science

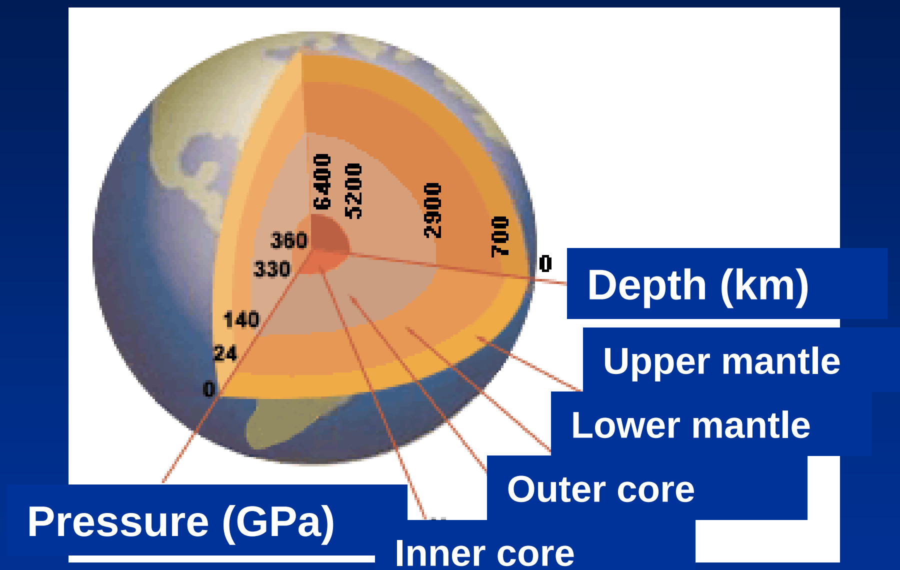
Alexandra Navrotsky
UC Davis

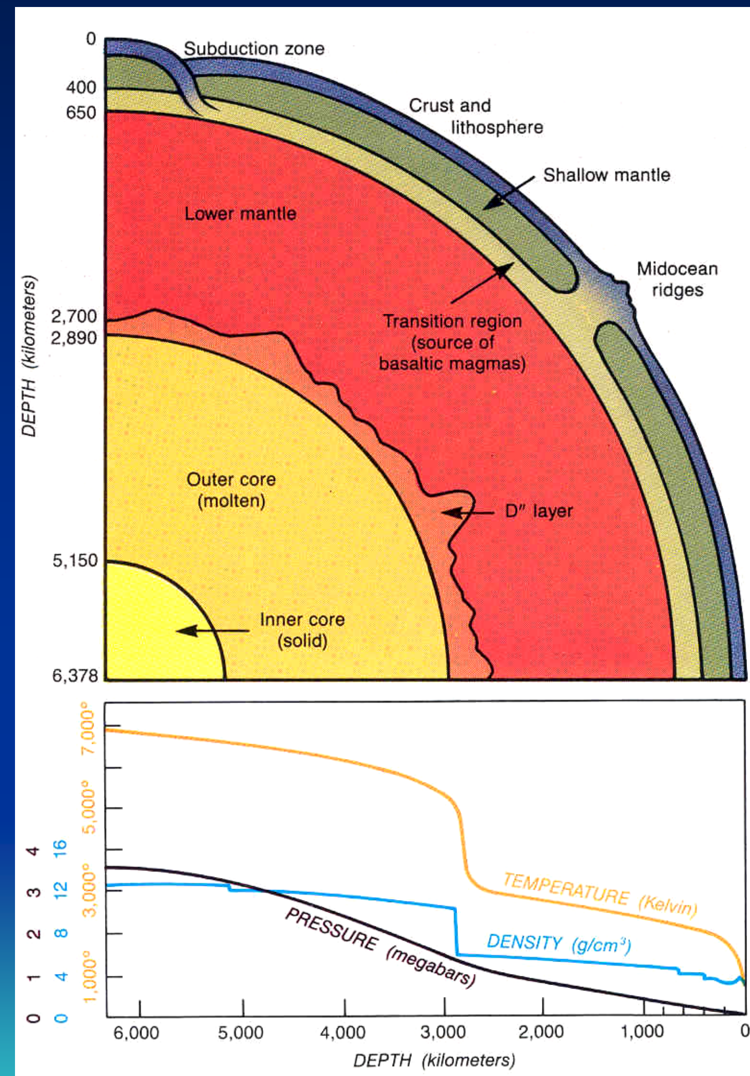
UC DAVIS
PETER A. ROCK
Thermochemistry Laboratory

There is nothing new under the sun. Whatever we discover as a seemingly new phenomenon, nature has done it somewhere in the universe on a huge scale for millions of years.........



The Earth





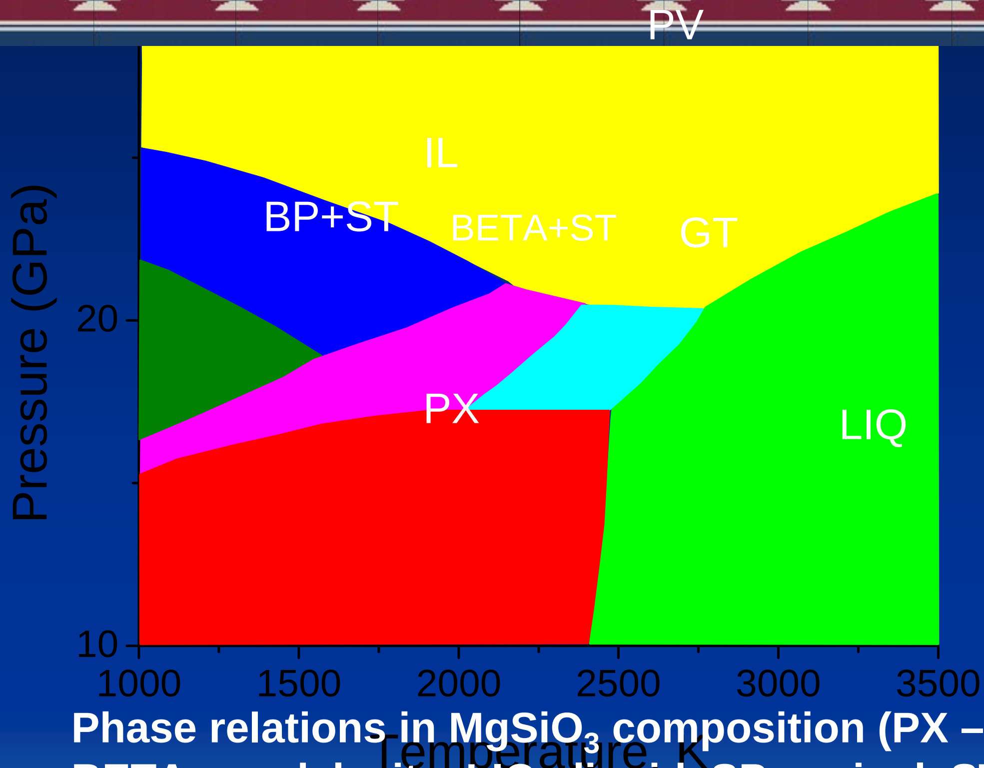
Concentric shells of different phase assemblages with sharp discontinuities between them

Olivine-spinelloid-spinel at 400 km

Spinel- perovskite + periclase at 670 km

Core-mantle boundary

Silicate Phase Transitions

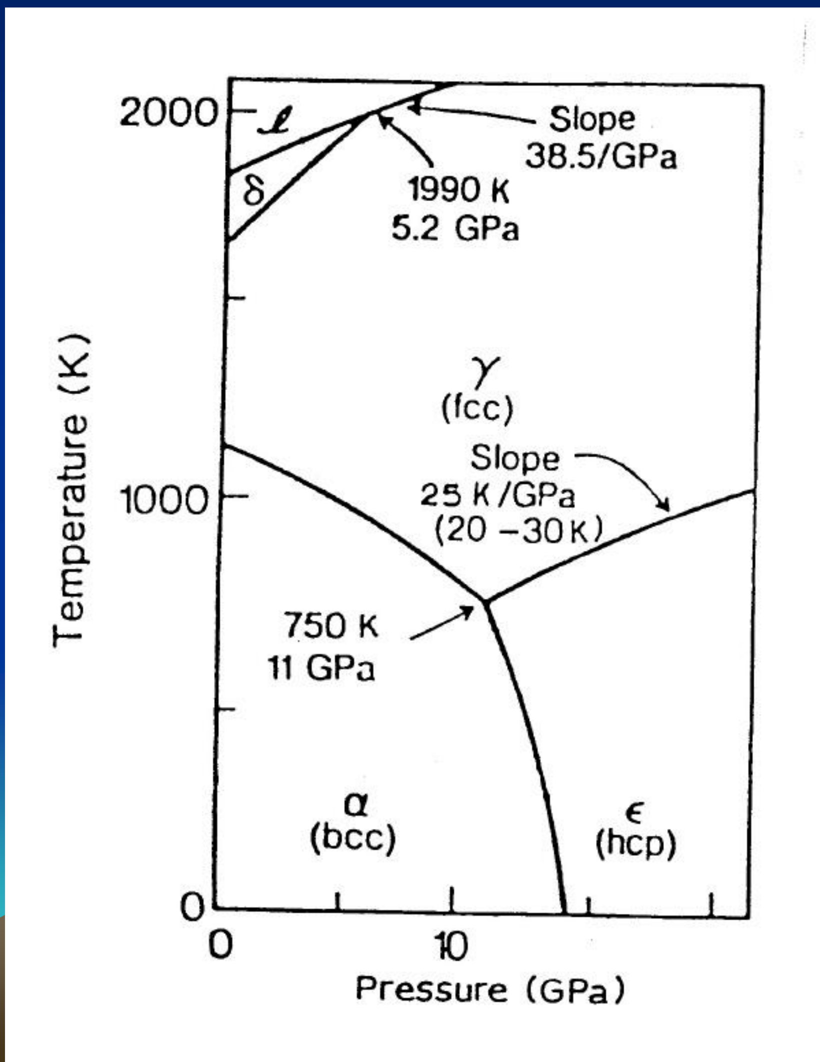


Phase relations in $MgSiO_3$ composition (PX – pyroxene, BETA - wadsleyite, LIQ –liquid, SP –spinel, ST – stishovite, IL – ilmenite, PV -perovskite (After Fei Saxena, Alexandra Navrotsky, 1990)

Lower Mantle

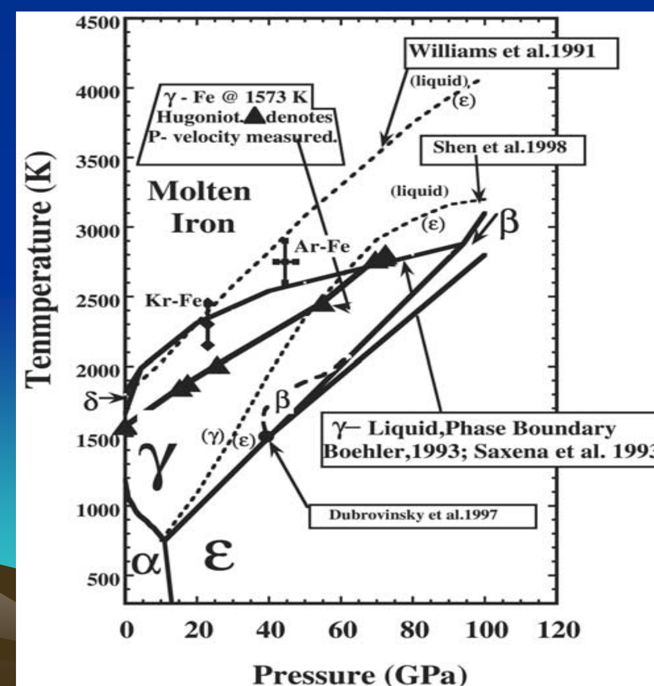
- Increase in coordination number of Si from 4 to 6, certainly in solids, probably in melts
- Many competing solid phases
- Increasing Fe content, decreasing oxygen fugacity, uncertain H (H_2O) and C (CO_2) content
- Pressure induced amorphization, complex melting/crystallization, strong changes in melt and glass structure…

Iron Phase Diagram



Inner/outer core boundary is at 3.3 Mband 5000-6000 K, extrapolation of melting curve is still uncertain

Effects of Ni and light elements (C, O, Si, S) not well known



Other Places, Other Times

- Condensation from the nebula
- The early Earth
- Other planets and moons
  - Terrestrial
  - Icy/rocky
  - Gaseous/fluid giants
  - Carbon rich

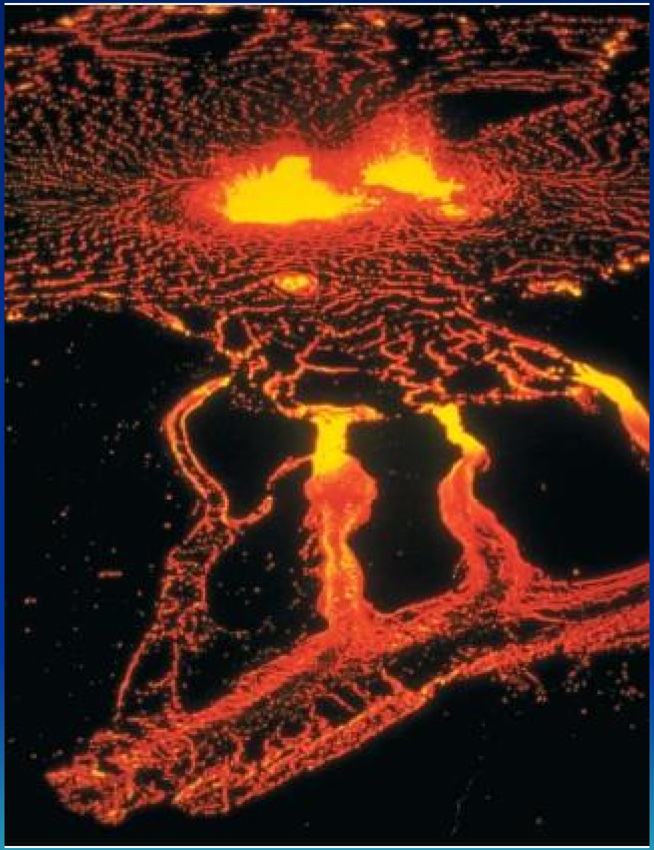
Systems and Phenomena

- Molten and glassy silicates
- Gels and amorphous low T materials
- Silicate – water miscibility
- Carbonate melts- carbonatites, diamonds
- Sulfide melts - ore bodies
- Molten metals - the outer core
- Pressure, shock, and radiation amorphized minerals
- *Speculative*
  - Polyamorphism and critical phenomena
  - Iron-rich metallic glasses
  - Si-C-O systems

Volcanism: Explosion vs. Lava Flow

Mt. St. Helens

Kilauea

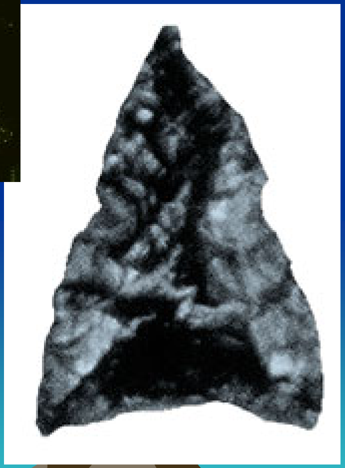


Effect of higher silica content

- Increased viscosity
- Increased H_2O solubility
- Increased degree of polymerization of SiO_4 and AlO_4 tetrahedra
- Increased glass forming ability
- Decreased heat of fusion/vitrification
- Stronger (less fragile) liquid
- More explosive

Obsidian - Natural Glass

Glass Mtn., OR



Ash flow tuff

Applications of aluminosilicate glasses to kietics of geologic processes

- **Obsidian hydration rims for age determination**
- **Glass transition temperature for cooling rates in igneous rocks containing glass**

Effect of Ti on glass transition in an alkali silicate glass

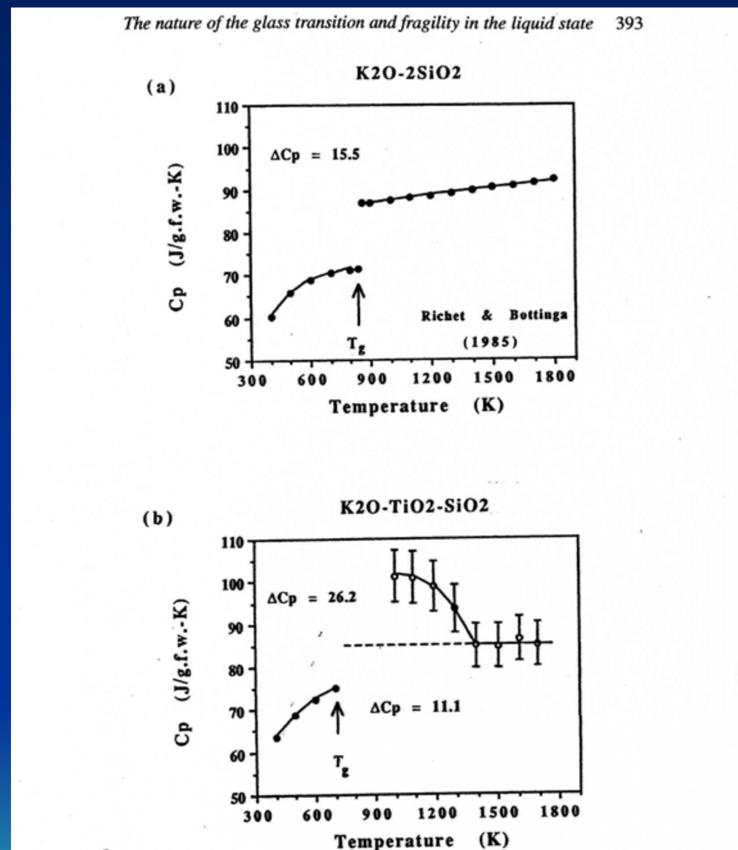


Figure 8.10. Comparison of heat capacity of silicate and titanosilicate glass and liquid Lange and Navrotsky 1993).

Polymorphic Phase Transitions in Liquids and Glasses

Peter H. Poole, Tor Grande, C. Austen Angell, Paul F. McMillan

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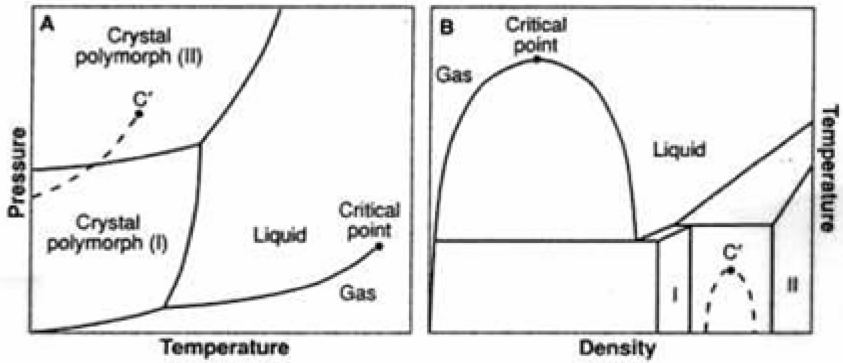


Schematic phase diagram of a pure substance exhibiting a liquid-liquid phase transition. (**A**) Solid lines locate the coexistence lines between the liquid, gas, and two crystal polymorphs. The liquid-gas coexistence line terminates in the critical point. The dashed line is the coexistence line for a liquid-liquid phase transition in the supercooled liquid, terminating in a critical point C′. (**B**) Projection of the lines given in (A) into the plane of temperature and density.

Polyamorphism

- YAG
- Organics
- **H_2O, SiO_2**
- **Silica - metal oxide immiscibility**
- **Water - salt systems with extensive cation hydration**
- **Metallic glasses**

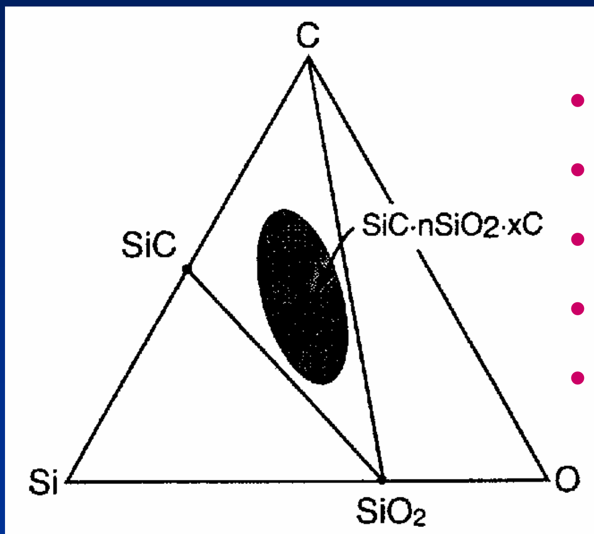
Metallic Glasses

- Well known in Fe, Ni, Co, Cr systems with B or Si
- Deep eutectics, multicomponent systems, complex short range structures
- Is met glass formation possibleunder extreme conditions, including the Earth’s core?

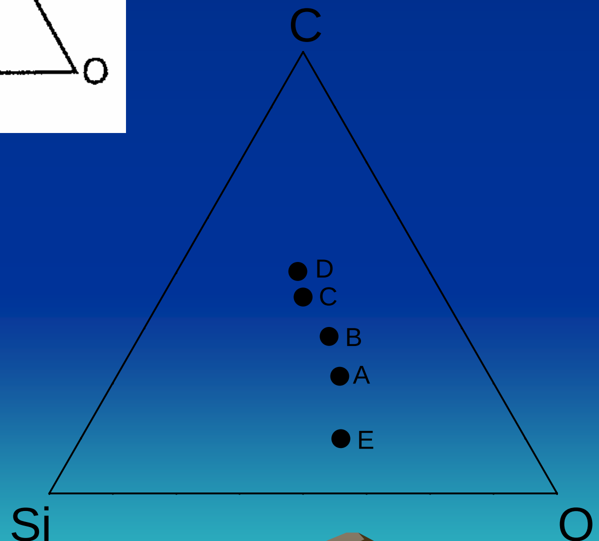
Si-C-N-O Materials

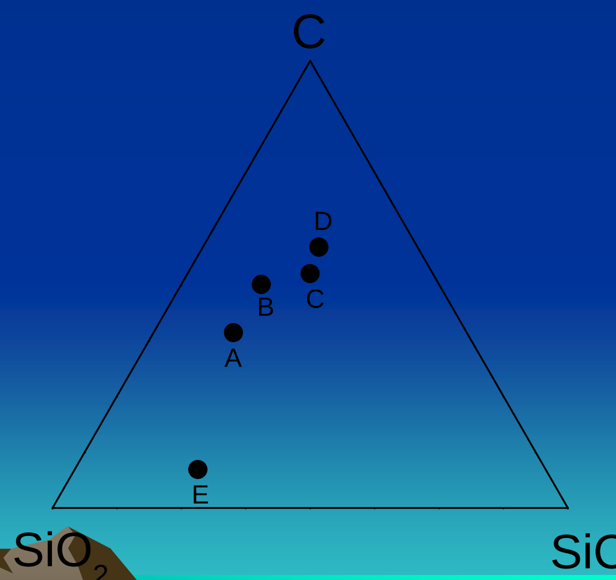
- CO polymers, photochemical reactions
- Tetrahedral C in CO_2 and silicates
- Carbothermic reduction of silica, iron oxides, etc. Occurs above 1500 oC under ambient conditions, what happens at high P,T, low fO2.
- Amorphous Si-O-C-N stable ceramics

Composition



- A: $Si_{0.295}O_{0.440}C_{0.265}$; $0.220\ SiO_2 + 0.075\ SiC + 0.190\ C$
- B: $Si_{0.271}O_{0.374}C_{0.355}$; $0.187\ SiO_2 + 0.084\ SiC + 0.271\ C$
- C: $Si_{0.278}O_{0.278}C_{0.444}$; $0.139\ SiO_2 + 0.139\ SiC + 0.305\ C$
- D: $Si_{0.259}O_{0.238}C_{0.503}$; $0.119\ SiO_2 + 0.140\ SiC + 0.363\ C$
- E: $Si_{0.364}O_{0.513}C_{0.124}$; $0.2565\ SiO_2 + 0.1075\ SiC + 0.0165$





Enthalpies of Formation from Crystalline SiO_2 + SiC + C

- ΔH values are exothermic (-7 to -130 kJ per g atom), implying energetic stability of amorphous phase relative to crystalline end members. No simple compositional dependence.
- Entropy of amorphous phase is higher than that of crystalline, so ΔG is also negative.
- Explains why samples do not crystallize until they decompose due to carbothermic reduction of silica above 1500 °C
- Behavior at high P???

Why Negative ΔH

- No crystalline ternary compounds, so this is surprising
- Nanostructure, silica domains, graphene sheets, and mixed bonds (Si bonded to both C and O) at interfaces
- Strain relaxation and mixed bonding make an interfacial stabilizing “glue”
- May explain why nanodomains do not grow into larger phase-separated regions
- Analogy to rare earth siiicate glasses? To metallic glasses?

Earth and Planetary Implications

- If these Si-C-O-N materials are stable, can they form by different routes, including during planetary accretion?
- Are they likely in “carbon planets”?
- They have strange viscoelastic properties which may be relevant
- What happens to them in the diamond stability field?