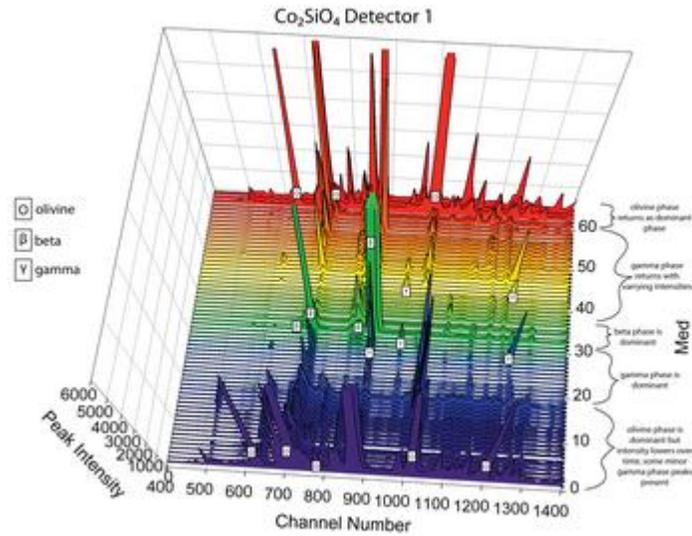


HIGH PRESSURE PHASE EQUILIBRIUM STUDIES

There are a number of different types of high pressure studies related to phase equilibria. There are true phase equilibrium studies that seek to characterize the range of pressure, temperature or chemical activity (e.g. for O₂) over which a given phase (or phase assemblage) is stable. Synthesis studies seek to discover and produce new phases. However, they are distinct from phase equilibrium studies. There are a number of circumstances that can lead to minerals forming outside their thermodynamic stability field. Another major area of interest is phase transformation mechanisms and kinetics.

Reversals: the difference between synthesis and phase equilibrium studies

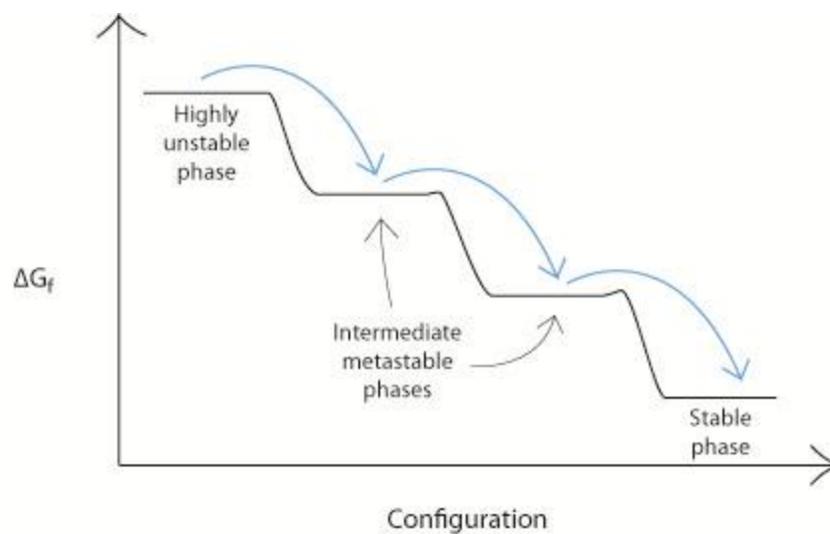
One of the most important features of a good phase boundary determination is the reversal. A reversal is a pair of experiments where the reactants and products in one experiment become the products and reactants in another experiment. The position of the phase boundary can be said to be somewhere between these bracketing experiments. In-situ experiments (e.g. synchrotron x-ray diffraction) are particularly efficient for conducting phase equilibrium studies because the transformation from one phase assemblage to the other can be run first one way and then back the other at a number of pressure and temperatures during a single experiment.



Example of a reversal for β/γ phase boundary in Co_2SiO_4 . [Click for larger image.](#)

Since phase boundaries are lines (or curves if volatiles are present) at minimum two reversal are required to fully describe a phase boundary. Reversals are necessary for two reasons: 1) Due to kinetics, phases can persist in some cases indefinitely outside of their stability field. Merely witnessing a phase at a given P and T, especially at lower temperatures, does not guarantee that it is the stable phase. 2) As mentioned above, phases can be synthesized outside of their stability field. Some of the reasons that this can occur are related to a phenomena referred to as Ostwald's step rule – which says that the first phase to form in a reaction is not always the one with the lowest free energy but the phase with a free energy closest to the free energy of the reactants. In order to start with a sample that is highly homogeneous, experimentalists may choose a gel or glass; the free energy of these reactants can be quite large.

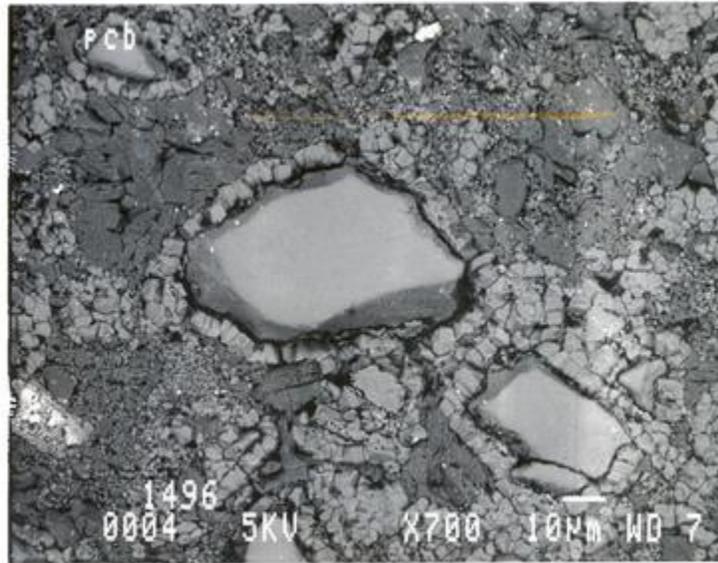
Reactants ground in a mortar and pestle can be highly strained (e.g. Kingma et al., 1993) which can also substantially raise their free energy. So for example, coesite can be produced from highly strained quartz at P and T conditions in the quartz stability field (Green, 1972). For these reasons if one wants to measure the position of a phase boundary or confirm that a given phase in fact has a stability field, reversals are required.



Ostwald's Step Rule

Experimental Concerns

The quality of a phase equilibrium study is highly dependent on how well known P, T and chemical activity are in the experiment. Discussions of uncertainty in P and T can be found in the multi-anvil and diamond anvil pages. Knowing the chemical activity of most elements in an experiment is quite straightforward; if the element was present in the capsule both before and after the experiment its activity is assumed to be one.



Beginner's mistake: Incomplete reaction between MgO , $\text{Mg}(\text{OH})_2$ and SiO_2 . Click for larger image.

However, there are some important exceptions for elements that are not necessarily trapped in the experiment; this includes volatiles like H_2 , H_2O and O_2 as well as elements that participate in solid solutions with sample assembly components abutting the sample (e.g. the capsule or gasket). The state of the art for containing volatiles in solid media apparatus (e.g. the multi-anvil) is to use welded noble metal capsules that are weighed before and after the experiment to guarantee that no mass is lost. However, this strategy may not always be feasible. This is especially true for in-situ experiments where x-ray transparency is required. The use of Au is limited by its melting point and since Fe dissolves in Pt, it cannot be used reliably for working in Fe bearing assemblages.

In solid medium experiments if a sample is not sealed in a welded noble metal capsule, the sample assembly exerts a great deal of control on the fugacity of volatiles. Pyrophyllite placed adjacent to the furnace can dehydrate and produce a wet environment, superglue in the hot parts of the assembly can combust and produce an environment that will reduce SiO_2 to Si metal. Graphite furnaces also produce a reducing environment that can destabilize Fe-bearing silicates; wrapping the sample in Fe or Ni foil is usually enough to prevent this. Similar issues occur in the DAC, where the chemical activity in the sample is affected by the confining medium and the gasket. Thus phase equilibrium studies require some thought about the chemical activity of the sample/sample assembly system in order to guarantee that the experiment that is conducted matches the experiment that is envisioned.

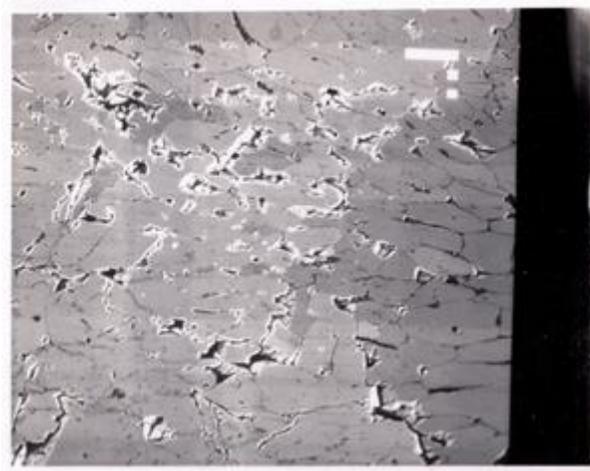
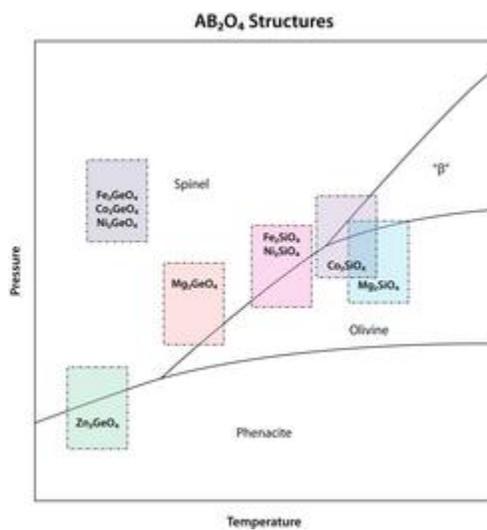


Image from Burnley and Navrotsky, 1996. [Click for larger image.](#)

Discovery and Synthesis of New Phases



Modified from Navrotsky, 1986. [Click for larger image.](#)

The simplest way to discover a new phase is to put reactants of interest together and bring them to some new pressure temperature condition and either observe them with x-rays at temperature and pressure or quench them and use x-ray diffraction to identify the phases present and search for new phases. However, there are more sophisticated strategies for searching P,T chemistry spaces for new phases. One strategy that has been around for a long time is to use one's knowledge of phase relations in one chemical system to make intelligent guesses about phase relations in another similar chemical system. For example, the observation that Mg₂GeO₄ formed in both an olivine and a denser spinel structured polymorph, led researchers in the 1930's to suggest that (Mg, Fe)₂SiO₄ olivine might also have a spinel structured polymorph which could account for the increase in seismic velocity at ~400 km depth.

Many compounds that share the same stoichiometry have phase diagrams that share the same topology. Structures that host elements with larger ionic radii at room pressure often faithfully predict the structures that elements with smaller radii will adopt at high pressure. Another clue that an undiscovered phase is present in a system is if the phase boundary between two phases (e.g. solid and melt) suddenly changes slope. Recently, first principle calculations (e.g. USPEX) have also been used to anticipate the existence of new phases.

Source:

https://serc.carleton.edu/NAGTWorkshops/mineralogy/mineral_physics/phase_equilibria.html