



## Mechanistic controls on variations in chemical composition of amphiboles as a function of T and P

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What controls the chemical compositions of minerals with changing temperature (T) and pressure (P)? There is now extensive information available on how minerals respond at the atomic scale to such changes, and this allows us to relate compositional variation in minerals as a function of T and P to details of their atomic arrangements in a mechanistic way.

Changing T and P result in thermal expansion and elastic compression. What do these changes mean with regard to atomic arrangements? First consider isodesmic structures (in which the strengths and arrangements of chemical bonds are fairly isotropic): thermal expansion and elastic compression each act in a fairly homogeneous fashion and the structure expands or contracts fairly uniformly. In anisodesmic structures (in which the strengths and arrangements of chemical bonds are anisotropic), thermal expansion and elastic compression each act in a heterogeneous fashion and the structure expands or contracts anisotropically. Consider the C2/m amphibole structure, a double-chain of tetrahedra and a strip of octahedra, both of which extend in the c-direction. This is a very anisodesmic structure, with regions that are strongly bonded and regions that are weakly bonded. This character is apparent in the thermal expansion of the structure of tremolite: The strongly bonded tetrahedra expand only slightly with increasing T, whereas the more weakly bonded octahedra expand considerably more with increasing T. As T increases, the octahedral strip expands more than the tetrahedral double-chain. In order for these two units to maintain their linkage, larger cations substitute at the T sites and smaller cations substitute at the M sites, compensating for the differential effects of thermal expansion. Thus high-T low-P amphiboles tend to be high in (T)Al and (C)Mg (e.g., magnesiohornblende, magnesiosadanagaite). With increasing P, the octahedral strip contracts more than the tetrahedral double-chain. Thus larger cations substitute at the M sites and the T-sites tend not to accept substitutions, compensating for the differential effects of elastic compression. Thus high-P low-T amphiboles tend to be Si-rich (e.g., glaucophane, winchite). So, what drives chemical change in amphiboles? It is the articulation requirements of the different elements of the structure with changing T and P.

What constrains this chemical change? In a structure such as amphibole, where the composition is changing, the bond topology is conserved, and any energetic differences between amphiboles of different composition involve only atom identities and their relative locations. The atom identities and their relative locations are the short-range arrangements of atoms in the structure. Stable arrangements of atoms in solids are controlled by the valence-sum rule of bond-valence theory: The sum of the bond valences to any atom is equal to the formal valence of that atom. A result of this constraint is that in patterns of SRO, atoms must cluster such that the local valence-sum rule is satisfied. Examination of patterns of SRO in amphiboles shows that only some patterns of order are stable, and that compositional variations can involve only these patterns, which, in turn, constrains compositional variation. Thus, for example, compositions close to tschermakite cannot occur, and pargasite and sadanagaite are the common amphiboles in high-T metamorphic rocks. Further examples will be given of these SRO constraints on chemical variation as a function of T and P in igneous and metamorphic rocks.