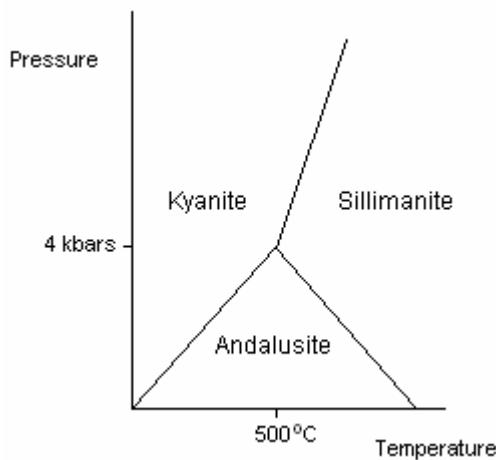


## Lecture 10: $\text{Al}_2\text{SiO}_5$ Polymorphs and Carbonates

### The $\text{Al}_2\text{SiO}_5$ Group

The  $\text{Al}_2\text{SiO}_5$  group of nesosilicates can be found in medium- to high-grade metamorphic rocks rich in aluminum. The group consists of three polymorphs: kyanite, sillimanite, and andalusite. These polymorphs all contain  $\text{Si}^{4+}$  in four-fold coordination and  $\text{Al}^{3+}$  in six-fold coordination, but sillimanite and andalusite also contain aluminum in four-fold and five-fold coordination, respectively. These structural differences are related to the metamorphic conditions under which the minerals form. Kyanite, for example, has the densest structure of all three polymorphs and forms under conditions of high pressure. The pressure and temperature range under which each of the polymorphs forms has been determined experimentally, as shown below.



Since the polymorphs of  $\text{Al}_2\text{SiO}_5$  form under a certain T-P range, they are commonly used as index minerals to define metamorphic zones. Andalusite, for example, generally indicates contact metamorphism aureoles while sillimanite generally indicates regional metamorphism.

### Carbonates

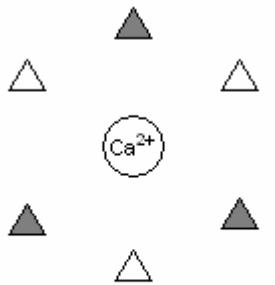
Anhydrous carbonates are a class of minerals composed of divalent metal ions and anionic  $(\text{CO}_3)^{2-}$  complexes. The  $(\text{CO}_3)^{2-}$  complexes do not share oxygens with each other and occur as individual units in layers perpendicular to the c axis. The metal ions occupy sites between these layers.

While all anhydrous carbonates contain layers of  $(\text{CO}_3)^{2-}$  complexes, they differ in the arrangement of these complexes within the layers and the coordination of metal ions. These structural differences provide a basis for organizing carbonates into three groups.

#### Calcite Group

Calcite	$\text{CaCO}_3$
Magnesite	$\text{MgCO}_3$
Siderite	$\text{FeCO}_3$
Rhodochrosite	$\text{MnCO}_3$
Smithsonite	$\text{ZnCO}_3$

Minerals in the calcite group contain relatively small metal cations in six-fold coordination, and the  $(\text{CO}_3)^{2-}$  complexes all point in the same direction. Their structures are very similar to the HCP structure of  $\text{NaCl}$ , with  $\text{Ca}^{2+}$  occupying the  $\text{Na}^+$  site and  $(\text{CO}_3)^{2-}$  complexes occupying the  $\text{Cl}^-$  site.



Triangles represent  $\text{CO}_3^{2-}$  complexes.  
Grey triangles are below the plane of the page. White triangles are above.

### Aragonite Group

Aragonite	$\text{CaCO}_3$
Witherite	$\text{BaCO}_3$
Strontianite	$\text{SrCO}_3$
Cerussite	$\text{PbCO}_3$

In the aragonite group, metal ions are larger than those in the calcite group and occupy nine-coordinated sites instead of six coordinated sites. The  $(\text{CO}_3)^{2-}$  complexes occupy two different structural layers in which the complexes point in different directions.

### Dolomite Group

Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Azurite	$\text{CaFe}(\text{CO}_3)_2$
Kutnahorite	$\text{CaMn}(\text{CO}_3)_2$

Minerals in the dolomite group have structures very similar to calcite, but with  $\text{Ca}^{2+}$  and either  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , or  $\text{Mn}^{2+}$  in alternating layers perpendicular to the c axis.