Epidote Group

Chemically complex
\((A, M, Si, O, OH)\)
- A sites contain large, high-coordination cations
  - Ca, Sr, lanthanides
- M sites are octahedrally-coordinated, trivalent
  (occasionally divalent) cations
  - Al, Fe\(^{3+}\), Mn\(^{3+}\), Fe\(^{2+}\), Mg\(^{2+}\)

Space group: P2\(_1\)/m
Crystal class: monoclinic 2/m
- \(a=8.98\) \(b=5.64\) \(c=10.22\) (angstroms)
- \(\alpha=1.670-1.715\) \(\beta=1.674-1.725\) \(\gamma=1.690-1.734\)
- \(Z=2\)
Solid solution extends from clinozoisite to epidote

Chemical formula
- Epidote: \(Ca_2(Al,Fe)Al_3O(\text{SiO}_4)(\text{Si}_2\text{O}_7)(OH)\)
- Clinozoisite: \(Ca_2Al_3O(\text{SiO}_4)(\text{Si}_2\text{O}_7)(OH)\)
- Zoisite is an orthorhombic polymorph (Pnmc) of clinozoisite
Epidote structure type
Two types of edge-sharing octahedra
- single chain of M(2)
- zig-zag chain of central M(1) and peripheral M(3)

These chains are crosslinked by SiO$_4$ and SiO$_7$ groups

Between the chains and crosslinks are relatively large cavities which house the A(1) and A(2) cations.

Silica tetrahedra
- Si (1) and Si(2) share O(9), forming an Si$_2$O$_7$ group
- Si (3) forms an isolated SiO$_4$ group

Each tetrahedron retains essentially its same shape and size in all structures

In a given bonding situation a particular Si-O bond type has nearly the same value in each mineral, however, the different Si-O bond types vary in length due to local charge imbalance.

MO$_6$ Octahedra
- Unequal occupancy of the 3 different octahedral positions, M(1), M(2), M(3).

M(2) octahedral chain contains only Al atoms
M(1) and M(3) substitute entirely with non-Al atoms
- the M(3) octahedra contain a larger fraction
A(1) and A(2) Polyhedra

Clinozoisite and epidote have A sites occupied entirely by calcium atoms. Other members have other divalent atoms such as Sr, Pb, or trivalent lanthanide elements, with the substitution of Ca found ONLY in the A(2) site.
- A(2) site is larger with higher coordination number
The size and shape of the A(1) polyhedron are quite similar between end members
The A(2) polyhedron is much more variable between members, due to the diverse occupancy of this site

Hydrous behavior under high P and T
(Pawley, Redfern, and Holland, 1996)
- Not much information
- Most equations of state for molar vol of water extrapolated from low-pressure data
- Essential for understanding water transport in the earth
  * metamorphic and melting reactions from crust through the upper mantle
  * subduction zones
- Findings show stability at high pressures
  * subduction zones (lower temperatures)

Thermal expansion of Clinozoisite and Zoisite
- differ mainly in nature of octahedral chains
- volume expansion of zoisite slightly greater
- both show b and c parameters expand much more than the a parameter

Imply Al octahedra expand on heating, forcing chains to lengthen (parallel to b) but presumably rotation of the cross-linkages, Si tetrahedral pairs, prevent the a axis from enlarging significantly
Thermal expansion of Clinozoisite

Thermal expansion of Zoisite

Compressibility of Zoisite, Clinozoisite, and Epidote

- The monoclinic end-members, clinozoisite and epidote, show identical compression behavior (3-6.7 Gpa)
  - c axis most compressible

- Orthorhombic Zoisite shows b axis most compressible

- Zoisite is far less compressible than clinozoisite
  - expect the opposite due to larger Ca1 & Ca2 sites in orthorhombic phase
  - Zoisite denser at ambient conditions, Clinozoisite denser in metamorphic and igneous conditions
Compression of Clinzoisite

![Clinzoisite Diagram](image)

**Figure 1.** Relative compression of clinzoisite. Variation of cell parameters normalized to volume at 1 bar, as a function of pressure. The curve for volume is a least-squares fit, giving $K_{0} = 3.5 \pm 0.5$ GPa (Mohs hardness 5.5). Bars for individual cell parameters are just guides for the eye. Error bars for $V^{1/2}$ are two standard deviations; error bars on individual axial ratios are larger than symbols.

Compression of Zoisite

![Zoisite Diagram](image)

**Figure 2.** Relative compression of zoisite. Variation of cell parameters normalized to volume at 1 bar, as a function of pressure. The curve for volume is a least-squares fit, giving $K_{0} = 2.0 \pm 0.1$ GPa (Mohs hardness 6.5). Bars for individual cell parameters are just guides for the eye. Error bars for $V^{1/2}$ are two standard deviations; error bars on individual axial ratios are larger than symbols.

Compression of Epidote

![Epidote Diagram](image)

**Figure 3.** Relative compression of epidote. Variation of cell parameters normalized to volume at 1 bar, as a function of pressure. The curve for volume is a least-squares fit, giving $K_{0} = 1.5 \pm 0.2$ GPa (Mohs hardness 6.5). Bars for individual cell parameters are just guides for the eye. Error bars for $V^{1/2}$ are two standard deviations; error bars on individual axial ratios are larger than symbols.