The pressure behavior of clinozoisite and zoisite: An X-ray diffraction study

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ABSTRACT

Compressibility data of clinozoisite and zoisite were measured by single-crystal X-ray diffraction in a diamond-anvil cell up to a pressure of about 50 kbar. In both polymorphs, the unit cell parameters varied linearly with pressure but in an anisotropic pattern: \( \beta_x = 2.1(1) \times 10^{-4}, \beta_y = 2.8(1) \times 10^{-4}, \beta_z = 3.3(1) \times 10^{-4} \) kbar\(^{-1}\) for clinozoisite, and \( \beta_x = 2.3(2) \times 10^{-4}, \beta_y = 2.9(1) \times 10^{-4}, \beta_z = 3.7(2) \times 10^{-4} \) kbar\(^{-1}\) for zoisite. The principal coefficients of the strain ellipsoid of clinozoisite are \( \beta_x = 2.0 \times 10^{-4}, \beta_y = 2.7 \times 10^{-4}, \beta_z = 3.3 \times 10^{-4} \) kbar\(^{-1}\); \( \beta_x \) and \( \beta_y \) were symmetrically oriented in the (010) plane with an angle of about 12° between \( \beta \) and the \( a \) axis, whereas \( \beta_z \) coincides with the \( b \) axis. Bulk moduli calculated as the reciprocal of cell-volume compressibility were 1300(20) kbar for the monoclinic and 1140(20) for the orthorhombic polymorph. \( K_0 \), determined by fitting the unit-cell parameters with a third-order Birch-Murnaghan equation of state, was 1270(45) kbar, with \( K' = 0.5(2) \) for clinozoisite and 1020(65) kbar with \( K' = 4.8(4) \) for zoisite.

Structural refinements of clinozoisite performed at 0.5, 19.4, and 42 kbar, and also under ambient conditions, showed that the compression mechanism included both shrinking of the polyhedra (i.e., octahedra and Ca polyhedra) and tilting of the SiO\(_4\) group, with reduction of the Si-O-Si angle. The different effect of these mechanisms explains the anisotropic compressional pattern in clinozoisite and the similar behavior observed in the two polymorphs.

Comparison of high-pressure and high-temperature data for clinozoisite showed that a given increase in pressure produced structural effects very similar to those seen after a proportional decrease in temperature. The calculated volume-expansivity-to-compressibility ratio of 38 bar/K indicates that the cell volume of clinozoisite remains unchanged with geothermal gradients of about 10 °C/km. The crystallographic data support the results of experimental petrology in indicating that epidote is a good candidate for transporting H\(_2\)O in down-going subduction slabs.

INTRODUCTION

Clinozoisite and zoisite are the Fe-poor members of the epidote group. They crystallize in either orthorhombic (zoisite, space group \( Pnma \)) or monoclinic (clinozoisite, space group \( P2_1/m \)) forms with the formula \( \text{Ca}_2\text{Al}_3\text{Fe}_p\text{Si}_{10}\text{O}_{28}\text{OH} \), where \( p \) is <0.04 (Kvick et al. 1988). Zoisite having a more restricted chemical range than clinozoisite. Dollase (1968) determined the structures of zoisite and clinozoisite and showed that the structure of zoisite could be related only approximately by a diagonal glide twin operation on \( (100) \) to the monoclinic cell, as previously proposed by Ito (1950). On the basis of transmission electron microscopy observations, Ray et al. (1986) described a polytypical relationship between the clinozoisite and zoisite structures: A displacement by \( \frac{1}{4}[001] \) on \( (001) \) planes between clinozoisite unit-cell modules yields the zoisite structure. The polytypes can be interchanged by introducing a shear between the various stacking modules.

The essential features of the epidote structure are chains of edge-sharing octahedra parallel to the \( b \) axis. The chains are connected by both single tetrahedra (SiO\(_4\)) and pairs of tetrahedra (Si\(_2\)O\(_7\)). Although in clinozoisite there are two types of chains, one with only M2 octahedra and the other with M1 octahedra and M3 octahedra attached on alternate sides along the chain extension, in zoisite the \( n \)-glide “twin” operation produces only one kind of chain. Large cavities are formed where Ca atoms are hosted.

Zoisite and clinozoisite are relatively common constituents of rocks of the epidote-amphibole facies and also occur in both hydrothermal systems and high-\( P \) eclogite facies terrains. The stability relationships between the two forms are not completely known. Ackerman and Raase (1973) considered that zoisite was the stable phase at low \( T \), whereas Jenkins et al. (1983) showed that it was the stable form relative to clinozoisite at 555 °C for Fe-free compositions. Prunier and Hewitt (1985), studying the coexisting phases in the Fe-bearing system, showed that zoisite is the stable high-\( T \), Fe-poor phase.