

## Single-crystal elasticity of zoisite $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$ by Brillouin scattering

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### ABSTRACT

The single-crystal elastic constants of zoisite  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$  were determined by Brillouin scattering at ambient conditions. The elastic tensor was obtained by an inversion of acoustic velocity data for three different crystal planes. The aggregate bulk modulus, shear modulus, and Poisson's ratio are  $K_{\text{S0}} = 125.3(4)$  GPa,  $G_0 = 72.9(2)$  GPa, and  $\sigma_0 = 0.26(1)$  for the VRH (Voigt-Reuss-Hill) average, respectively. The maximum azimuthal anisotropy of zoisite is 22% for compressional velocity and 33% for shear velocity. The maximum shear splitting is 21% along the [001] direction. Our results resolve the discrepancies in bulk modulus and axial compressibilities reported from static compression studies, and provide the first experimental constraints on the shear modulus. Trends in the elastic moduli of minerals in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (CASH) system are evaluated.

**Keywords:** Zoisite, single crystal, elasticity, Brillouin scattering

### INTRODUCTION

Hydrous phases in subduction zones are potential agents that can transport water to the deep earth. Properties of these hydrous minerals, especially elastic moduli, are necessary to model seismic wave speeds and hence place constraints on recycling of H<sub>2</sub>O through subduction zones (Hacker et al. 2003). Zoisite  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$  is a hydrous mineral containing 2 wt% water that is potentially important in subduction zones. It has a large stability field that extends up to 5.0 GPa at 700 °C and 6.6 GPa at 950 °C in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O (CASH) system (Poli and Schmidt 1998). In the basalt + H<sub>2</sub>O system, zoisite remains stable to pressures of 3.1 GPa at 650 °C (Forneris and Holloway 2003). Breakdown of zoisite at this pressure may be a source of fluid release at 100–120 km depth depending on the thermal structure of the subducting slab (Poli and Schmidt 1995).

Zoisite belongs to epidote group  $[\text{Ca}_2(\text{Al,Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})]$ , which occur in high- and ultrahigh-pressure metamorphic rocks from a wide variety of geological settings, including continental collisions and subduction zones (Hacker et al. 2003; Enami et al. 2004). Figure 1 shows the crystal structure of zoisite (Fesenko et al. 1955; Fesenko et al. 1956; Dollase 1968). Zoisite is the only member of the epidote group that is orthorhombic, instead of monoclinic. However, the structures of all epidote minerals are similar. Monoclinic epidotes, including clinozoisite, have two distinct edge sharing octahedral chains that run along [010]. The octahedral sites are mainly occupied by Al but can also contain Fe<sup>3+</sup>. Zoisite has only one type of octahedral chain parallel to [010] made up of edge sharing octahedra designated M1,2. The second octahedral site, M3, is more distorted and is attached to M1,2 by edge sharing. The parallel octahedral chains are linked by SiO<sub>4</sub> and Si<sub>2</sub>O<sub>7</sub> tetrahedral groups for both types of epidote minerals. Calcium ions reside in two large positions between

the octahedral chains and exhibit sevenfold coordination. Hydrogen is bonded to an oxygen in the octahedral chains (Franz and Liebscher 2004).

Zoisite is structurally related to some other Ca-Al silicates that may also be important in subduction zones, including lawsonite  $\text{CaAl}_2\text{Si}_2\text{O}_7(\text{OH})_2 \cdot (\text{H}_2\text{O})$  and pumpellyite  $\text{Ca}_2\text{MgAl}_2(\text{SiO}_4)(\text{SiO}_7)(\text{OH})_2 \cdot (\text{H}_2\text{O})$ . The lawsonite structure, for example, also consists of chains of edge-sharing AlO<sub>6</sub> octahedra but linked by Si<sub>2</sub>O<sub>7</sub> groups only. The large cavities are occupied by Ca atoms and H<sub>2</sub>O molecules.

Only a limited amount of Fe<sup>3+</sup>-Al substitution is observed in zoisite and so it is chemically more restricted to compositions close to end-member  $\text{Ca}_2\text{Al}_3\text{Si}_3\text{O}_{12}(\text{OH})$  compared with the monoclinic epidotes. The highest Fe<sup>3+</sup> content found in zoisite is  $X_{\text{Fe}} = 0.21\text{--}0.23$  (Vogel and Bahezre 1965; Brunsmann et al. 2000).

Knowing the bulk modulus of zoisite is necessary to calculate seismic wave velocities and for volume determination at high pressures in phase equilibria calculations. The bulk modulus has been determined from static pressure-volume measurements using X-ray diffraction in both multi-anvil apparatus and diamond anvil cells (Holland et al. 1996; Comodi and Zanazzi 1997; Pawley et al. 1998; Grevel et al. 2000). Existing results show large discrepancies. The zero-pressure isothermal bulk modulus  $K_{\text{T0}}$  ranges from 102(6.5) GPa (Comodi and Zanazzi 1997) to 279(9) GPa (Holland et al. 1996). Neglecting the anomalous result of Holland et al. (1996), the range of possible bulk moduli for zoisite translate into a 3% uncertainty in the bulk sound velocity at 6 GPa (Hacker et al. 2003). Even more importantly, the shear and compressional sound velocities are unknown because of lack of constraint on the shear modulus. For the monoclinic epidotes, a large range of bulk moduli have also been reported from previous experiments ranging from 106.2 to 207 GPa (Ryzhova et al. 1966; Holland et al. 1996; Qin et al. 2003).

In this study, we used Brillouin scattering and X-ray diffraction to determine the full elastic tensor of zoisite. In doing so, we

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could resolve discrepancies in the bulk modulus and determine the shear modulus and elastic anisotropy for the first time. Zoisite is a good choice for initial studies of the elasticity of epidote minerals because of its higher symmetry and limited range of chemical variability (Franz and Liebscher 2004). We also compared the elasticity of zoisite to that of other minerals in the CASH system.

## EXPERIMENTS

Three platelets were cut from a gem-quality zoisite sample of unknown origin. Energy-dispersive single-crystal X-ray diffraction was performed at beamline X17C of the National Synchrotron Light Source. The unit-cell parameters were determined to be  $a = 16.207(5)$ ,  $b = 5.540(5)$ , and  $c = 10.056(2)$  Å with a calculated density  $3.343(3)$  g/cm<sup>3</sup> in good agreement with literature values (Franz and Liebscher 2004). The chemical composition was measured by electron microprobe and showed the sample to be pure zoisite with Fe, Mn, and Mg below detection limits. Figure 2 shows the Raman spectra of zoisite under ambient conditions. 29 modes were observed in this study and are compared with previous work (Huang 1999) in Table 1. Peak positions are generally in good agreement with Huang (1999) but we are able to identify several additional modes. The symmetric OH stretching vibration is observed at  $3150.2$  cm<sup>-1</sup>.

All three platelets were carefully polished parallel on both sides to 0.5 mm thickness using alumina paper down to a grit size of 1 μm. The Brillouin spectra were measured using a six-pass Sandercock tandem Fabry-Perot interferometer in a forward symmetric scattering geometry under ambient conditions. The sample was excited by a solid-state laser with a wavelength of 532.15 nm and power of about 150 mW. The acoustic velocities,  $v$ , are determined from the measured Brillouin frequency shift  $\Delta\nu_B$ :

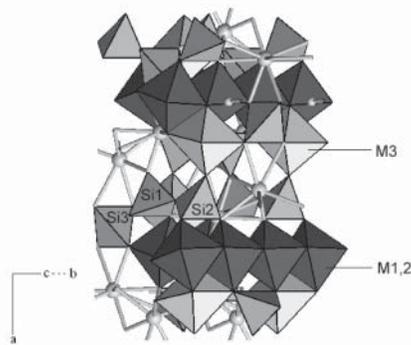
$$v = \frac{\Delta\nu_B \lambda_0}{2 \sin(\theta/2)} \quad (1)$$

where  $\lambda_0$  is the incident wavelength,  $\theta$  is the scattering angle ( $70^\circ$  in this study). Details of the Brillouin system are given elsewhere (Speziale and Duffy 2002).

Measurements were made in a total of 37 directions at  $5^\circ$  steps for each platelet. For each spectrum, the average collection time was around 20 minutes. Our Brillouin spectra are of excellent quality with a high signal-to-noise ratio. One quasi-longitudinal and two quasi-transverse waves were observed in most directions for all three platelets (Fig. 3). The uncertainty of the measurement was within  $\pm 0.5\%$  of the measured velocities.

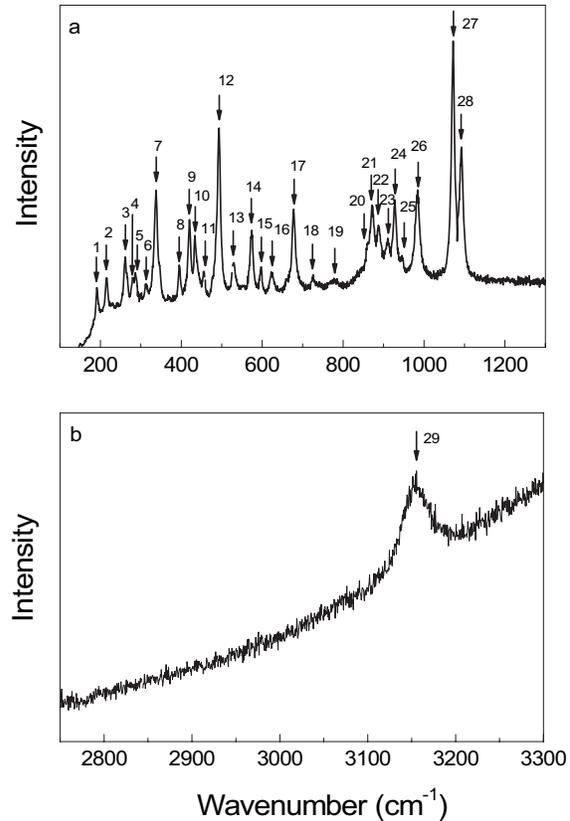
## RESULTS

Zoisite has orthorhombic symmetry (space group  $Pnma$ ) and nine independent elastic constants. For each platelet, the direction cosine that describes the phonon propagation direction can be described by an azimuthal angle together with the three Eulerian

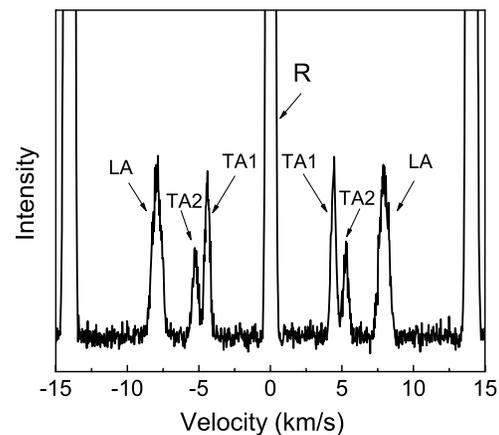


**FIGURE 1.** The crystal structure of zoisite. Zoisite is characterized by a single octahedron chain with site M1,2. M3 octahedra are attached to M1,2 by edge sharing. There are three distinct Si sites. Si1 and Si2 form a  $\text{Si}_2\text{O}_7$  group. Si3 is an isolated tetrahedron. The large spheres represent Ca atoms. The small spheres are hydrogen sites.

angles that relate the laboratory and crystal coordinate systems (Shimizu 1995). In fitting all the velocity data for the three platelets together, there are thus a total of 18 parameters (nine elastic constants, nine Eulerian angles) to be constrained. These



**FIGURE 2.** Raman spectra of zoisite under ambient conditions. (a) Wavenumber ranges from 100 to  $1300$  cm<sup>-1</sup>; (b) Raman spectrum of OH stretching vibration.



**FIGURE 3.** Brillouin spectrum of zoisite at ambient conditions (sample 1, azimuthal angle =  $30^\circ$ ). R = unshifted Rayleigh line; LA = longitudinal mode; TA1, TA2 = two transverse modes. TA2 is the fast transverse mode.

**TABLE 1.** Peak positions in Raman spectrum of zoisite

No.	This study (cm <sup>-1</sup> )	Huang 1999 (cm <sup>-1</sup> )	No.	This study (cm <sup>-1</sup> )	Huang 1999 (cm <sup>-1</sup> )	No.	This study (cm <sup>-1</sup> )	Huang 1999 (cm <sup>-1</sup> )	No.	This study (cm <sup>-1</sup> )	Huang 1999 (cm <sup>-1</sup> )
1	191.7	186	2	215.2	217	3	261.4	257	4	280.2	269
5	287.1		6	312.1	310	7	337.4	338	8	395.3	396
9	419.8		10	434.8	431	11	455.6		12	492.9	490
13	529.6	528	14	573.7	572	15	597.1	594	16	623.3	620
17	677.8	678	18	727.0		19	777.5		20	860.3	
21	871.7	869	22	889.0		23	909.0		24	927.8	926
25	945.8		26	983.4	982	27	1017.7	1070	28	1092.3	1091
29	3150.2	3151									

were obtained by non-linear least squares fitting to Christoffel's equation (Every 1980):

$$\det|C_{ijkl}n_jn_l - \rho v^2\delta_{ik}| = 0 \quad (2)$$

where,  $\rho$  is the density,  $v$  is the velocity of phonon,  $n_i$  are the direction cosines of the phonon propagation directions, and the  $C_{ijkl}$  are the elastic constants. Table 2 shows the best-fitting  $C_{ij}$  values. Here we have adopted the compact Voigt notation for the components of the elastic tensor (Nye 1985). Orientations of two of the three crystal platelets were determined by energy-dispersive single-crystal X-ray diffraction at beamline X17C of Brookhaven National Laboratory (Hu et al. 1994). The X-ray orientations were used as starting models in the inversion. Table 3 shows the Eulerian angles obtained from inversion of the Brillouin scattering data compared with those from single-crystal X-ray diffraction. The uncertainty on Eulerian angles that results from the inversion is typically within 1.5°. The single-crystal X-ray orientations are similar, but can show differences from Brillouin results up to 5°. The difference is likely to due to the remounting of the crystal that was necessary for the X-ray measurements but tradeoffs among the Eulerian angles for a given plane may also contribute as discussed below.

Figure 4 shows the experimentally obtained velocity data together with values calculated from the best fitting elastic constants. The root-mean-square (RMS) deviation between measured and calculated acoustic velocities was 39 m/s. For the longitudinal moduli  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  and shear moduli  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ , the precision of the recovered value is better than 0.6% (1 $\sigma$  level), while it is better than 2.6% for the off-diagonal moduli  $C_{12}$ ,  $C_{13}$ ,  $C_{23}$ . The covariance matrix was calculated and indicates that individual constants are well resolved and do not suffer significant "trade-offs" among pairs of elastic constants (Press et al. 1988; Brown et al. 1989). The greatest trade-offs are between  $C_{12}$  and  $C_{13}$  and between  $C_{23}$  and  $C_{13}$ , but the magnitude of the covariance coefficients are less than 2% of the magnitude of the constants themselves.

## DISCUSSION

### Individual moduli and elastic anisotropy of zoisite

The individual elastic moduli of zoisite can be compared to values for other hydrous Ca-Al silicates such as lawsonite (Sinogeikin et al. 2000) and hirschildite (O'Neill et al. 1993) (Table 4). In general, the longitudinal, shear, and off-diagonal moduli of zoisite span similar ranges as those observed for the other materials, but the maximum values for each type of modulus in zoisite exceeds those in the other minerals. The longitudinal modulus along the direction of the octahedral chains is interme-

**TABLE 2.** Single-crystal elastic moduli of zoisite

Modulus	Value (GPa)	Modulus	Value (GPa)	Modulus	Value (GPa)
$C_{11}$	279.8(6)	$C_{44}$	51.8(3)	$C_{12}$	94.7(11)
$C_{22}$	249.2(6)	$C_{55}$	81.4(3)	$C_{13}$	88.7(10)
$C_{33}$	209.4(9)	$C_{66}$	66.3(3)	$C_{23}$	27.5(7)

Note: Numbers in parentheses are 1- $\sigma$  uncertainty in the last digit(s).

**TABLE 3.** Eulerian angles from single crystal X-ray diffraction and Brillouin scattering

Experimental technique	Sample 2		Sample 3	
	$\theta$	$\chi$	$\theta$	$\chi$
X-ray	56.3°	94.8°	106.3°	6.8°
Brillouin	51.8(14)°	97.3(13)°	106.3(7)°	5.7(6)°

**TABLE 4.** Single-crystal elastic moduli of zoisite, lawsonite, and hirschildite

Modulus	Zoisite	Lawsonite*	Hirschildite†
$C_{11}$ (GPa)	279.8(6)	226(2)	186.5(11)
$C_{22}$ (GPa)	249.2(6)	214(2)	186.5(11)
$C_{33}$ (GPa)	209.4(9)	259(2)	186.5(11)
$C_{44}$ (GPa)	51.8(3)	65(1)	63.9(5)
$C_{55}$ (GPa)	81.4(3)	60(1)	63.9(5)
$C_{66}$ (GPa)	66.3(3)	17(1)	63.9(5)
$C_{12}$ (GPa)	94.7(11)	69(2)	56.5(14)
$C_{13}$ (GPa)	88.7(10)	65(2)	56.5(14)
$C_{23}$ (GPa)	27.5(7)	82(2)	56.5(14)

\* From Sinogeikin et al. (2000).

† From O'Neill et al. (1993). The composition is Ca<sub>2</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>1.72</sub>(H<sub>2</sub>O<sub>4</sub>)<sub>1.28</sub>.

diated in value for zoisite, which is also the case for lawsonite. Among the shear moduli,  $C_{55}$  for zoisite is 23% larger than  $C_{44}$  and 55% larger than  $C_{66}$ . One exceptional feature of the elasticity of zoisite is that  $C_{23}$  is much lower than  $C_{12}$  and  $C_{23}$  or any of the off-diagonal moduli for lawsonite and hirschildite. Data inversions in which  $C_{23}$  was fixed at higher values gave poor fits to the velocity data.

The maximum shear velocity for zoisite is 5.47 km/s along [011] (polarization [0, 0.62, -0.79]). The minimum shear velocity is 3.94 km/s along [001] (polarization [010]). [001] is the direction of the maximum shear splitting [( $v_{S,max[001]} - v_{S,min[001]}$ )/ $v_{S,aggr}$  = 0.21]. Zoisite has much smaller shear anisotropy  $A_S = [(v_{S,max} - v_{S,min})/v_{S,aggr} = 0.33]$  than lawsonite at ambient  $P$  and  $T$  ( $A_S = 0.74$ ) (Sinogeikin et al. 2000). However, lawsonite exhibits strong shear softening at ambient  $T$  as discussed below and its anisotropy is much reduced upon heating to 450 °C ( $A_S = 0.40$ ) (Schilling et al. 2003). The longitudinal anisotropy of zoisite  $A_P = [(v_{P,max} - v_{P,min})/v_{P,aggr} = 0.22]$  is smaller than the shear anisotropy. It is comparable to that of lawsonite ( $A_P = 0.24$ ) (Sinogeikin et al. 2000).

### Aggregate elasticity and comparison with previous studies

Table 5 presents the Voigt and Reuss bounds and VRH average (Voigt-Reuss-Hill) for the isotropic aggregate bulk and shear modu-

lus. The aggregate Poisson's ratio is 0.26(1), which is given by

$$\sigma = \frac{3K - 2G}{2(3K + G)} \quad (3)$$

where  $K$  is the bulk modulus,  $G$  is the shear modulus.

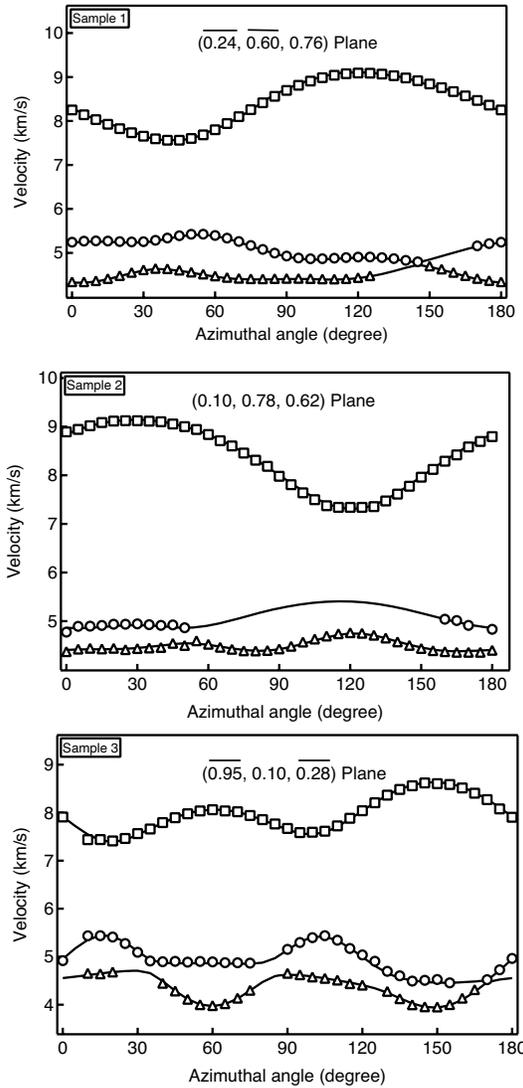
The isothermal bulk modulus,  $K_T$ , was calculated from the measured adiabatic value,  $K_S$ , using

$$K_T = K_S / (1 + \alpha\gamma T) \quad (4)$$

where  $T$  is temperature (300 K),  $\alpha$  is the thermal expansion coefficient, and  $\gamma$  is the Gruneisen parameter given by

$$\gamma = \frac{\alpha K_S V}{C_p} \quad (5)$$

$V$  is the molar volume and  $C_p$  is the specific heat. Thermodynamic values used for the adiabatic to isothermal correction are



**FIGURE 4.** Measured compressional and shear wave speeds of zoisite as a function of direction for three platelets of zoisite. Symbols represent experimental velocities. Solid lines are best fitting results.

shown in Table 6.

Our resulting  $K_{T0} = 123.4(4)$  GPa is in agreement with those of Pawley et al. (1998) and Grevel et al. (2000) who used the Birch-Murnaghan equation of state to fit pressure-volume data (Table 7). Our result is also within 5% of that reported from first principles calculations using density functional theory ( $K_{T0} = 117.5$  GPa) (Winkler et al. 2001a). On the other hand, our value is 17% higher than  $K_{T0} = 102.6$  GPa reported by Comodi and Zanazzi (1997). The determination of the bulk modulus and its pressure derivative in static compression studies relies on the fits to the slope of the measured  $P$ - $V$  curve. Static compression studies also suffer from a well-known tradeoff between fitted values of the pressure derivative of the bulk modulus,  $K'_{T0}$ , and  $K_{T0}$ . The limited pressure ranges in previous compression studies could lead to large uncertainties in the bulk modulus.

Using  $V_0$ ,  $K_{T0}$  values from our X-ray and Brillouin data, we calculated the pressure volume isotherm using the third-order Birch-Murnaghan equation of state by assuming  $K'_{T0} = 4$  (Fig. 5). In general, our compression curve is broadly consistent with earlier measurements and the agreement is especially good for the equation of state of Grevel et al. (2000).

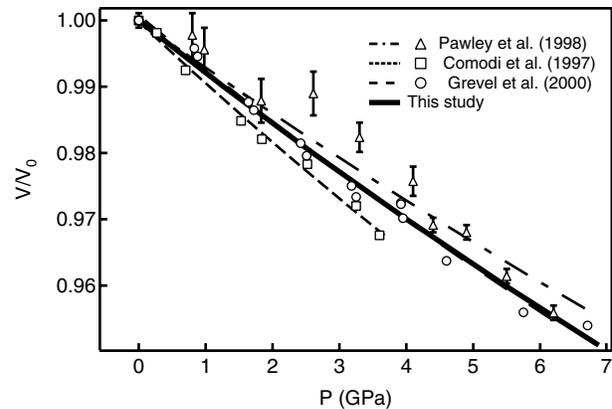
Previous theoretical and experimental studies that examined both zoisite and clinozoisite found that the bulk modulus of clinozoisite is 20% greater than that of zoisite (Comodi and Zanazzi 1997; Winkler et al. 2001a). However, in the experi-

**TABLE 5.** Aggregate elastic moduli of zoisite

This study	Reuss	Voigt	VRH
$K_{S0}$ (GPa)	121.6(4)	128.9(4)	125.3(3)
$G_0$ (GPa)	70.6(2)	75.1(2)	72.9 (2)
$v_p$ (km/s)	8.03	8.28	8.16
$v_s$ (km/s)	4.60	4.74	4.67
$\sigma_0$	0.26(1)	0.26(1)	0.26(1)

**TABLE 6.** Thermodynamic parameters of zoisite under ambient conditions

Parameter	Value	Reference
Thermal expansion, $\alpha$	$3.29 \times 10^{-5} \text{ K}^{-1}$	Pawley et al. (1998); Grevel et al. (2000)
Molar volume, $V$	135.9(2) $\text{cm}^3$	This study
Gruneisen parameter, $\gamma$	1.59	Calculated
Heat capacity, $C_p$	352 J/(K-mol)	Poli and Schmidt (1998)



**FIGURE 5.** Volume compression of zoisite as a function of pressure at room temperature from Brillouin scattering (thick solid line) and static compression experiments. Error bars are smaller than symbols when not shown.

**TABLE 7.** Isothermal bulk modulus and shear modulus of zoisite and related minerals

Mineral	Reference	$P_{max}$ (GPa)	$K_{T0}$ (GPa)	$K_T$ (GPa)	$K_T^*$	$G_0$ (GPa)
Zoisite	This study	0	125.3(3)	123.4(4)		72.9(2)
	Pawley et al. (1998)	6.2		125(3)	4 (fixed)	
	Grevel et al. (2000)	7		125.1(2.1)	4 (fixed)	
	Comodi and Zanazzi (1997)	3.6		102(6.5)	4.8(4)	
Clinozoisite	Winkler et al. (2001b)	0		117.5(1.7)		
	Comodi and Zanazzi (1997)	5.1		127.0(4.5)	0.5(2)	
	Winkler et al. (2001a)	0		136(4)		
Epidote	Holland et al. (1996)	5.21		162(4)	4 (fixed)	
	Ryzhova (1966)	0	106.2			61.2
	Qin et al. (2003)	20		207(15)	4 (fixed)	
Lawsonite	Sinogeikin et al. (2000)	0	125(2)	123.2(20)		51.8(7)

\*  $K_T^* = (\partial K_T / \partial P)_T$

mental static compression study of Comodi and Zanazzi (1997), fits were performed using  $K_{T0}^* = 0.5$  for clinozoisite and  $K_{T0}^* = 4.8$  for zoisite. If a value of  $K_{T0}^* = 4$  were adopted for the former and the equation of states refitted,  $K_T$  would decrease to 117 GPa, which is now smaller than that of zoisite. Thus, at present there are no experimental results that can unambiguously confirm the theoretical finding that there is a significant difference between the bulk moduli of zoisite and clinozoisite.

For orthorhombic crystals, the linear compressibilities along the three crystallographic axes are given by Nye (1985):

$$\begin{aligned}\beta_a &= s_{11} + s_{12} + s_{13} \\ \beta_b &= s_{21} + s_{22} + s_{23} \\ \beta_c &= s_{31} + s_{32} + s_{33}\end{aligned}\quad (6)$$

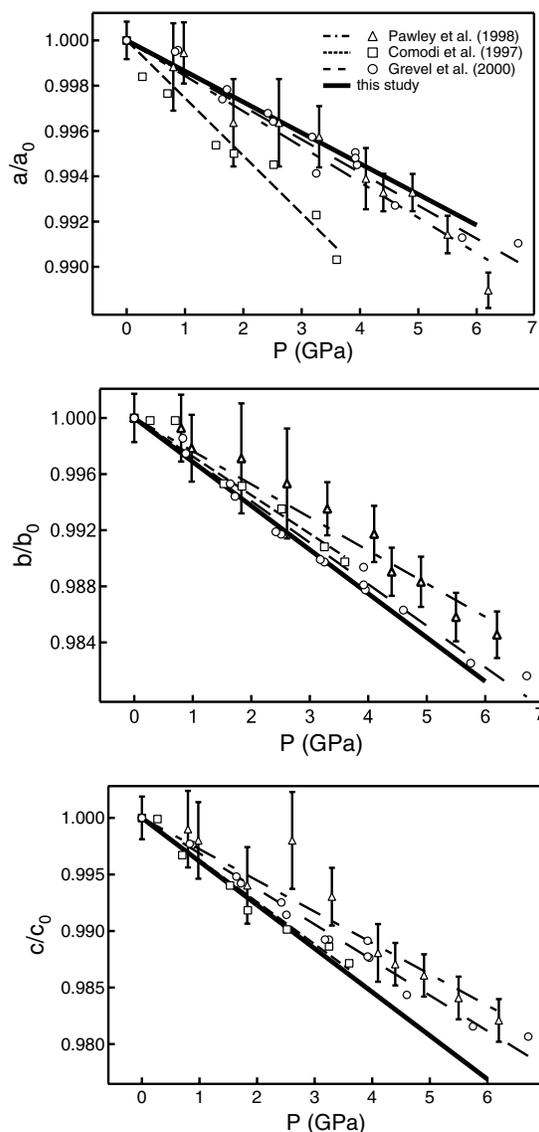
where  $\beta_i$  is the linear compressibility in the  $i$  direction, and  $s_{ij}$  are the isothermal elastic compliances. The conversion of adiabatic elastic constants to isothermal ones (Davies 1974) was carried out using parameters in Table 2. From our measured elastic constants, the values calculated for zoisite at ambient conditions are:

$$\begin{aligned}\beta_a &= 1.36(3) \times 10^{-3} \text{ GPa}^{-1} \\ \beta_b &= 3.13(2) \times 10^{-3} \text{ GPa}^{-1} \\ \beta_c &= 3.85(2) \times 10^{-3} \text{ GPa}^{-1}\end{aligned}\quad (7)$$

Figure 6 shows relative axial compressibilities of zoisite computed using elastic constants in comparison with those determined by static compression studies. In this case, we have not included any pressure effects on the  $s_{ij}$  and hence our axial compressibilities are close to straight lines (solid lines in Fig. 6). In reality, the effect of the decreased compressibility with pressure means our measurements give a lower bound to the actual axial compression curves. For the  $a$  and  $b$  axes, our results are in a general agreement with Grevel et al. (2000). While for the  $c$  axis, our result instead agrees best with that of Comodi and Zanazzi (1997). If the pressure effect is considered, this will lead to a better agreement in  $b$  and  $c$  axes with previous studies but poorer agreement for the  $a$  axis.

#### Elasticity in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system

Figure 7 shows selected minerals in the CASH system. The chemical compositions are listed in Table 8. Minerals in this system can be grouped by similarities in chemical compositions. Some phases are polymorphs: zoisite and clinozoisite;



**FIGURE 6.** Relative compression of unit-cell parameters of zoisite derived from Brillouin scattering data (thick solid line) compared with static compression studies. Error bars are smaller than symbols when not shown.

kyanite, sillimanite, and andalusite; quartz and coesite. Lawsonite, diaspore, and portlandite are chemically hydrous forms of anorthite, corundum, and lime, respectively, but with different crystal structures. Hibschite is the hydrous phase of grossular with which it forms a solid solution. The hydrous Ca-Al silicates: lawsonite and zoisite contain 11.5 and 2 wt% H<sub>2</sub>O, respectively. Hibschite has variable H<sub>2</sub>O content, but elasticity data have been reported for a sample with composition Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>1.72</sub>(H<sub>4</sub>O<sub>4</sub>)<sub>1.28</sub> containing 10.9 wt% H<sub>2</sub>O (O'Neill et al. 1993).

Figure 8 shows the bulk and shear moduli of minerals in the CASH system. Although a wide range of structures, compositions, and water contents are represented, both the bulk and shear modulus show a general, monotonic increase of moduli with density. With the exception of anorthite-lawsonite, incorporation of water decreases the density and elastic moduli of minerals in the CASH system: the elastic moduli of diaspore, portlandite, hibschite are smaller than the chemically related anhydrous phases corundum, lime, and grossular. The modulus-density trend for the hydrous-anhydrous pairs tends to follow the general behavior of the CASH system as a whole.

Lawsonite and zoisite have similar structures. Lawsonite consists of chains of edge sharing AlO<sub>6</sub> octahedra in [100] direction and are linked by Si<sub>2</sub>O<sub>7</sub> tetrahedra along [001] direction. Water is present as both H<sub>2</sub>O molecules and OH groups, and lawsonite contains 11.5 wt% water, which is much greater than that of zoisite (2 wt%). OH groups are bonded to Al-octahedra for both structures. H<sub>2</sub>O molecules and Ca atoms occupy large cavities in

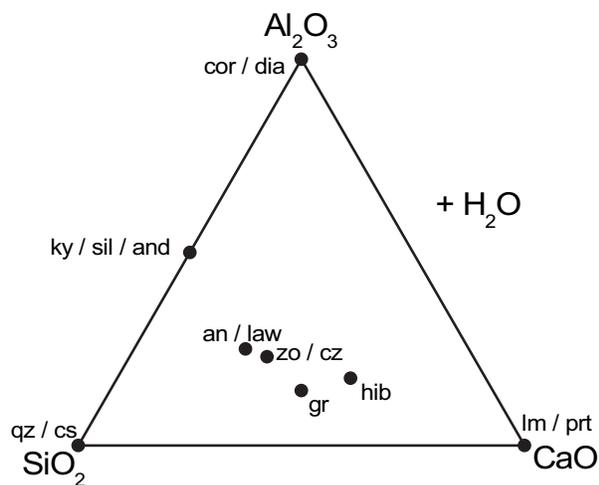
the lawsonite structure. At high pressures and temperatures up to 980 °C at 6.5 GPa, lawsonite decomposes into zoisite, kyanite, quartz (coesite), and water (Schmidt and Poli 1994).

The elastic constants of lawsonite have been determined from Brillouin scattering (Sinogeikin et al. 2000; Schilling et al. 2003). Zoisite and lawsonite have very similar bulk moduli, but zoisite has a 40% larger shear modulus than lawsonite (52 GPa). This is likely related to a phase transition in lawsonite at *T* near 0 °C (Sondergeld et al. 2000). Lawsonite exhibits shear softening of the elastic constant *C*<sub>66</sub> as the transition temperature is approached. The low shear modulus of lawsonite is strongly affected by the softening of *C*<sub>66</sub> (Table 4). As temperature increases, the shear modulus of lawsonite actually increases (Schilling et al. 2003). Due to the proximity of the phase transition in lawsonite at ambient conditions, it is difficult to predict its elasticity at subducting slab conditions.

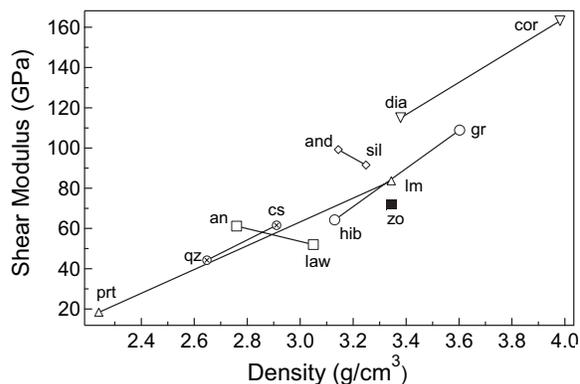
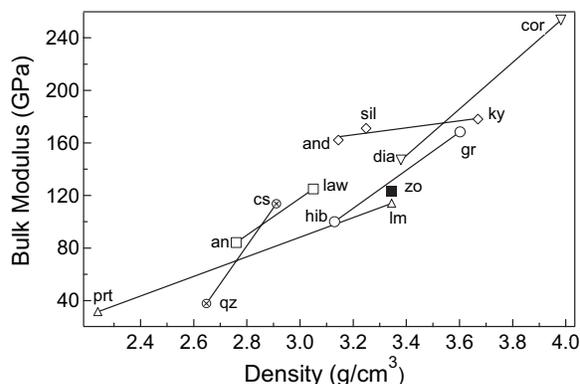
The density and bulk modulus of lawsonite are greater than its anhydrous counterpart, anorthite, but it has a smaller shear modulus in comparison with anorthite. These features are a reflection of both the elastic instability in lawsonite discussed above as well as the large structural differences between the two minerals. Al in anorthite is in fourfold coordination, but Al in

**TABLE 8.** Chemical formula of minerals in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system

Mineral name	abbr.	Chemical formula	Mineral name	abbr.	Chemical formula
anorthite	an	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	lawsonite	law	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> (OH) <sub>2</sub> ·H <sub>2</sub> O
grossular	gr	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	hibschite	hib	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>1.72</sub> (H <sub>4</sub> O <sub>4</sub> ) <sub>1.28</sub>
corundum	cor	Al <sub>2</sub> O <sub>3</sub>	diaspore	dia	AlOOH
lime	lm	CaO	portlandite	prt	Ca(OH) <sub>2</sub>
zoisite	zo	Ca <sub>2</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub> (OH)	clinozoisite	czo	Ca <sub>2</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub> (OH)
quartz	qz	SiO <sub>2</sub>	coesite	cs	SiO <sub>2</sub>
kyanite	ky	Al <sub>2</sub> SiO <sub>5</sub>	sillimanite	sil	Al <sub>2</sub> SiO <sub>5</sub>
andalusite	and	Al <sub>2</sub> SiO <sub>5</sub>			



**FIGURE 7.** Selected minerals in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. Chemical compositions and abbreviations are given in Table 8.



**FIGURE 8.** Bulk and shear moduli of minerals in the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system. Solid lines connect structurally or chemically related species. Data are from: ky (Winkler et al. 2001b); sil, and (Vaughan and Weidner 1978); an (Hearmon 1984); law (Sinogeikin et al. 2000); cor (Ohno et al. 1986); dia (Jiang et al. 2005); lm (Oda et al. 1992); prt (Laugesen 2005); gr (Bass 1989); hib (O'Neill et al. 1993); qz (Hearmon 1979); cs (Weidner and Carleton 1977). Abbreviations are listed in Table 8.

lawsonite is in sixfold coordination.

In general, Figure 8 shows that structurally and chemically diverse minerals in the CASH system show a general increase in both bulk and shear modulus with density. Structural effects are clearly also important or even dominant as in the case of lawsonite and anorthite. The hydrous Ca-Al silicates (lawsonite, hibschite, zoisite) show an increase in shear modulus with decreasing water content (and increasing density). As discussed above, the shear modulus of lawsonite may be anomalous, and the values for hibschite and zoisite are likely to be more representative of hydrous Ca-Al silicates generally.

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