Influence of octahedral site chemistry on the elastic properties of biotite

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Abstract
Brillouin light scattering spectroscopy was used along with detailed composition information obtained from electron probe microanalysis to study the influence of octahedral site chemistry on the elastic properties of natural biotite crystals. Elastic wave velocities for a range of directions in the ac and bc crystallographic planes were obtained for each crystal by application of the well-known Brillouin equation with refractive indices and phonon frequencies obtained from the Becke line test and spectral peak positions, respectively. In general, these velocities increase with decreasing iron content, approaching those of muscovite at low iron concentrations. Twelve of thirteen elastic constants for the full monoclinic symmetry were obtained for each crystal by fitting analytic expressions for the velocities as functions of propagation direction and elastic constants to corresponding experimental data, while the remaining constant was estimated under the approximation of hexagonal symmetry. Elastic constants $C_{11}$, $C_{22}$, and $C_{66}$ are comparable to those of muscovite and show little change with iron concentration due to the strong bonding within layers. In contrast, nearly all of the remaining constants show a pronounced dependence on iron content, a probable consequence of the weak interlayer bonding. Similar behaviour is displayed by the elastic stability, which exhibits a dramatic decrease with increasing iron content, and by the elastic anisotropy within the basal cleavage plane, which decreases as the amount of iron in the crystal is reduced. This systematic dependence on iron content of all measured elastic properties indicates that the elasticity of biotite is a function of octahedral site chemistry and provides a means to estimate the elastic constants and relative elastic stability of most natural biotite compositions if the iron or, equivalently, magnesium, concentration is known. Moreover, the good agreement between the elastic constants of Fe-poor (Mg-rich) biotite and those of phlogopite obtained from first-principles calculation based on density functional theory indicates that the latter approach may be of use in predicting the elastic properties of biotites.

Keywords Biotite · Elastic properties · Octahedral site chemistry · Brillouin light scattering · Electron probe microanalysis

Introduction
Micas are common rock-forming phyllosilicate minerals displaying monoclinic symmetry and comprising approximately 5–12% of the continental crust (Almqvist and Mainprice 2017). The perfect {001} cleavage and platy habit of the mica group lead to preferred orientation of their grains. In sedimentary rocks preferred orientation arises as a depositional or diagenetic feature. In shales, composed predominantly of clay minerals, which are closely related in structure to micas, such preferred orientation leads to their fissility. In metamorphic rocks preferred orientation of micas (and other minerals) is a response to crystallisation (or recrystallisation) in a stress field, causing the development of a foliation (or schistosity, (Vernon 2018) perpendicular to the direction of the primary stress. At the highest temperatures of metamorphism, and in the presence of an anisotropic stress field, compositional segregation, combined with foliation, may lead to the development of very strongly layered gneisses (gneissosity, (Vernon 2018).

The presence of fissility, foliation, or gneissosity causes anisotropy in the velocity of seismic waves through the Earth. This was recognised in the nineteenth century and with the development of improved instrumentation and processing techniques has become a tool that is used both
in exploration geophysics and deep Earth studies (Helbig and Thomsen 2005; Romanowicz and Wenk 2017; Chandler et al. 2021).

The anisotropy of rocks can provide information on rock microstructure and crystal anisotropy bears on efforts to use inclusions of one mineral in another to obtain measures of pressure at the time of inclusion (Healy et al. 2020). Complete and accurate characterization of the elastic properties of rocks and the minerals that compose them is therefore important to understanding the composition and structure of the Earth. On a microscopic scale, knowledge of the elasticity of sheet silicates like micas provides insight into the nature of bonding and acoustic wave behaviour in layered materials. Moreover, the use of micas in applications such as flexible electronic devices also requires that the elastic properties be known (Ma et al. 2016; Xu et al. 2018).

The micas

The silicates are, volumetrically, the most important mineral group in the Earth’s crust. Their structures are based on tetrahedra, i.e. sites in which each central cation (commonly Si or Al) is coordinated by four oxygen atoms arrayed at the apices of a tetrahedron. Sharing of the apical oxygens between adjacent tetrahedra, together with substitution or larger cations on sites that arise between tetrahedra give rise to a wide variety of silicate structures and symmetries.

A key determinant of structure type is the number of oxygens per tetrahedron that are shared with adjacent tetrahedra. In the sheet silicates three of the four oxygen atoms of each tetrahedral site are shared, giving rise to the (Si, Al)-O tetrahedral sheet as the common structural characteristic of these minerals. Within the sheet silicates the micas form a large and important group. Their distinguishing feature is a structure based on a double sheet of tetrahedra between which is sandwiched a layer of octahedral sites (coordination number six, see Fig. 1) in which four of the six apices of each octahedron are coordinated to the oxygens of the tetrahedra and two to sites that can be occupied by hydroxyl, fluorine or chlorine. There are two tetrahedral sheets per octahedral sheet and the combined tetrahedral-octahedral-tetrahedral layer is often called a TOT sheet. The TOT sheets carry a net negative charge that is compensated by large cations (K, Na, etc.) lying between them. Various stacking sequences of the TOT sheets are possible but the most common gives rise

![Fig. 1 Crystal structures of biotite and muscovite. a Biotite structure (Takeda and Ross 1975) with two T = Si, Al tetrahedral layer shown with light grey spheres which sandwich an octahedral layer. Mg (or Fe) octahedral layer shown with medium grey spheres. Interlayer potassium cations shown with black spheres. b Muscovite structure (Guggenheim et al. 1987) with interlayer cations shown with black spheres, tetrahedral cations shown with light grey spheres, and octahedral cations shown with medium grey spheres](image)
to monoclinic symmetry. Figure 1 was created using VESTA (Momma and Izumi 2011) software along with data publicly available through the American Mineralogist database (Downs and Hall-Wallace 2003) for biotite (Takeda and Ross 1975) and muscovite (Guggenheim et al. 1987).

**Biotite and muscovite**

Biotite \( (K_2(Mg,Fe)_6[Si_6Al_2O_20])(OH,F,Cl)_4 \) is trioctahedral with three octahedral sites per formula unit (six in the conventional unit cell, which we use here) completely or almost completely filled (see left panel of Fig. 1). Muscovite \( (K_2Al_4[Si_6Al_2O_20])(OH,F,Cl)_4 \) is dioctahedral, meaning that one of every three octahedra is vacant (see right panel of Fig. 1). In biotite, substitution of trivalent \( (Fe^{3+}, Al^{3+}) \) or quadrivalent \( (Ti^{4+}) \) cations on octahedral sites can be compensated by either octahedral vacancies or by replacement of Si by Al on tetrahedral sites beyond the ideal one out of four, and there can be extensive solid solution towards siderophyllite (an end member with Fe and Al mixing on octahedral sites). Similarly, in muscovite altervalent substitution on the octahedral sites can be compensated by changing the composition of the tetrahedra, although such substitutions are less common than in biotite. The chemical diversity of the micas accounts for their widespread occurrence in igneous, metamorphic and sedimentary rocks of widely differing chemistry and paragenesis.

**Elasticity of micas**

Despite its importance and utility, the elasticity of many micas remains merely estimated or unexplored. This is largely due to chemical variability and the low symmetry of these crystals. While complete sets of elastic constants have been measured for muscovite (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993), analogous data for the biotite group have not been reported. Experimentally-determined elastic constants for biotite are limited to estimates obtained via ultrasonic techniques for two phlogopite samples and a biotite sample of unspecified composition with the symmetry approximated as hexagonal rather than the true monoclinic (Aleksandrov et al. 1961). This precludes direct comparison with theoretical results for the full monoclinic elastic constants tensor for phlogopite (Chheda et al. 2014) and muscovite (Militzer et al. 2011), but differences in some constants among these samples hint at the dependence of biotite elasticity on composition. This effect has not, however, yet been quantified.

In this paper, the results of Brillouin light scattering experiments on natural crystals of biotite are reported. The crystals were selected a priori to be compositionally different, with the composition later quantified by electron probe microanalysis. Directional dependences of elastic wave velocities in the \( ac \) and \( bc \) crystal planes were measured from Brillouin peak frequency shifts and refractive indices determined from the Becke line test. These velocities, together with sample densities, permitted twelve of thirteen elastic constants and related mechanical properties to be determined for each of the samples. The results show that the elastic properties of biotite depend on octahedral site chemistry. Comparison is also made to new and published results for muscovite and to elastic constants of phlogopite determined from first-principles calculations.

**Theory**

**Brillouin light scattering**

Brillouin spectroscopy is a technique used to probe thermally-excited acoustic phonons (elastic waves) in a medium via the inelastic scattering of light. For a 180° backscattering geometry such as that used here, conservation of energy and momentum applied to the scattering process (Dil 1982; Speziale and Duffy 2014) yield the phonon velocity via the well-known Brillouin equation

\[
v = \frac{\Omega}{q} = \frac{f\lambda_i}{2n}.
\]

Here, \( f = \Omega/2\pi = |f_i - f_j| \) is the Brillouin peak frequency shift and \( q = 4\pi n/\lambda_i \) is the magnitude of the wavevector of the probed phonon, where \( n \) is the refractive index of the target material and \( \lambda_i \) the wavelength of the incident light.

**Elastic waves**

Acoustic modes may be considered as sound waves in a crystal since their wavelengths are much greater than the primitive unit cell dimensions. The equation that describes the motion of these waves is

\[
\rho \frac{\partial^2 u_i}{\partial t^2} = C_{ijkl} \frac{\partial^2 u_j}{\partial x_i \partial x_l},
\]

where \( \rho \) is the density of the medium, \( C_{ijkl} \) is the elastic stiffness tensor, \( u_i(x_i, t) \) is the particle displacement as a function of position, \( x_i \), and time, \( t \), with \( i, j, k, l = 1, 2, 3 \) (Hayes and Loudon 2012; Every 1980).
Assuming plane wave solutions to Eq. 2 of the form
\[ u = e^{i(k \cdot r - \omega t)} \], where \( r \) is the position vector, and \( k \) and \( \omega \) are, respectively, the phonon wavevector and angular frequency, yields the secular equation
\[ |\Gamma_{ik} - \rho^2 \delta_{ik}| = 0, \tag{3} \]
where \( \Gamma_{ik} = \frac{C_{ijkl} \rho^2}{\rho^2} n_i n_j \) is the Christoffel matrix, \( n_i \) and \( n_j \) are direction cosines, and \( \delta_{ik} \) is the Kronecker delta (Hayes and Loudon 2012).

For monoclinic symmetry the elastic constants tensor takes the form (Nye 1985),
\[ C_{ij} = \begin{bmatrix}
    C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\
    C_{12} & C_{22} & C_{23} & 0 & C_{25} & 0 \\
    C_{13} & C_{23} & C_{33} & 0 & C_{35} & 0 \\
    0 & 0 & 0 & C_{44} & 0 & C_{46} \\
    C_{15} & C_{25} & C_{35} & 0 & C_{55} & 0 \\
    0 & 0 & 0 & C_{46} & 0 & C_{66}
\end{bmatrix}, \tag{4} \]

Here we used the standard monoclinic orientation with \( a \neq b \neq c \) with the unique \( b \)-axis and \( \beta \neq 90^\circ \). Figure 2 shows the orientation for a monoclinic biotite structure. Voigt notation has been introduced to reduce the number of subscripts on the elastic constants from four to two by replacing each of the couples \( ij \) and \( kl \) with a single subscript via the scheme: 11 \( \rightarrow \) 1; 22 \( \rightarrow \) 2; 33 \( \rightarrow \) 3; 23, 32 \( \rightarrow \) 4; 13, 31 \( \rightarrow \) 5; and 12, 21 \( \rightarrow \) 6 (Malgrange et al. 2014).

For elastic waves propagating in the \( ac \) plane (010) at angle \( \theta \) to the crystallographic \( c \)-axis, \( n_x = \sin \theta \), \( n_y = 0 \), and \( n_z = \cos \theta \), and Eq. 3 becomes for the pure transverse (T) mode,
\[ C_{eff} = C_{66} \sin^2 \theta + C_{44} \cos^2 \theta + 2C_{46} \sin \theta \cos \theta, \tag{5} \]
and
\[ C_{eff}^{\pm} = \frac{1}{2}(-b \pm \sqrt{b^2 - 4c}), \tag{6} \]
where,
\[ b = -[\sin^2 \theta (C_{11} + C_{55}) + 2 \sin \theta \cos \theta (C_{15} + C_{35}) + \cos^2 \theta (C_{33} + C_{55})], \]
and
\[ c = \sin^4 \theta (C_{11}C_{55} - C_{15}^2) + 2 \sin^3 \theta \cos \theta (C_{11}C_{55} - C_{13}C_{15}) + \sin^2 \theta \cos^2 \theta (C_{11}C_{33} - C_{13}^2 + 2C_{15}C_{35} - 2C_{13}C_{55}) + 2 \sin \theta \cos^3 \theta (C_{33}C_{15} - C_{13}C_{35}) + \cos^4 \theta (C_{33}C_{55} - C_{35}^2), \]
with effective elastic moduli \( C_{eff} = \rho v^2 \). The “+” term in Eq. 6 refers to the quasi-longitudinal (QL) mode and the “−” term refers to the quasi-transverse (QT) mode.

For propagation in the \( bc \) crystallographic plane (100), the effective moduli are roots of a cubic equation having the form
\[ C_{eff}^3 - aC_{eff}^2 + \beta C_{eff} - \gamma = 0, \tag{7} \]
where
\[ a = [(C_{66} + C_{22}) \sin^2 \theta + (C_{55} + C_{33}) \cos^2 \theta + C_{44}], \]
\[ \beta = \sin^4 \theta (C_{44}C_{66} + C_{22}C_{44} + C_{22}C_{66} - C_{46}^2) + \sin^2 \theta \cos^2 \theta (C_{44}C_{66} - C_{23}^2 - C_{25}^2 - 2C_{23}C_{44} - 2C_{46}C_{25} + C_{35}) + C_{44}C_{55} + C_{33}C_{66} + C_{22}(C_{33} + C_{55}) - C_{46}^2 \] + \cos^4 \theta (C_{33}C_{44} - C_{35}^2 + C_{33}C_{55} + C_{44}C_{55}),
and
\[ \gamma = [\sin^6 \theta (C_{22}C_{44}C_{66} - C_{22}C_{46}^2) + \sin^4 \theta \cos^2 \theta (2C_{22}C_{35}C_{46} + C_{22}C_{44}C_{55}) + 2C_{22}C_{33}C_{66} - C_{25}^2C_{44} - C_{23}^2C_{66} + 2C_{23}C_{25}C_{46} + 2C_{23}C_{25}C_{46} - 2C_{44}C_{23}C_{66}) + \cos^2 \theta \sin^2 \theta (C_{33}C_{55}C_{22} - C_{35}C_{22} - C_{33}C_{46} + C_{33}C_{44}C_{66}) - C_{25}C_{33} - C_{23}C_{55} + 2C_{25}C_{35}C_{44} - 2C_{25}C_{33}C_{46} + 2C_{25}C_{23}C_{35} + 2C_{23}C_{35}C_{46} - 2C_{23}C_{44}C_{55}) + \cos^6 \theta (C_{44}C_{55}C_{33} - C_{35}^2C_{44}), \]
where \( \theta \) is again the angle between the \( c \)-axis and the phonon propagation direction.

The roots of Eq. 7 are known from the theory of algebraic equations (Mensch and Rasolofosaon 1997) and are given by
\[ M' = X^i + \frac{\alpha}{3}, \quad i = 1, 2, 3 \]
where
\[ X^i = 2\sqrt{R} \cos \left( \frac{\phi}{3} + (i - 1) \frac{2\pi}{3} \right), \quad i = 1, 2, 3, \]
with
\[ R = \sqrt{\left( \frac{1}{3} \left( \alpha^2 - \beta \right) \right)^3}, \]
and
\[ \phi = \arccos \left( \frac{2\alpha^3 - 3\alpha \beta + \gamma}{2R} \right). \]
Experimental details

Samples

General physical characteristics

The biotite samples used in this study were natural crystals deliberately selected to have a range of colours to maximize the likelihood that they possessed substantially different levels of major cations Fe and Mg. Platelets with areas of ~ 1 cm² and thicknesses of a few hundred μm were cleaved from these larger bulk samples to allow loading onto the sample stage and to expose a pristine surface for Brillouin light scattering experiments. For the purposes of comparison, two muscovite samples were also analyzed.

Chemical composition

Chemical analysis was carried out on fragments mounted in epoxy cement with the {001} cleavage plane orientated vertically and polished to a final grade of 0.25 micron using diamond abrasive. The samples were carbon coated and examined initially using a JEOL JSM-7100F Scanning Electron Microscope (SEM). Reconnaissance chemical analysis by energy dispersive x-ray spectroscopy (Thermo™) allowed us to confirm the identification of the mica species and identify potential sites for analysis by electron microprobe.

Following SEM investigation the samples were analysed using a JEOL JXA-8230 Electron Probe Microanalyzer (EPMA) operating at an accelerating voltage of 15kV, beam current of 20nA and beam diameter of 5 microns in wavelength dispersive (WDS) mode. The $K_{\alpha}$ emission lines were counted using a TAP diffracting crystal for Si, Al, Mg, and Na, a LIFH crystal for Fe, Ti and Mn, a PETL crystal for K, Ca, and Cl and a LDE1 crystal for F. Counts were collected for the emission peak and for positions on both the low and high wavelength side of the peak. Total background counting time was the same as that for the emission peak. The following standards were used: Si, Na albite; Al, pyrope; K K-feldspar; Ca, Mg diopside; Fe almandine; Ti rutile; Mn rhodonite; Cl turgutite; F apatite. A secondary standard (Astimex biotite) was analysed intermittently to test for instrument drift.

Estimated detection limits (3σ, weight percent) for those elements expected to be present in trace to minor quantities are as follows: Mn, Ti 0.015; Na 0.02, Ca 0.006; Cl 0.01; F 0.07. Table 1 presents the mean of the analyses for each sample as weight percent oxide recalculated to 22 oxygen atoms and assigned to the tetrahedral (T), octahedral (O) or large cation (X) sites. The hydroxyl content (apfu) was estimated by difference on the assumption of full occupancy of the OH, F, Cl site. The number of analyses per sample was as follows: Muscovite #2, one, Biotite #1, six, and ten analyses for each of Biotite #3, #2 and Muscovite #1. With the exception of Muscovite #2, for which we have no information, the samples show some inhomogeneity. This was assessed by comparing the observed variation in chemistry with the expected variation based on microprobe counting statistics. The magnitude of inhomogeneity is, however, much smaller than the differences in chemistry among the samples.

Refractive indices

Figure 2 shows the optical orientation of biotite, with the crystallographic $b$ axis chosen coincident with the two fold symmetry axis. Refractive indices of the biotite samples were obtained using the Becke line test (Nesse 2012). Polarized light was provided by a Nikon Eclipse i50 Pol polarizing light microscope and Cargille optical liquids of known refractive indices and graduated at intervals of 0.002 were used as immersion liquids. Measurements of refractive indices $\gamma$ and $\beta$ were made on sample fragments that were placed on the perfect {001} cleavage. The remaining refractive index $\alpha$ was determined by mounting each sample on a spindle stage with cleavage plane perpendicular to the stage surface. Refractive index values determined using this approach are presented in Table 2 and are considered accurate to ± 0.001.

Density determination

Mass densities for the biotite samples used in this work were required to determine elastic constants. The equation $\rho = Ax^b + C$, with $A = -0.141$, $B = -0.523$, and $C = 3.085$, was found to yield a good empirical fit to published density versus $x = [\text{Fe}] / [\text{Mg}]$ data for biotites of known composition (Coats and Fahey 1944; Bilgrami 1956; Hutton 1947; Larsen et al. 1938; Nockholds and Richey 1939; Pagliani 1940). This was used, together with the composition data obtained from electron probe microanalysis, to estimate the density for the samples of this work. Figure 3 shows the fitting results with $\chi^2$ quoted in the legend. The uncertainty in density determined using this approach is ~ 5%. It is important to note that the empirical equation above should not be used to estimate the density of a biotite for which [Fe]/[Mg] lies outside the range of those of the samples studied in present work as it may yield inaccurate or unphysical values, particularly for small [Fe]/[Mg] values.

The density of muscovite was taken as fixed and set equal to the average of two previously published values: $(2832 + 2844)/2kg \cdot m^{-3} = 2838 \text{ kg} \cdot m^{-3}$ (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993).
Brillouin light scattering apparatus

Brillouin spectra were obtained under ambient conditions utilizing a 180° backscattering geometry. P-polarized light of wavelength $\lambda_i = 532$ nm and power of 60 mW from a Nd:YVO$_4$ single mode laser was incident on the target sample at angles $5^\circ \leq \theta_i \leq 75^\circ$, corresponding to probed phonon propagation directions ranging from $\sim 3^\circ$ to $\sim 37^\circ$ from the crystallographic c-axis. Focusing of incident light onto the sample and collection of scattered light was accomplished using a high-quality anti-reflection-coated camera lens of focal length $f = 5$ cm and $f/# = 5.6$. After exiting this lens, the scattered light, on which no polarization analysis was performed, was processed by a spatial filter (40-cm lens, 450 μm-diameter pinhole, and 20 cm lens) and subsequently frequency-analyzed by an actively stabilized 3+3 pass tandem Fabry-Perot interferometer (JRS Scientific Instruments). The free spectral range of the interferometer was set to 40 GHz and the finesse was $\sim 100$. The light transmitted by the interferometer was incident on a pinhole of diameter 700 μm and detected.
by a low-dark count rate ($\ll 1 \text{s}^{-1}$) photomultiplier tube where it was converted to an electrical signal and sent to a computer for storage and display. A schematic diagram of the apparatus is shown in Fig. 4 and a photograph can be found in Ref. (Andrews 2018).

Table 2  Principal refractive indices of biotites and muscovite determined using the Becke line test

| Sample | Colour | $n_a$ | $n_\beta$ | $n_\gamma$ | $n_{avg}$ | 2V |
|--------|--------|-------|-----------|------------|------------|----|
| Biotite 12.7% Fe, 0.2% Mg | Green | 1.551 | 1.665 | 1.665 | 1.613 | $\ll 20^\circ$ |
| Biotite 8.1% Fe, 4.5% Mg | Green | 1.575 | 1.657 | 1.657 | 1.629 | $\ll 10^\circ$ |
| Biotite 1.1% Fe, 12.3% Mg | Pale Brown | 1.544 | 1.597 | 1.597 | 1.579 | Too small to measure |
| Muscovite 2.1% Fe, 0.5% Mg | Very Pale Brown-Green | 1.543 | 1.567 | 1.618 | 1.576 | $\sim 35^\circ - 40^\circ$ |
| Muscovite 0.5% Fe 0.4% Mg | Pale Brown | 1.558 | 1.603 | 1.610 | 1.590 | – |
| Biotite (Ref. Coats and Fahey (1944)) 5.1% Fe, 0.1% Mg | Green-Grey | 1.570 | 1.640 | 1.640 | 1.620 | – |
| Biotite (Ref. Bilgrami (1956)) 1.0% Fe, 4.0% Mg | – | 1.575 | 1.617 | 1.621 | 1.604 | 30° |
| Biotite (Ref. Hutton (1947)) 2.8% Fe, 3.1% Mg | Dark Brown | 1.57 | 1.64 | 1.64 | 1.620 | – |
| Biotite (Ref. Larsen et al. (1938)) 2.1% Fe, 4.4% Mg | – | 1.586 | 1.643 | 1.643 | 1.623 | 0° - 8° |
| Biotite (Ref. Nockholds and Richey (1939)) 3.4% Fe, 0.1% Mg | Blue-Green | 1.582 | 1.625 | 1.625 | 1.610 | – |
| Biotite (Ref. Pagliani (1940)) 0.2% Fe, 7.4% Mg | Violet-Brown | 1.544 | 1.583 | 1.585 | 1.571 | – |

Fig. 2  a) $a$, $b$ and $c$ are the crystallographic axes, $\beta$ and $\gamma$ are the principal refractive indices. Incident laser beam shown with $\theta_i$ indicating angle from $c$-axis. Not shown principle refractive index $\alpha$. b) Biotite structure (unique $b$ axis and $\beta \neq 90^\circ$) (Takeda and Ross 1975) viewed down from $b$. Projection of unit cell shown along with the Cartesian coordinate system, $z \parallel c$, $x \parallel a^*$ and $y \parallel b$. Note: $b \parallel b^*$
Results & discussion

Spectra

Figure 5 shows a series of Brillouin spectra collected from the Fe-rich biotite crystal containing 12.7% Fe and 0.2% Mg. Three sets of Brillouin doublets were observed and attributed to T, QT, and QL acoustic modes due to the similarity of the frequency shifts to those of muscovite (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993). The frequency shifts of all of these peaks showed significant variation with angle of incidence, reflecting the expected large elastic anisotropy of biotite. The Brillouin peak intensities also show interesting dependence on $\theta_i$. This is especially true for the QT and QL peaks for which the ratio $I_{QT}/I_{QL}$ changes from essentially zero to a large value over the range of angles probed. Spectra of other samples were qualitatively similar, although the T peaks in the sample with 8.1% Fe and 4.5% Mg were noticeably weaker than for the other samples (see Fig. 1 in Supplementary Materials).

Elastic wave velocities

Figure 6 shows the T, QT, and QL mode velocities in the $ac$ and $bc$ crystallographic planes as measured from the $c$-axis. These velocities were calculated from Eq. 1 using the associated Brillouin peak frequency shifts and, because birefringence effects were negligible (no obvious peak splitting), the average refractive index for each sample (Nesse 2012). For propagation directions near the $c$-axis, the T and QT velocities are relatively low and increase with increasing angle away from the $c$-axis in both the $ac$ and $bc$ planes. The QL mode velocity remains relatively constant for angles close to the $c$-axis and increases for propagation directions greater than $\approx 20 - 25^\circ$. Studies on muscovite (Vaughan and Guggenheim 1986) and phlogopite (Chheda et al. 2014) show a similar dependence of sound velocities on propagation direction over common ranges.
It can also be seen from Fig. 6 that the elastic wave velocities for biotite, nearly without exception, increase with decreasing Fe concentration (or, equivalently, increasing Mg concentration), and approach those of muscovite for the biotite sample with the lowest Fe concentration. The same type of behaviour was observed in ultrasonic studies on muscovite, phlogopite, and a biotite of unknown composition, where, for nearly all propagation directions for which measurements were made, the velocities for the phlogopites and the biotite were lower than the corresponding velocities for muscovite (Alekandrov et al. 1961). This may be due in part to the relatively large atomic mass of Fe compared to Mg and Al, resulting in a lower vibrational frequency and therefore a lower velocity, but it could also be due to other factors such as differences in chemical bonding.

Fig. 5 Brillouin spectra of an Fe-rich biotite crystal (12.7% Fe, 0.2% Mg). The probed phonons propagated in the (010) plane. Angles of incidence, $\theta_1$, are indicated on the right side of the graph. The corresponding angles between the crystallographic $c$-axis and the phonon propagation directions, $\theta$, are given on the left side of the graph. T, QT, and QL refer to peaks due to pure transverse, quasi-transverse, and quasi-longitudinal acoustic modes, respectively.

Fig. 6 Quasi-longitudinal (top), quasi-transverse (center), and pure transverse (bottom) mode velocities versus direction (i.e., angle from the crystallographic $c$-axis) in the $ac$ and $bc$ crystallographic planes. ◆ - muscovite 2.1% Fe, 0.5% Mg; □ - muscovite 0.5% Fe, 0.4% Mg; ▼ - biotite 1.1% Fe, 12.3% Mg; ▲ - biotite 8.1% Fe, 4.5% Mg; ◼ - biotite 12.7% Fe, 0.2% Mg. The vertical and horizontal error bars are approximately the size of the symbols.

### Elastic constants

#### Determination of elastic constants

Table 3 and Fig. 7 give the elastic constants for the biotite and muscovite samples of the present work along with values obtained in previous studies. All of the constants for the samples of the present work except $C_{12}$ were obtained using a custom non-linear least-squares fitting routine written in MATLAB and based on the Levenberg-Marquardt algorithm. This routine executed a global fit of the expressions for $C_{eff} = \rho v_{m}^{2}(\theta, C_{ij})$, where $m = T, QT,$ and QL, given in Sect. 2.2 to experimental data by minimizing the square of the difference between experimental and calculated $\rho v_{m}^{2}(\theta, C_{ij})$ values for all three modes and measured propagation directions in the $ac$ and $bc$ planes simultaneously through adjustment of the $C_{ij}$. Initial guesses of elastic constants were those determined for biotite with assumed hexagonal symmetry and muscovite found in the literature (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993; Aleksandrov et al. 1961). Embedded in the fitting routine was the constraint that the elastic constants, when appropriately combined, satisfy the conditions for elastic stability (i.e., that the elastic energy be positive) for a crystal with monoclinic symmetry (Mouhat and Coudert 2014). These are that the
Table 3  Elastic constants (in GPa) and selected elastic constant ratios for biotite and muscovite obtained in the present work and for biotite, muscovite, and phlogopite obtained in previous studies

| Sample                        | $C_{11}$ | $C_{22}$ | $C_{33}$ | $C_{44}$ | $C_{55}$ | $C_{66}$ | $C_{12}$ | $C_{13}$ | $C_{15}$ | $C_{23}$ | $C_{25}$ | $C_{35}$ | $C_{46}$ | $C_{22}/C_{11}$ | $C_{35}/C_{44}$ | $C_{23}/C_{13}$ |
|-------------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------------|----------------|----------------|
| Biotite                       | 178      | 176      | 42       | 4.4      | 11       | 77       | 24       | 14       | −9.3     | 22       | 27       | 1.8      | −7.7     | 0.99           | 2.50            | 1.57            |
| 12.7% Fe, 0.2% Mg             | ± 5.4    | ± 3.6    | ± 0.3    | ± 0.2    | ± 1.3    | −6.9     | ± 4.6    | ± 5.2    | ± 1.5    | ± 0.9    | ± 3.8    | ± 0.05   | ± 0.30   | ± 1.14         |                 |                 |
| Biotite                       | 183      | 183      | 48       | 7.9      | 16       | 75       | 33       | 21       | −12      | 22       | 27       | −2.7     | −6.2     | 1.00           | 2.02            | 1.04            |
| 8.1% Fe, 4.5% Mg              | ± 5.4    | ± 5.5    | ± 0.6    | ± 0.2    | ± 1.7    | −4.7     | ± 2.1    | ± 4.5    | ± 3.5    | ± 1.3    | ± 2.2    | ± 0.06   | ± 0.15   | ± 0.44         |                 |                 |
| Biotite                       | 178      | 171      | 52       | 12.2     | 17       | 76       | 26       | 28       | −13      | 22       | 22       | −8.5     | −6.2     | 0.96           | 1.39            | 0.78            |
| 1.1% Fe, 12.3% Mg             | ± 5.2    | ± 3.5    | ± 1.2    | ± 0.5    | ± 1.5    | −5.4     | ± 1.6    | ± 5.1    | ± 2.5    | ± 1.9    | ± 3.4    | ± 0.05   | ± 0.08   | ± 0.33         |                 |                 |
| Muscovite                     | 182      | 182      | 66       | 13.8     | 17       | 71       | 40       | 22       | −2.3     | 24       | 18       | −3.8     | 1.3      | 1.00           | 1.23            | 1.09            |
| 2.1% Fe, 0.5% Mg              | ± 4.0    | ± 3.8    | ± 1.1    | ± 0.5    | ± 1.4    | −2.2     | ± 3.3    | ± 2.7    | ± 3.4    | ± 1.7    | ± 2.0    | ± 0.04   | ± 0.09   | ± 0.23         |                 |                 |
| Muscovite                     | 180      | 183      | 56       | 17.3     | 23       | 77       | 26       | 22       | −12      | 19       | 29       | −2.7     | −7.2     | 1.02           | 1.33            | 0.86            |
| 0.5% Fe, 0.4% Mg              | ± 3.6    | ± 3.6    | ± 1.2    | ± 0.5    | ± 1.3    | −1.9     | ± 2.9    | ± 4.6    | ± 4.5    | ± 1.0    | ± 2.2    | ± 0.04   | ± 0.07   | ± 0.28         |                 |                 |
| Muscovite (Composition Unknown)| 181.0    | 178.4    | 58.6     | 16.5     | 19.5     | 72.0     | 48.8     | 25.6     | −14.2    | 21.2     | 1.1      | −5.2     | 0.99           | 1.18            | 0.83            |
| Vaughan and Guggenheim (1986)  | ± 1.2    | ± 1.3    | ± 0.6    | ± 0.6    | ± 0.7    | ± 2.5    | ± 1.5    | ± 0.8    | ± 1.8    | ± 3.7    | ± 0.9    | ± 3.7    | ± 0.67   | ± 0.99         |                 |                 |
| Muscovite (Composition Unknown)| 176.5    | 179.5    | 60.9     | 15.0     | 13.1     | 70.7     | 47.7     | 20.0     | −1.2     | 23.0     | 11.1     | −0.7     | 0.7      | 1.02           | 0.87            | 1.15            |
| McNeil and Grimsditch (1993)  | ± 1.1    | ± 1.3    | ± 0.6    | ± 0.2    | ± 1.2    | ± 1.1    | ± 0.6    | ± 5.3    | ± 0.5    | ± 0.01   | ± 0.07   | ± 0.12   | ± 0.07   | ± 0.12         |                 |                 |
| Phlogopite (DFT-GGA) Chheda et al. (2014) | 181.2    | 184.7    | 62.1     | 13.5     | 20.0     | 67.9     | 47.6     | 12.2     | −15.7    | 12.1     | −4.9     | −1.2     | −5.9     | 1.02           | 1.48            | 0.99            |
| Phlogopite (DFT-LDA) Chheda et al. (2014) | 199.5    | 201.2    | 82.2     | 17.0     | 25.3     | 72.4     | 54.1     | 25.4     | −13.1    | 24.4     | −4.5     | −2.8     | −6.4     | 1.01           | 1.49            | 0.96            |
| Muscovite (DFT-LDA) Militzer et al. (2011) | 194.3    | 188.0    | 91.1     | 25.2     | 30.5     | 71.3     | 68.1     | 43.2     | −14.3    | 39.5     | 1.7      | 1.1      | −0.6     | 1.03           | 1.21            | 0.91            |

aElastic constant is zero for hexagonal symmetry.

bRatio is unity for hexagonal symmetry.

cUncertainties in ratios calculated by the authors of the present work using standard error formulae.
diagonal elements of the elastic constants tensor, \( C_{ii} \), be greater than zero and that

\[
\begin{align*}
(C_{11} C_{22} C_{33} + C_{15}(-C_{23}^2 + C_{22} C_{33})) \\
- 2C_{12} C_{23} C_{25} C_{35} - C_{12}^2 C_{35}^2 + C_{11} C_{22} C_{35} \\
+ 2C_{15} C_{12} C_{23} C_{25} - C_{12} C_{25} C_{33} - C_{13} C_{22} C_{35} \\
+ C_{12} C_{25} C_{35} + C_{11} C_{23} C_{55} + C_{12} C_{33} C_{55} \\
- C_{11} C_{22} C_{33} C_{55} + C_{13}(-C_{25}^2 + C_{22} C_{35}) \\
+ 2C_{12} C_{13} (C_{25} - C_{23} C_{35} - C_{23} C_{55}) (C_{46} - C_{44} C_{66}) > 0,
\end{align*}
\]

(8)

\[
\begin{align*}
C_{44}(-C_{13} C_{25} C_{33} + C_{15} C_{23} - C_{22} C_{33}) \\
+ 2C_{11} C_{23} C_{25} C_{35} + C_{12} C_{35}^2 - C_{11} C_{22} C_{35} \\
- 2C_{15} (C_{13} C_{23} C_{25} - C_{12} C_{25} C_{33} - C_{13} C_{22} C_{35}) \\
+ C_{12} C_{25} C_{35} - C_{11} C_{23} C_{55} - C_{12} C_{33} C_{55} \\
+ C_{11} C_{23} C_{33} C_{55} + C_{15} (C_{25}^2 - C_{22} C_{35}) \\
+ 2C_{12} C_{13} (-C_{25} C_{35} + C_{23} C_{55}) > 0,
\end{align*}
\]

(9)

\[
\begin{align*}
- C_{44} (C_{13}^2 - C_{25}^2) - 2C_{12} C_{13} C_{23} + C_{12} C_{33} \\
+ C_{11} (C_{23}^2 - C_{22} C_{33}) > 0,
\end{align*}
\]

(10)

\[
\begin{align*}
C_{11} C_{22} C_{33} - C_{13}^2 C_{23} C_{33} + 2C_{12} C_{13} C_{23} \\
- C_{11} C_{23}^2 C_{23} - C_{12} C_{33}^2 > 0,
\end{align*}
\]

(11)

and

\[
C_{11} C_{22} - C_{12}^2 > 0.
\]

(12)

In all cases, the quality of the fits was excellent as can be seen for Fe-rich and Fe-poor biotite in Fig. 8 (see also Fig. 2 of Supplemental Materials). The standard error of regression (SER) for the highest- and lowest-quality least-squares fits have been calculated as points of reference. The best fit (SER = 1.28 GPa) was obtained for Fe-rich biotite (12.7% Fe, 0.2% Mg) and the lowest-quality fit (SER = 1.69 GPa) was obtained for the biotite sample with 8.1% Fe and 4.5% Mg. Figure 3 in the Supplemental Materials shows a representative series of residual plots for the Fe-poor (1.1% Fe, 12.3% Mg) sample. The uncertainties in the elastic constants were estimated by averaging the difference between individual best-fit constants and corresponding members of second and third sets of elastic constants obtained by increasing and decreasing, respectively, all experimental \( \rho \nu^2_m(\theta, C_f) \) values by 2% and re-executing the fitting routine.

\( C_{12} \) could not be determined using the least-squares fitting procedure described above because it does not appear in the expressions for \( C_{eff} \) given in Sect. 2.2. Estimates of this constant, however, were obtained by approximating the symmetry of biotite and muscovite as hexagonal, in which case \( C_{12} = C_{11} - 2C_{66} \). It is emphasized that this expression is used here only as a means to estimate \( C_{12} \) and is not expected to hold in general for the samples of the present study due to the true symmetry being monoclinic.

Table 4 presents Voigt and Reuss bulk and shear moduli (\( K_V \) and \( G_V \)) in GPa and universal elastic anisotropy index (Ranganathan and Ostoja-Starzewski 2008) for biotite and muscovite obtained in the present work and for biotite, muscovite, and phlogopite obtained in previous studies.

### Table 4

| Sample                          | \( K_V \)         | \( K_R \)         | \( G_V \)         | \( G_R \)         | \( A^U \)        |
|---------------------------------|-------------------|-------------------|-------------------|-------------------|------------------|
| Biotite - 12.7% Fe, 0.2% Mg     | 57.3 ± 4.2        | 35.3 ± 2.8        | 41.0 ± 3.0        | 9.4 ± 0.8         | 23.3 ± 2.4       |
| Biotite - 8.1% Fe, 4.5% Mg      | 63.0 ± 4.3        | 42.0 ± 2.9        | 43.0 ± 3.0        | 16.0 ± 1.1        | 14.9 ± 1.3       |
| Biotite - 1.1% Fe, 12.3% Mg     | 61.4 ± 4.1        | 43.0 ± 2.9        | 42.9 ± 2.7        | 19.4 ± 1.2        | 12.5 ± 1.0       |
| Muscovite - 2.1% Fe, 0.5% Mg    | 66.9 ± 5.0        | 43.3 ± 3.2        | 52.0 ± 3.9        | 25.0 ± 1.9        | 12.0 ± 1.1       |
| Muscovite - 0.5% Fe, 0.4% Mg    | 61.0 ± 4.8        | 45.8 ± 3.6        | 46.9 ± 3.7        | 26.9 ± 2.1        | 10.1 ± 1.0       |
| Muscovite (Comp Unknown)        | 67.7 ± 1.5        | 48.7 ± 1.1        | 43.1 ± 0.94       | 27.6 ± 0.6        | 9.2 ± 0.2        |
| Muscovite (Comp Unknown)        | 66.5 ± 2.6        | 49.0 ± 1.8        | 42.0 ± 1.6        | 23.0 ± 0.9        | 10.5 ± 0.5       |
| Phlogopite (DFT-GGA)            | 61.0 ± 4.7        | 43.0 ± 8.2        | 43.3 ± 1.3        | 24.1 ± 2.9        | 10.4 ± 1.2       |
| Phlogopite (DFT-GGA)            | 86.1              | 73.1              | 47.0              | 38.2              | 7.3              |
| Phlogopite (DFT-LDA)            | 77.2 ± 5.6        | 62.9 ± 7.2        | 47.6 ± 1.1        | 31.2 ± 2.0        | 8.9 ± 0.6        |
| Muscovite (DFT-LDA)             | 68.8              | 50.1              | 43.0              | 31.0              | 8.3              |

Monoclinic character

The non-zero values of \( C_{15}, C_{23}, C_{35}, \) and \( C_{46} \), along with the fact that \( C_{44} \neq C_{55} \), and \( C_{13} \neq C_{23} \) (see Table 3) reaffirm the monoclinic character of biotite. \( C_{15}, C_{23}, C_{35}, \) and \( C_{46} \) all differ significantly from zero with \( C_{15} \) and \( C_{46} \) having negative values for each of the three biotites and \( C_{35} \) being negative for two of the samples. Interestingly,
while $C_{11} \approx C_{22}$ for each of the biotite samples, $C_{44}$ is considerably smaller than $C_{55}$ for all three, with the ratio $C_{55}/C_{44}$ decreasing from about 2.5 to 1.4 as the Fe content decreases. Similar behaviour is seen for $C_{23}/C_{13}$, which ranges from $\sim 1.6$ for Fe-rich biotite to $\sim 0.8$ for biotite with low Fe content. Collectively, these results indicate a relatively high degree of elastic anisotropy, ostensibly concentrated in the shear properties, and highlight the deficiencies associated with the previously-invoked approximation of hexagonal symmetry (Aleksandrov et al. 1961).

**Dependence on primary cation concentration**

As can be seen in Table 3 and Fig. 7, the dependences of biotite elastic constants on primary cation concentration are varied. $C_{11}, C_{22}, C_{66},$ and $C_{23}$ are nearly independent of Fe (or Mg) concentration, taking on very similar values for all three samples of the present work (ranges: $C_{11} \sim 3\%$, $C_{22} \sim 7\%$, $C_{66} \sim 3\%$, $C_{23} \sim 0\%$). The remaining constants show significant dependence on [Fe] (see Fig. 9). $C_{33}, C_{44}, C_{55},$ and $C_{13}$ all increase with decreasing Fe concentration, while $C_{15}$ and $C_{35}$ decrease with decreasing Fe concentration (see Table 5). $C_{25}$ has the same value for the two biotites of higher Fe concentration, with the value for the sample with the smallest Fe concentration being lower by $\sim 15\%$. In contrast, $C_{46}$ is lowest for the Fe-rich biotite and takes on a common, $\sim 20\%$ higher value for the two samples of lower Fe concentration.

The composition information in Table 1 shows that, by far, the most significant sample-to-sample difference among the biotite crystals is in Fe and Mg content, suggesting that the behaviour of the elastic constants is a manifestation of the structural response of the crystal to Fe–Mg substitution in the octahedral sheets, a well-known and common substitution mechanism in biotite. The structural changes that occur as a result of this substitution are functions of cation radius and include rotation of tetrahedra and flattening of octahedra in the tetrahedral and octahedral sheets, respectively (Cibin...
et al. 2005; Hewitt and Wones 1975; Tombolini et al. 2002).

Elastic constants $C_{11}$, $C_{22}$, and $C_{33}$ will be relatively insensitive to these changes due to the strong intralayer bonding within a tetrahedral–octahedral–tetrahedral (TOT) sheet. In contrast, the weak interlayer bonding between adjacent TOT sheets will, in general, result in the remaining constants displaying a stronger dependence on Fe concentration. With the exception of $C_{23}$, this is precisely the behaviour that is observed.

**Table 5**

| Fit Parameter | $C_{11}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{45}$ | $C_{46}$ | $C_{55}$ |
|---------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| $C_{Fe-Poor}$ | $C_{0-Poor}$ | $C_{Fe-Poor}$ | $C_{0-Poor}$ | $C_{Fe-Poor}$ | $C_{0-Poor}$ | $C_{Fe-Poor}$ | $C_{0-Poor}$ | $C_{Fe-Poor}$ |
| $C_{Fe-Poor}$ | 0.0167 | 0.0572 | 0.0345 | 0.0444 | 0.0249 | 0.0208 | -0.1060 | 0.0168 |
| $C_{0-Poor}$ | 1.032 | 1.091 | 1.065 | 1.0747 | 1.062 | 0.991 | 1.150 | 0.995 |

**Elastic stability**

Figure 10 shows the value of the left-hand side of stability conditions Eqs. 8–12, each normalized to the corresponding value at lowest Fe concentration, as a function of Fe concentration. While the values of the left-hand sides of Eqs. 11 and 12 are nearly independent of Fe concentration, those of Eqs. 8–10 exhibit a dramatic decrease with increasing Fe concentration, being reduced, at the highest Fe concentration, to $\sim 10\%$ of the respective low-Fe concentration values. Given that violation of one or more of the stability conditions results in an unstable crystal, the latter behaviour suggests that biotite becomes progressively less stable with increasing Fe content in the octahedral sheet. The same conclusion is reached when one considers the stability condition that the diagonal components of the elastic constants tensor be positive definite. $C_{11}$, $C_{22}$, and $C_{33}$ are nearly independent of [Fe], but $C_{33}$, $C_{44}$, and $C_{55}$ show relatively large or very large decreases with increasing Fe concentration (see Table 3 and Fig. 9).

The decrease in elastic stability with increasing Fe concentration is likely related to the accompanying increase in average octahedral cation radius. In fact, synthetic trioctahedral micas of the form $KFe_{2+}AlSi_3O_{10}(OH)_2$ with octahedral cation radius greater than that of Fe$^{2+}$ are not stable, the instability being attributed to the inability of the tetrahedral layer to further expand by rotation of tetrahedra, resulting in smaller tetrahedral layers on a larger octahedral layer (Hazen and Wones 1972). A second study shows that the stability is limited not only by tetrahedral rotation angle, but also by the absolute size of the octahedra (Toraya 1981). In the $KFe_{2+} AlSi_3O_{10}(OH)_2 - KFe_{2+}AlSi_3O_{10}(OH)_2$ system, the misfit between the tetrahedral and octahedral sheets decreases by substitution of large Fe$^{2+}$ or Mn$^{2+}$ ions for Mg$^{2+}$ ions. This induces variations of shared edge lengths in edge-shared octahedra which, in turn, increases the mutual repulsion between octahedral cations, resulting in a corresponding decrease in elastic stability (Toraya 1981). Previous studies have also shown that annite, an Fe-rich biotite, is much less stable than the Fe-poor biotite phlogopite (Eugster and Wones 1962). Also consistent with this argument is that Mg silicates have, in general, a higher melting point than their Fe analogues (Gower 1957). The results obtained in the present study are consistent with those of the above works and also show that the elastic stability exhibits a progressive decrease from Fe-poor (Mg-rich) biotite to Fe-rich (Mg-poor) biotite.
Comparison to theory

Due to the similarity in compositions, the elastic constants of the Fe-poor (Mg-rich) biotite sample can be compared to those of phlogopite obtained from first-principles calculations based on density functional theory (Chheda et al. 2014). As seen in Table 3 and in Fig. 7, most of the elastic constants for Fe-poor biotite are within ≤10% of the corresponding values obtained for phlogopite using the generalized gradient approximation (GGA) or the local density approximation (LDA). $C_{11}, C_{22}, C_{33}, C_{44},$ and $C_{55}$ show better agreement with values obtained using the GGA, while constants $C_{66}, C_{13}, C_{15}, C_{23},$ and $C_{46}$ compare very well with values obtained using the LDA. Experimental values of $C_{25}$ and $C_{35}$ agree neither with the GGA nor the LDA values. It is also interesting to note that the ratios $C_{22}/C_{11}, C_{55}/C_{44},$ and $C_{23}/C_{13}$ for phlogopite obtained from the GGA and LDA calculations are nearly identical to one another and, furthermore, are consistent with those for the Fe-poor biotite (see Table 3). Moreover, $C_{33}, C_{44},$ and $C_{55}$ for the Fe-poor biotite are smaller than the corresponding values for phlogopite obtained using the GGA, while $C_{15}$ for the Fe-poor biotite is larger than the LDA-calculated value for phlogopite. These behaviours (i.e., $C_{ij}^{Fe-poor} \leq C_{ij}^{Phlog}, i = 3, 4, 5,$ and $C_{ij}^{Fe-poor} \leq C_{ij}^{Phlog}$) are as would be expected given the systematic dependence (strictly increasing or strictly decreasing) of these constants on Fe concentration as demonstrated in the present work, and the fact that elastic constants determined using the GGA and LDA tend to represent lower and upper bounds on the $C_{ij}$, respectively. We note that our results in Table 3 also indicate that $C_{13}$, like $C_{33}, C_{44},$ and $C_{55}$, is a strictly decreasing function of [Fe] and while its behaviour does not mimic that of these other constants in the sense that $C_{13}^{Fe-poor} \leq C_{13}^{Phlog}$ calculated using the GGA, the value of $C_{13}^{Phlog}$ obtained using the LDA is $\sim 0.9 \times C_{13}^{Fe-poor}$.

The first-principles calculations cited above yield an elastic constants tensor for trioctahedral phlogopite that is similar to that of dioctahedral muscovite, leading the authors to conclude that the elastic properties of micas are rather insensitive to octahedral site chemistry (Chheda et al. 2014). While it is
true that the tensors are similar, the systematic changes with Fe concentration of several of the biotite elastic constants in the present work suggest that the octahedral site chemistry does in fact play an important role in determining the elastic properties of these micas.

Comparison to muscovite

The biotite elastic constants can be compared to those of muscovite determined in the present and previous studies (see Table 3 and Fig. 7) (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993). $C_{11}$, $C_{22}$, and $C_{33}$ values for biotites are very similar to those for muscovites. This is not unexpected because, for both of these mica subgroups, the intralayer bonding is strong and the layers are composed of many of the same types of atoms arranged in a like fashion. $C_{22}$ also displays this behaviour, although the reason for its similarity to the corresponding value for muscovite is not obvious. The values of $C_{33}$, $C_{44}$, and $C_{55}$ approach those of muscovite as Fe concentration decreases (or, equivalently, Mg concentration increases). The same general behaviour is observed for concentration decreases (or, equivalently, Mg concentration increases). The same general behaviour is observed for $C_{11}$. It is difficult to make meaningful comparisons for $C_{15}$, $C_{25}$, $C_{35}$, and $C_{46}$ because of the very large variation in the values of these constants for muscovite.

The elastic anisotropy within the basal cleavage plane of biotite can be compared to that for muscovite via the ratios $C_{22}/C_{11}$ and $C_{55}/C_{44}$—both of which would be equal to unity if the basal plane displayed elastic isotropy. As Table 3 shows, for all biotite and muscovite samples, $C_{22}/C_{11} \approx 1.0$. In contrast, $C_{55}/C_{44}$ differs substantially from this value, being largest for Fe-rich biotite (2.5) and approaching values similar to those for muscovite as Fe content decreases. This result indicates that the basal plane anisotropy of Fe-rich biotite is strongest for the shear properties and is considerably higher than that of muscovite and decreases with decreasing Fe content in the octahedral sheet (Vaughan and Guggenheim 1986; McNeil and Grimsditch 1993).

Implications

Brillouin light scattering spectroscopy was used to probe the elastic properties of natural biotite crystals with compositions quantified by electron probe microanalysis. The systematic dependence of elastic wave velocities, elastic stiffness constants, elastic stability, and basal plane anisotropy on iron content suggests that biotite elasticity is a function of octahedral site chemistry and provides a means to estimate the elastic properties of most biotite compositions with known iron or magnesium content. Moreover, the overall agreement between the experimentally determined elastic constants of a Mg-rich biotite and those for phlogopite obtained from first-principles calculation based on density functional theory suggests that the latter approach holds promise in describing the elastic properties of biotites.

Supplementary Information

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Data Availability

Additional data and code available upon request.

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