Elasticity of calcium and calcium-sodium amphiboles

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ARTICLE INFO

ABSTRACT

Measurements of single-crystal elastic moduli under ambient conditions are reported for nine calcium to calcium-sodium amphiboles that lie in the composition range of common crustal constituents. Velocities of body and surface acoustic waves measured by Impulsive Stimulated Light Scattering (ISLS) were inverted to determine the 13 moduli characterizing these monoclinic samples. Moduli show a consistent pattern: $C_{33} > C_{22} > C_{11}$ and $C_{23} > C_{12} > C_{13}$ and $C_{44} > C_{55} \sim C_{66}$ and for the uniquely monoclinic moduli, $|C_{35}| \gg C_{46} \sim |C_{25}| > |C_{15}| \sim 0$. Most of the compositionally-induced variance of moduli is associated with aluminum and iron content. Seven moduli ($C_{11}\ C_{12}\ C_{13}\ C_{22}\ C_{44}\ C_{55}\ C_{66}$) increase with increasing aluminum while all diagonal moduli decrease with increasing iron. Three moduli (C_{11}, C_{13} and C_{44}) increase with increasing sodium and potassium occupancy in A-sites. The uniquely monoclinic moduli ($C_{15}\ C_{25}$ and C_{35}) have no significant compositional dependence. Moduli associated with the a^* direction ($C_{11}\ C_{12}\ C_{13}\ C_{55}$ and C_{66}) are substantially smaller than values associated with structurally and chemically related clinopyroxenes. Other moduli are more similar for both inosilicates. The isotropically averaged adiabatic bulk modulus does not vary with iron content but increases with aluminum content from 85 GPa for tremolite to 99 GPa for pargasite. Increasing iron reduces while increasing aluminum increases the isotropic shear modulus which ranges from 47 GPa for ferro-actinolite to 64 GPa for pargasite. These results exhibit far greater anisotropy and higher velocities than apparent in earlier work. Quasi-longitudinal velocities are as fast as ~9 km/s and (intermediate between the a^*- and c-axes) are as slow as ~6 km/s. Voigt-Reuss-Hill averaging based on prior single crystal moduli resulted in calculated rock velocities lower than laboratory measurements, leading to adoption of the (higher velocity) Voigt bound. Thus, former uses of the upper Voigt bound can be understood as an *ad hoc* decision that compensated for inaccurate data. Furthermore, because properties of the end-member amphiboles deviate substantially from prior estimates, all predictions of rock velocities as a function of modal mineralogy and elemental partitioning require reconsideration.

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1. Introduction

Amphiboles are abundant in crustal igneous and metamorphic rocks. They exhibit a wide range of compositions as a result of extensive solid solution behavior, accommodating all of the abundant cation species (silicon, aluminum, magnesium, iron, calcium, sodium, and potassium). The structure also contains ~2 wt% bound water. When subducted, dehydration reactions in rocks containing amphiboles release water at depth that probably affects the evolution of magma in arc volcanism and is likely associated with intermediate and deep earthquakes (Hacker et al., 2003a) as well as seismic tremor/slow slip (Audet et al., 2010).

Since amphiboles are ubiquitous, the description of the crustal seismic structure requires characterization of their elastic properties (*e.g.* Christensen and Mooney, 1995; Christensen, 1996; Hacker et al., 2003b; Barberini et al., 2007; Tatham et al., 2008; Llana-Funez and Brown, 2012; Ji et al., 2013; Selway et al., 2015). However, knowledge concerning their single-crystal elasticity and compositional dependences has remained elusive. In the pioneering work that continues to be cited, Aleksandrov and Ryzhova (1961a) reported single crystal elastic moduli for two "hornblendes" of unspecified composition based on only slightly over-determined sets of ultrasonic velocity measurements on megacrysts under ambient conditions. As previously demonstrated in studies of feldspars (Brown et al., 2006, 2016; Waeselmann et al., 2016), results from these early studies have proven to be systematically in error.

That the early ultrasonic results under-estimate velocities most likely was a result of open cleavage surfaces and cracks. Also

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contributing was an inadequate sampling of velocities as a function of propagation direction. Based on the lack of reported chemistry and probable systematic errors, these early results are considered here in the context of having incorrectly influenced various interpretations of crustal seismic structure that were grounded on mineral properties. In particular, in order to better match laboratory measurements, the compensating use of the upper Voigt bound when calculating aggregate rock velocities has been common. In contrast, Watt and O'Connell (1980) demonstrated that, in well-characterized and nearly crack-free samples, velocities in two-phase aggregates fell within the Hashin-Shtrikman bounds which lie between the extremal Voigt and Reuss bounds (see also Watt et al., 1976).

A few determinations of single-crystal elastic properties are available within the broad range of amphibole compositions. Bezacier et al. (2010) gave elastic moduli for a crystal having a composition near the glaucophane end-member. High pressure X-ray cell parameter determinations have been reported for tremolite, pargasite, and glaucophane (Comodi et al., 1991) and for synthetic glaucophane (Jenkins et al., 2010).

Hacker et al. (2003b) compiled available (isotropically averaged) elasticity data for important rock-forming minerals including amphiboles. They excluded the Aleksandrov and Ryzhova (1961a) moduli as probably being in error and relied on the Christensen (1996) rock velocity measurements to estimate properties of an average crustal "hornblende." To constrain properties of other end-member compositions, they used bulk moduli from the Holland and Powell (1998) thermodynamic database plus the Comodi et al. (1991) compression measurements. Although an isothermal bulk modulus can be inferred from pressure-induced strains, the shear modulus, necessary to estimate body wave velocities, cannot be determined solely from the hydrostatic X-ray data. Instead, Hacker et al. (2003b) estimated shear moduli on the basis of the reported bulk moduli and an assumed Poisson's ratio. They noted that this was a remaining source of uncertainty.

As noted in Section 6.3, an isothermal bulk modulus measured under hydrostatic compression (which is equivalent to the elastic aggregate lower-bound Reuss average) is significantly smaller than the appropriate Voigt-Reuss-Hill or Hashin-Shtrikman bulk modulus used for calculation of seismic velocities. Bulk moduli for some amphiboles given by Hacker et al. (2003b) appear to represent the Reuss bound. They combined lower bound moduli (in some cases) in an upper-bound Voigt average for calculations of velocities in rocks as mixtures of minerals. Thus, the accuracy of their analysis relied on how well the two errors off-set each other.

Here, elastic moduli are reported for nine amphiboles that lie in the range of compositions commonly found in crustal rocks (Schumacher, 2007). Elastic wave velocities (quasi-longitudinal, quasi-transverse and surface acoustic waves – SAW) were measured using Impulsive Stimulated Light Scattering (ISLS) (Abramson et al., 1999). A joint inversion allowed accurate determination of the 13 elastic moduli for these monoclinic minerals. The dependences of moduli on composition are determined through linear regression. From these, relationships to crystal structure and seismic velocities can be explored. Ultimately, more accurate predictions of seismic properties of rocks can be undertaken on the basis of modal mineralogy and elemental partitioning.

2. Amphibole chemistry and structure

As reviewed by Hawthorn and Oberti (2007), the monoclinic ($C2/m$) calcium (including common hornblende) to calcium-sodium amphiboles have a generalized formula of

$$A_{0-1}B_2C_5T_8O_{22}(OH)_2$$
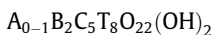
where the A-site is occupied by sodium or potassium or remains vacant and the B-site is occupied by sodium or calcium. The octahedrally coordinated C-sites contain iron (divalent or trivalent), magnesium, or aluminum (designated as ^{vi}Al). The tetrahedral T-sites contain silicon and aluminum (typically up to two aluminum per eight sites, occasionally more, and designated as ^{iv}Al). Other common minor chemical components (Ti, Mn, Co, Cr) are found in size and valence-state appropriate sites. Fluorine and chlorine can substitute for OH^{-1}.

The naming conventions associated with the chemical compositions of calcium and sodium amphiboles (Hawthorne et al., 2012, see also Leake et al., 1997) are illustrated in Fig. 1 using three compositional variables. Although complete solid-solution substitution is possible within this compositional space, several of the stoichiometric compositions are given discrete names. Tremolite is $[]Ca_2$-$Mg_5Si_8O_{22}(OH)_2$ (where the brackets denote the vacant A-site) while winchite has one calcium and one sodium in the B-site. Glaucophane has all sodium in the B-site with coupled substitutions of a trivalent cation in C-sites required to balance charge. Hornblende is both an end-member in Fig. 1 and is a generalized term for calcium amphiboles with intermediate tetrahedral aluminum compositions. In addition, solid-solution substitution of iron for magnesium gives rise to iron end-members for all phases shown in Fig. 1 with ferro- added to the name (e.g. ferro-pargasite).

Amphiboles have I-beam structures of two double tetrahedral chains that are bonded to each other by an octahedral sheet containing five C-site cations. The I-beams are oriented along the c-axis with A-site cations (when present) bonding the I-beams along the a-axis and B-site cations serving to bond I-beams along the b-direction. Clinopyroxenes share similar chemical variations in a structure that is closely related to the amphiboles, both being inosilicates but the pyroxenes have single tetrahedral chains aligned along the c-axis. The general formula of the clinopyroxene is BCT_2O_6 with the B and C sites being equivalent to those found in the amphiboles. End member pyroxenes include diopside ($CaMgSi_2O_6$) hedenbergite ($CaFeSi_2O_6$), and jadeite ($NaAlSi_2O_6$).

Having a wide range of solid-solution substitutions for essentially the same crystal structure, amphiboles provide a natural laboratory for the exploration of chemical controls on elasticity. Variations in elastic moduli are anticipated from changes of ionic sizes and charges, as a result of cation substitutions in the A, B, C and T sites. Comparisons of elasticity between pyroxenes and amphiboles provide further opportunities to explore factors influencing elastic behavior.

3. Sample sources and characterization

The sources, localities (when known), X-ray determined cell parameters, and densities of nine amphiboles are given in Table 1. Individual crystals as 2–3 mm mineral separates were obtained either from disaggregated crystalline rocks or were broken off larger previously collected crystals. Chemical homogeneity of samples from each source was confirmed by application of analytic methods to all individual samples used in the study.

Microprobe analyses for all samples are reported in Table S1 of the supporting materials. A lack of chemical zoning was confirmed in all crystals and the reported analyses are the averages of point determinations across each crystal. Structural formula, based on Probe-AMPH (Tindle and Webb, 1994), are given in Table 2 and are plotted in perspective in Fig. 1. Samples 1 and 2 with ~1 sodium in the B-site are classified as calcium-sodium amphiboles. The remaining seven samples are calcium amphiboles. The chemistry of the glaucophane sample used by Bezacier et al. (2010) and the average calcium amphibole composition reported by Schumacher (2007) are also included in Table 2. As noted by