

1 **Elasticity of Plagioclase Feldspars**

2 J. Michael Brown  
3 Department of Earth and Space Sciences  
4 Box 35-1310  
5 University of Washington  
6 Seattle, WA 98195  
7 brown@ess.washington.edu

8  
9 Ross J. Angel\*  
10 Virginia Tech Crystallography Laboratory  
11 Department of Geosciences  
12 Virginia Tech  
13 Blacksburg VA 24060-0420 USA

14  
15 Nancy Ross  
16 Virginia Tech Crystallography Laboratory  
17 Department of Geosciences  
18 Virginia Tech  
19 Blacksburg VA 24060-0420 USA

20  
21

22

23

24 \*Now at: Department of Geosciences, University of Padova, Via G. Gradenigo 6, I-35131  
25 Padova, Italy.

26

27        **Abstract:**

28        Elastic properties are reported for seven plagioclase feldspars that span compositions from albite  
29        ( $\text{NaSi}_3\text{AlO}_8$ ) to anorthite ( $\text{CaSi}_2\text{Al}_2\text{O}_8$ ). Surface acoustic wave velocities measured using  
30        Impulsively Stimulated Light Scattering and compliance sums from high-pressure X-ray  
31        compression studies accurately determine all 21 components of the elasticity tensor for these  
32        triclinic minerals. The overall pattern of elasticity, and the changes in individual elastic  
33        components with composition can be rationalized on the basis of the evolution of crystal  
34        structures and chemistry across this solid-solution join. All plagioclase feldspars have high  
35        elastic anisotropy;  $a^*$  (the direction perpendicular to the  $b$ - and  $c$ -axes) is the softest direction by  
36        a factor of 3 in albite. From albite to anorthite the stiffness of this direction undergoes the  
37        greatest change, increasing two-fold. Small discontinuities in the elastic components, inferred at  
38        boundaries between the three structural phases ( $C\bar{1}$ ,  $I\bar{1}$ , and  $P\bar{1}$ ), appear consistent with the  
39        nature of the underlying conformation of the framework-linked tetrahedra and the associated  
40        structural changes. Body wave velocities measured plagioclase-rich rocks, reported over the last  
41        five decades, are consistent with calculated Hill-averaged velocities using the current moduli.  
42        This confirms longstanding speculation that previously reported elastic moduli for plagioclase  
43        feldspars are systematically in error. The current results provide greater assurance that the  
44        seismic structure of the mid and lower crust can be accurately estimated on the basis of specified  
45        mineral modes, chemistry, and fabric.

46

47        **Index Terms:** 3620 3909 3924 7205 7220

## 48 1. Introduction

49 Knowledge of the complete elastic properties of the constituent minerals of rocks is a  
50 prerequisite for predicting and interpreting the seismic response of Earth's crust. Plagioclase  
51 feldspars are a dominant mineral group in both the continental and oceanic crust. Both their  
52 isotropic and the anisotropic elastic responses, associated with mineral fabric or (lattice)  
53 preferred orientations (the so-called LPO) are needed for the range of naturally occurring  
54 compositions, at temperatures and pressures appropriate for the crust. However, because they  
55 have triclinic symmetry, 21 individual elastic moduli are necessary to describe their single  
56 crystal properties and, as a consequence, their full elastic tensors have never been previously  
57 determined except for one end-member [Brown *et al.*, 2006]. Here, all moduli at one bar are  
58 reported for seven samples that span plagioclase compositions.

59 Plagioclase feldspars found in crustal rocks have major element compositions that fall along the  
60 anorthite ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) – albite ( $\text{NaAlSi}_3\text{O}_8$ ) join (given here as the anorthite content,  $\text{An}_x$  with  $x$   
61 ranging from 0 to 100), with the exchange of  $\text{Ca}^{2+}$  for  $\text{Na}^+$  coupled to a change in the Al,Si ratio.  
62 The chemistry and phases of crustal feldspars is further discussed in the Auxiliary Materials. All  
63 feldspars have a fully polymerized three-dimensional framework of  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra.  
64 The framework is built up from rings of four tetrahedra that lie approximately perpendicular to  
65 the  $b$ -axis (Figure 1a). These 4-rings are linked to form the “crankshaft” [Megaw, 1970] chains  
66 that extend along the  $a$ -axis and are characteristic of the feldspar structure type (Figure 1b).  
67 Sheets of chains are further linked together along the  $b$ -axis to form the cavities for the extra-  
68 framework cations,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  (Figure 1c). Despite the three-dimensional connectivity of the  
69 tetrahedral framework of feldspars, compression measurements [e.g. Angel *et al.*, 1988; Benusa  
70 *et al.*, 2005], and determinations of the elastic tensor [Brown *et al.*, 2006] have shown that all  
71 feldspars, irrespective of either framework composition or the extra-framework cation, are as  
72 elastically anisotropic as sheet silicates. This anisotropy arises from the topology of the  
73 framework. The “crankshaft” chains (Figure 1b) can be closed up or extended relatively easily  
74 (e.g. Smith and Brown, [1988] page 55) because this can be accomplished by cooperative  
75 rotations of effectively rigid tetrahedra without any deformations of the tetrahedra [Angel *et al.*,  
76 2012; 2013]. As a consequence, changes in the distribution of Al,Si between the tetrahedral sites  
77 has only a small effect on the bulk moduli of plagioclase feldspars [Sochalski-Kolbus *et al.*,  
78 2010].

79 Efforts to connect the seismic response of Earth's interior to the elasticity of its constituents have  
80 involved high-pressure laboratory studies [e.g. *Christensen and Mooney*, 1995]). In the case of  
81 plagioclase-rich rocks, the compositional dependence of compressional wave velocities to 1 GPa  
82 was reported by *Birch* [1961]; additional data at high pressure on essentially mono-mineralic  
83 aggregates (including determinations of shear wave velocities) are reported in [*Simmons*, 1964;  
84 *Liebermann and Ringwood*, 1976; *Seront et al.*, 1993; *Mueller et al.*, 2002]. Application of  
85 pressures greater than 0.2-0.5 GPa is typically assumed sufficient to adequately close cracks so  
86 that measured velocities are representative of the intrinsic mineral elasticity. However, low  
87 aspect ratio cracks may not close under such pressures and velocities may remain systematically  
88 below intrinsic values.

89 Prior measurements of the compressibility of the feldspars (the response to hydrostatic pressure)  
90 (e.g. *Angel* [2004]) are not sufficient to fully determine the elastic modulus or compliance  
91 tensors. Thus, the only primary source of data for the full elastic properties of plagioclase  
92 feldspar crystals as a function of composition is the pioneering one-bar ultrasonic measurements  
93 of twinned megacrysts by *Ryzhova* [1964], and this work has been extensively cited.  
94 Unfortunately, as documented in *Brown et al.* [2006], the data acquisition scheme used by  
95 *Ryzhova* [1964], could not adequately determine all 13 elastic tensor components in the pseudo-  
96 monoclinic samples, nor the values of the additional 8 components that are allowed in crystals  
97 with triclinic symmetry.

98 The elastic properties of a mineral aggregate in which the cracks are fully closed must fall  
99 between the Voigt (upper) and Reuss (lower) bounds that can be calculated from the single-  
100 crystal elastic moduli and compliances. [*Hill*, 1963]. In the absence of microstructure knowledge  
101 (e.g. *Mainprice et al.* [2011]), the Hashin-Shtrikman bounds provide the tightest possible  
102 estimates for aggregate behavior [*Watt et al.*, 1976]. Results in a number of studies  
103 [*Christensen*, 1966; *Liebermann and Ringwood*, 1976; *Seront et al.*, 1993; *Brown et al.*, 2006]  
104 have indicated that moduli reported by *Ryzhova* [1964] might be biased to low values, possibly  
105 as a result of the samples having open cracks. Alternatively, accepting *Ryzhova's* result leads to a  
106 match between measured rock velocities and the calculated Voigt bound [*Seront et al.*, 1993].  
107 For feldspar-rich rocks, this lies well above the Hashin-Shtrikman upper bound. This empirical  
108 correlation indicates that either the rock velocities are in error or that one of the other

109 characteristics of the rock (either the texture or the elastic properties of the constituent phases) is  
110 in error.

111 The elastic moduli reported here are interpreted in terms of the underlying structural  
112 conformation, changes in composition, and the structural states of plagioclase minerals. These  
113 data provide an ideal opportunity for reassessing the interpretation of measured compressional  
114 and shear wave velocities in feldspar-rich rocks, and also for addressing more general issues of  
115 the elastic response of aggregates. The extreme elastic anisotropy of feldspars, with the Reuss  
116 and Voigt bounds on the shear modulus differing by 30% and the bulk moduli differing by 20%  
117 make them ideal for resolving the question as to whether or not rock properties fall close to the  
118 (Hill) average between the upper and lower bounds and within the tighter Hashin-Shtrikman  
119 bounds recommended by *Watt et al.* [1976].

## 120 **2. Sample sources and characterization**

121 The sources, chemistry, localities, and structural state of seven samples are given in Table S1 of  
122 the Auxiliary Materials. Together with the end-member albite [*Brown et al.*, 2006], the six  
123 additional samples measured in this study were chosen so as to cover the compositional range of  
124 plagioclase feldspars and to represent the variety of structural states ( $C\bar{1}$ ,  $I\bar{1}$ , and  $P\bar{1}$ ) most  
125 commonly found in natural plagioclases. Changes in the patterns of Al,Si order within the  
126 tetrahedra result in symmetry changes that can be identified by changes in the diffraction patterns  
127 [*Bown and Gay*, 1958; *Angel et al.*, 1990]. The degree of Al,Si order can be determined from the  
128 tetrahedral bond lengths determined by structure refinements [*Ribbe*, 1983; *Kroll and Ribbe*  
129 1983; *Salje*, 1985]. The change in the Al,Si ratio away from a simple integer ratio means that  
130 some Al,Si disorder is induced by the chemical substitution away from the end-member  
131 compositions of albite and anorthite. Single-crystal X-ray diffraction data were therefore  
132 collected from one crystal from each sample on a variety of Oxford Diffraction CCD  
133 diffractometers. Full details of the data collections, structure refinements and final refined  
134 structural parameters are reported in the Auxiliary Materials crystallographic information file  
135 (*cif*). In summary, six of the samples are well ordered and are thus “low plagioclases” with  
136 thermodynamic and elastic properties typical of plagioclases in crustal rocks.  $An_{60}$  is a relatively  
137 disordered “high-plagioclase” [*Kroll and Ribbe*, 1980] on the basis of its unit-cell parameters and  
138 refined structure. TEM observations of the  $An_{48}$  sample confirmed that it is a Bøggild

139 intergrowth, a composite crystal containing coherent lamellae of approximate compositions  $An_{45}$   
140 (symmetry  $C\bar{1}$ ) and  $An_{55}$  (symmetry  $I\bar{1}$ ). In Table 1 cell parameters, unit cell volumes, and  
141 densities (calculated from the chemistry and cell volumes) are given for the samples.

142 Following *Brown et al.* [2006], we chose the following convention to align the non-orthogonal  
143 crystallographic axes with respect to the Cartesian axial system used for the description of the  
144 elastic tensor. The Y-axis is aligned parallel to the crystallographic  $b$ -axis. The X-axis is set in  
145 the  $a^*$  direction (perpendicular to the  $b$ - and  $c$ -axes). The Z-axis is chosen to satisfy a right-  
146 handed coordinate system. This convention is different from that used by *Ryzhova* [1964] who  
147 also set the Y-axis parallel to the  $b$ -axis, but then set the Z-axis parallel to  $c^*$ . Relative to our  
148 system, these coordinates are rotated  $\sim 26^\circ$  about the  $b$ -axis. Although *Ryzhova's* convention was  
149 motivated by the nature of the underlying crystal structure (placing the extension direction of the  
150 crankshaft chain within the structures of plagioclase feldspars parallel to the X-axis) it results in  
151 compressional velocities in the X-Z plane that enjoy no simple relationship to the Cartesian  
152 coordinates. With the convention used here, maxima and minima of the compressional velocities  
153 lie closer to the coordinate axes, with the extreme values determined principally by a single  
154 elastic modulus. We use the convention that the elastic moduli (stiffnesses) are represented by  
155 the 6 by 6 matrix  $C_{ij}$ . The inverse of this matrix is the compliance matrix  $S_{ij}$ . These matrixes are  
156 related to the full tensor representation of elasticity by the Voigt notation [*Nye*, 1957].

### 157 **3. Experimental methods:**

#### 158 **3.1 X-ray Compressibility Determinations:**

159 Adding to measurements previously reported [*Angel*, 2004], the unit-cell compressions of the  
160  $An_{48}$ ,  $An_{60}$ , and  $An_{96}$  samples used in this study were measured in diamond-anvil cells by single-  
161 crystal diffraction using a Huber 4-circle diffractometer [*Angel et al.*, 1997] run by the Single  
162 software [*Angel & Finger*, 2011]. Pressures were determined from the measured unit-cell volume  
163 of a quartz crystal included in the cell with each sample and its equation-of-state [*Angel et al.*,  
164 1997]. Unit cell data for the other plagioclase compositions were taken from *Angel* [2004].  
165 Values of the components of the compressibility matrix  $\beta_i = S_{i1} + S_{i2} + S_{i3}$  at room pressure  
166 were determined in two ways. For the three elements corresponding to normal strains ( $i = 1-3$ ),  
167 Birch-Murnaghan equations of state were fit to the variations with pressure of the cubes of the  
168 unit-cell dimensions corresponding to the X, Y, and Z Cartesian axial directions to obtain the

169 room-pressure values of compressibility. This approach cannot be applied to the shear elements  
170 of the compressibility matrix ( $i = 4-6$ ). Therefore for both these and the normal strains, the  
171 components of the incremental Eulerian finite strain  $\varepsilon_i$  were calculated from the unit-cell  
172 parameters of each pair of consecutive data points to yield the compliance tensor component  
173 sums  $\beta_i = -\varepsilon_i/\Delta P$ , in which  $\Delta P$  is the pressure increment between data points. Plots of each of  
174 the 6 compliance sums against the average pressure of the pair of data points were then  
175 extrapolated back to zero to provide a constraint on the room pressure values of the  
176 compressibility matrix elements for each crystal. For the normal compressibilities ( $\beta_i$ ,  $i = 1-3$ )  
177 the two methods yielded the same values within the estimated uncertainties (Figure 2). Their  
178 variation with composition across the  $C\bar{1}$  and  $I\bar{1}+P\bar{1}$  phases (*i.e.* for  $An_0$ -  $An_{50}$  and for  $An_{50}$ -  
179  $An_{100}$  separately) was then fitted with appropriate polynomials as shown in Figure 2. An  
180 additional distinction was made between the  $I\bar{1}$  and  $P\bar{1}$  phases for  $\beta_5$  and  $\beta_6$ . The values from  
181 these fits were then used as constraints in the subsequent analysis to determine the full set of  
182 elastic parameters from the measured wave velocities.

### 183 **3.2 Acoustic Velocity and Elastic Parameters Determinations:**

184 Surface acoustic wave (SAW) velocities were measured using the method of Impulsive  
185 Stimulated Light Scattering (ISLS) [Abramson *et al.*, 1999]. Details of the experiment and the  
186 method to determine elastic parameters for triclinic feldspars are described in Brown *et al.*  
187 [2006]. New in this work was the use of the “Trust Region Interior Reflective Method”  
188 [Coleman and Li, 1994, 1996] to find an optimal set of elastic moduli that best fit measured  
189 surface-wave velocities and the compressibilities (Figure 2) determined in the high-pressure X-  
190 ray measurements. A “multi-start” approach was adopted in which optimization is initiated  
191 many times from sets of elastic moduli that are randomly generated in the range of an *a priori*  
192 “trust region” (set to insure that the elasticity tensor remains positive definite). The best solution  
193 is identified and, within the stated uncertainties, is thought to be unique for each data set. A  
194 Monte Carlo analysis provided support for this conjecture. Synthetic data with random errors  
195 and propagation coverage comparable to the actual data were generated from known sets of  
196 elastic moduli. The inversion method used here recovered the *a priori* moduli within the  
197 estimated uncertainties.

198 Elastic moduli  $C_{ij}$  and their associated  $2\sigma$  uncertainties for all plagioclase samples are listed in  
199 Table 2. The first nine moduli in each column are those allowed to be non-zero under  
200 orthorhombic symmetry ( $C_{11}$   $C_{22}$   $C_{33}$   $C_{44}$   $C_{55}$   $C_{66}$   $C_{12}$   $C_{13}$   $C_{23}$ ). The next four ( $C_{15}$   $C_{25}$   $C_{35}$   $C_{46}$ ), in  
201 addition to the first nine, are allowed to be non-zero for monoclinic symmetry. Compliances ( $S_{ij}$ )  
202 are listed in Table S2 of the Auxiliary Materials. Note that individual compliances are *not* the  
203 simple inverse of the modulus component with the same indices [Nye, 1957]. The values  
204 reported here for albite differ slightly from those in *Brown et al.* [2006] as a result of refitting the  
205 original velocity data with modified estimates for the uncertainties of the X-ray compliance  
206 sums. We have adopted a uniform uncertainty of  $0.0001 \text{ GPa}^{-1}$  for all of the compliance sums  
207 derived from the high-pressure X-ray measurements. This value is a conservative global estimate  
208 that exceeds both the formal fitting error, the data scatter of individual high-pressure data points,  
209 the spread in values determined by different methods of data reduction (section 3.1), and is the  
210 maximum misfit of smoothed trend lines fit through the data as a function of composition.  
211 Magnitudes of uncertainties for components  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{12}$ ,  $C_{13}$ , and  $C_{23}$  scale with  
212 uncertainties in X-ray compressibilities. Other moduli/compliances are fully constrained by the  
213 SAW data and their values and uncertainties are not impacted by the X-ray data. The  $2\sigma$   
214 uncertainties listed in the table were calculated from the covariance matrix [*Brown et al.* 1989]  
215 that included uncertainties in both the velocities (set to be 0.3%) and the X-ray determined  
216 compressibilities. Table S3 of the Supplementary Materials contains X-ray compliance  
217 determinations, all measured and predicted SAW velocities, and optimization results.

## 218 **4. Discussion**

### 219 **4.1 Elastic Moduli, Compliances, and Body Wave Velocities**

220 The elastic moduli and compliances are plotted in Figure 3 as a function of composition.  
221 Boundaries between the three symmetrically distinct phases of plagioclase ( $C\bar{1}$ ,  $I\bar{1}$ ,  $P\bar{1}$ ) are  
222 also indicated. Within the range of composition of each phase, the data are linked by low order  
223 curves to guide the eye; most points lie within estimated uncertainty of these curves. Although a  
224 few components exhibit linear or mildly non-linear trends over the entire range of composition  
225 (for example  $C_{11}$  and  $S_{11}$ ), the majority of components cannot be adequately represented over the  
226 entire compositional range with a single low-order polynomial. Additional compositional data



227 are needed to fully constrain behavior across the phase boundaries. Nevertheless, several  
228 components appear to have discontinuities larger than experimental uncertainties.

229 The orthorhombic elastic moduli (upper two rows of Figure 3) are larger (with the exception of  
230  $C_{23}$  which is discussed below) and have smaller percentage changes with composition than the  
231 remainder of the off-diagonal components. However, as shown below, the non-orthorhombic  
232 components have non-negligible effects on calculated body wave velocities.

233 For diagonal matrix elements  $ii$  with  $i = 1-3$ , the most compliant direction is parallel to  $a^*$  (since  
234  $X$  is set parallel to  $a^*$ ,  $C_{11}$  is small and  $S_{11}$  is large). With increasing substitution of  $Ca^{2+}$  for  $Na^{1+}$   
235 (and the coupled substitution of  $Al^{3+}$  for  $Si^{4+}$ ),  $C_{11}$  stiffens significantly. The trend for  $C_{11}$  from  
236 albite to anorthite is essentially linear while  $S_{11}$  has distinctly nonlinear behavior; small  
237 discontinuities at the phase boundaries shown by the curves are comparable to the uncertainties.  
238 The other two longitudinal moduli and compliances associated with the  $Y$  and  $Z$  axes ( $C_{22}/S_{22}$   
239 and  $C_{33}/S_{33}$ ) are nearly identical at  $An_0$  and diverge slightly for  $An_{100}$ .  $C_{22}/S_{22}$  appear to have  
240 discontinuities at the  $C\bar{1}$  to  $I\bar{1}$  transition that are larger than uncertainties. Although a  
241 continuous curve might be constructed through the  $C_{33}$  and  $S_{33}$  compositional trends,  
242 discontinuous segments are shown in the figure. The overall strong anisotropy of the elastic  
243 properties of albite and the decrease in anisotropy with increasing anorthite content is also  
244 reflected in the anisotropy of the thermal expansion coefficients [*Tribaudino et al.*, 2011] and  
245 must therefore reflect the fundamental anisotropy of the response of the three-dimensional  
246 tetrahedral framework of the feldspar structure to applied stresses and strains.

247 The diagonal shear components (matrix elements  $ii$  with  $i = 4-6$ , top rows, middle panels) relate  
248 applied shear strains with stresses having the same sense of shear direction. These components  
249 are well constrained by the SAW data as evidenced by the small experimental uncertainty. That  
250 low degree polynomial curves do not fit data within uncertainty in the  $C\bar{1}$  range of composition  
251 may be a result of including the  $An_{48}$  sample. Since this crystal is a Bøggild intergrowth with  
252 lamellae of both  $C\bar{1}$  and  $I\bar{1}$  phases, elastic behavior intermediate between the two phases might  
253 be expected.  $C_{44}$  and  $C_{66}$  change little across the entire compositional series while  $C_{55}$  shifts  
254 from being nearly equal to  $C_{44}$  for albite to being nearly equal to  $C_{66}$  for anorthite. This change  
255 occurs entirely within the  $C\bar{1}$  range of composition.

256 The off-diagonal longitudinal moduli and compliances (matrix elements 12, 13, and 23) relate  
257 compressive stresses to compressive strains in orthogonal directions.  $C_{12}$  and  $C_{13}$  are nearly equal  
258 and both double in the range from albite (~30 GPa) to anorthite (~60 GPa). The compliances,  $S_{12}$   
259 and  $S_{13}$  are appropriately negative; a compressive stress along the X-axis generates an expansion  
260 in the orthogonal directions (Y and Z axes). However, the  $C_{23}$  modulus is anomalously small for  
261 albite and increases with anorthite content. A small value for  $C_{23}$  means that application of  
262 normal strain in just the Y direction results in a small normal stress in the Z direction. That  $S_{23}$  is  
263 positive for the  $C\bar{1}$  plagioclases is unusual in that this indicates that a compressive stress along  
264 the Y axis gives rise to *contraction* along the Z-axis. Coesite also exhibits the same behavior  
265 [Weidner and Carleton, 1977] and has a similar, but not identical, tetrahedral framework to the  
266 feldspars. The structures of both minerals include 4-rings of tetrahedra that can undergo a  
267 torsional tilt that does not distort the tetrahedra (Figure 1a) [Angel et al., 2003, 2012].  
268 Simulations of the whole framework of feldspar show that the connectivity between these rings  
269 results in the torsion of all rings shortening the Y and Z directions simultaneously but leads to  
270 large expansion of the X direction (Figure 6 in [Angel et al., 2012]). Thus the negative values of  
271  $S_{12}$  and  $S_{13}$  and the positive value of  $S_{23}$  for  $C\bar{1}$  plagioclases indicates that the elastic response of  
272 feldspars to individual normal stresses is, like their response to hydrostatic stress, accommodated  
273 by the mutual rotation of effectively rigid tetrahedra. Further modeling of the monoclinic  
274 feldspars [Angel et al., 2013] shows that while distortions and changes in relative size of the  
275 tetrahedra (e.g. due to changes in Al,Si ordering) do not affect the overall pattern of anisotropy  
276 of the structure, they do generate changes in the unit-cell parameters and can modify the  
277 anisotropy by a few percent. Therefore it is not surprising that the weak co-variation of the *b*-  
278 and *c*-axes with the torsional tilt, which leads to the positive value of  $S_{23}$  for  $C\bar{1}$  plagioclases is  
279 further weakened as the pattern of Al,Si order changes to that of the  $I\bar{1}$  and  $P\bar{1}$  phases and  $S_{23}$   
280 becomes zero within uncertainty: a compressive stress along Y causes no strain in the Z  
281 direction.

282 The scales and limits of the ordinates are held constant to facilitate comparisons of the remaining  
283 (non-orthorhombic) elastic elements in Figure 3 (bottom two rows). All of these parameters are  
284 well determined solely on the basis of the surface wave velocity measurements. The  
285 discontinuities between the  $C\bar{1}$ ,  $I\bar{1}$ , and  $P\bar{1}$  phases shown in these figures provide additional  
286 support for the divisions adapted in interpreting the X-ray compliance sums as shown in Figure

287 2. The three panels on the left give moduli and compliances associated with the mapping of  
288 compressive stresses to shear strains (matrix elements  $ij$  with  $i=1-3$  and  $j=4-6$ ). The far right  
289 panels gives the mapping between shear stresses and resulting shear strains in orthogonal  
290 directions. Most of the  $S_{ij}$  are small, ranging from -4 to +4 TPa<sup>-1</sup> and the trends for individual  
291 elastic elements within each phase are complex and varied. Further, with the exception of  $S_{46}$ , the  
292 values of the elements allowed under the aristotype monoclinic symmetry of feldspars (i.e.  $S_{15}$ ,  
293  $S_{25}$ ,  $S_{35}$  and  $S_{46}$ ) are no larger than those elements whose values would be zero in monoclinic  
294 feldspars. However, the smaller discontinuities associated with the  $C\bar{1}$  to  $\bar{1}1$  transition in the  
295 values of the ‘monoclinic’ elements  $S_{i5}$  relative to those for the ‘triclinic’ elements  $S_{i4}$  and  $S_{i6}$   
296 indicate that the elastic response of the plagioclases is still dominated by the response of the  
297 tetrahedral framework. This is supported, as we discuss below, by the observation that the  $C_{ij}$   
298 with  $j=6$  have generally larger discontinuities than those with  $j=4-5$ . This means that the change  
299 in shear stiffness of the X-Y plane ( $j=6$ ) from  $C\bar{1}$  to  $\bar{1}1$  is larger than that of the perpendicular  
300 planes X-Z and Y-Z ( $j=4-5$ ). Ignoring the cell-doubling along the  $c$ -axis that arises from the  
301 change in Al/Si ordering pattern, the transition results in small changes in the  $\alpha$  and  $\beta$  unit-cell  
302 angles but a significant increase in the  $\gamma$  angle from  $\sim 90^\circ$  for  $C\bar{1}$  plagioclases to  $\sim 91.5^\circ$  for  $\bar{1}1$   
303 plagioclases. Thus, the biggest change in the shear elastic moduli between  $C\bar{1}$  and  $\bar{1}1$  phases  
304 corresponds to the biggest difference between their unit-cell parameters.

305 Compressional and shear velocities in single crystals with respect to propagation directions  
306 relative to crystal axes are shown in Figure 4. For purely orthorhombic symmetry, velocities  
307 would exhibit mirror symmetry about the Cartesian coordinate axes. Although these triclinic  
308 velocities exhibit orthorhombic trends (e.g. the maximum and minimum compressional velocities  
309 lie close to the Cartesian axes), perturbations associated with the lower symmetry of the feldspar  
310 structure are clearly evident. Strong anisotropy of compressional velocities is observed in the X-  
311 Y and X-Z planes with the low velocities (<6 km/s) in the X direction ( $a^*$  crystallographic  
312 direction) and velocities exceeding 8 km/s along Y and Z. Shear wave velocities show strong  
313 anisotropy in the Y-Z plane; the highest shear velocities and greatest polarization dependence  
314 occur near the bisector of the  $b$ - and  $c$ - axes. At these points, the velocity of the fastest shear  
315 wave approaches the compressional wave velocity. With increasing anorthite content,  
316 compressional and shear velocities become less anisotropic (as indicated by more circular  
317 velocity trends).

## 318 4.2 Elasticity and structure

319 The overall pattern of elasticity variation and the resultant variation in compressibility elements  
320 across the plagioclase join (as shown in Figures 2-4) reflects the evolution of the structures of  
321 these feldspars. The dominant change in the framework conformation across the whole join is the  
322 reduction in the values of the same tetrahedral tilts (#2 and #3 in the notation of [Megaw, 1970;  
323 Angel *et al.*, 2012]) that follow exactly the same trend as found in alkali feldspars [Angel *et al.*,  
324 2012, 2013]. This results from maximizing the length of the shortest O-O distances in the  
325 structure as the volume of the structure is changed [Angel *et al.*, 2012, 2013]. In the plagioclase  
326 feldspars, the relative values of the diagonal compressional moduli  $C_{ii}$  and compliances  $S_{ii}$  and  
327 the first three compressibilities  $\beta_i$  ( $i=1-3$ ) can be explained in terms of these same tilts. The X  
328 direction is soft because the coupled changes in tilts 2 and 3 results in large strains in this  
329 direction, without changes in the short O-O distances (see Fig 8 in Angel *et al.* [2012]). The Y  
330 and Z directions are about 3 times stiffer than X under both hydrostatic compression (as  
331 represented by elements  $\beta_2$  and  $\beta_3$  in Figure 2) and normal stress ( $S_{22}$  and  $S_{33}$  in Figure 3)  
332 because the combination of tilts 2 and 3 does not produce large strains in these directions. The  
333 values, and the unusual positive sign of  $S_{23}$ , of the off-diagonal compliances  $S_{ij}$  ( $i,j=1-3, i \neq j$ ) that  
334 define the normal strains in directions perpendicular to an applied normal stress can be explained  
335 by the same mechanism. Other mechanisms that might be available to accommodate stress  
336 applied to the structures will be stiffer because they either generate smaller strains and shorten  
337 O-O distances (tilts 1 and 4) or they involve deformation of the stiff tetrahedra. The overall  
338 decrease in anisotropy that is observed in the compressibility, and in the normal compliances  $S_{ii}$ ,  
339 on going from albite towards anorthite cannot be directly due to the substitution of Al for Si in  
340 the framework but must, in some way, be the result of the coupled substitution of the Na of the  
341 albite component by Ca of the anorthite component.

342 The different changes in various moduli, compliances and compressibilities between the  $C\bar{1}$ ,  $\bar{1}\bar{1}$ ,  
343 and  $P\bar{1}$  plagioclases are related to the magnitudes of the corresponding changes in structure.  
344 First, the changes in the normal compressibilities  $\beta_i$  and normal compliances  $S_{ij}$  ( $i,j=1,3$ ) are  
345 relatively small compared to their values (Figures 3-5), confirming that the values of these elastic  
346 elements are controlled by the topology of the framework and not by its detailed conformation as  
347 represented by the values of tilts. Most of the other elastic properties ( $\beta_i$ ,  $S_{ij}$ ,  $C_{ij}$ ;  $i,j = 4-6$ ) show

348 relatively small jumps in values at the phase transition from  $C\bar{1}$  to  $I\bar{1}$ , but significant changes in  
349 slopes; this is consistent with the observation that the tilts of the framework of  $I\bar{1}$  plagioclase  
350 evolve smoothly with composition away from those of  $C\bar{1}$  plagioclase close to the transition.  
351 Note that even if the transition is thermodynamically continuous as indicated by the trends in  
352 structure, discontinuities are allowed in the elastic properties at the transition point (e.g.  
353 [Carpenter & Salje 1998]). Neither the structural data nor the one available set of elasticity data  
354 for the  $P\bar{1}$  plagioclases is sufficient to identify trends in elasticity within that phase. Nonetheless,  
355 it is clear that the large jumps in the values of some individual compliances, especially  $S_{i6}$  which  
356 indicate significant changes in the shear stiffness of the X-Z plane, are related to the change in  
357 the pattern of the shears of the 4-rings of tetrahedra within the structure. Within  $C\bar{1}$  structures  
358 there is only one type of ring, so each layer of tetrahedral rings in the X-Z plane contains rings  
359 all sheared in the same sense, while consecutive X-Z layers are sheared in the opposite sense.  
360 Naïve mechanical considerations would suggest that stiffness of the structure in response to  
361 shear in the X-Z plane would be significantly different when the layers contain rings sheared in  
362 opposite senses (as in  $I\bar{1}$  structures) and when the rings are sheared by far greater angles of more  
363 than  $10^\circ$  in both senses in  $P\bar{1}$  anorthites.

364 In summary, the measured patterns of compressibilities (response to hydrostatic stress) and of  
365 compliances and moduli (response to individual stresses and strains) for plagioclase feldspars are  
366 not just internally consistent. They are also consistent with what is known about the structures  
367 and the changes in structures with composition and between the three symmetrically distinct  
368 phases. However, it is important to note that, while we can relate all of the changes in elasticity  
369 to changes in structural conformations, it is not possible to determine whether these changes are  
370 the direct influence of stronger bonds for Ca relative to Na interacting with framework oxygen  
371 atoms, or a consequence of shorter O-O distances as the Ca content is increased and the  
372 conformation of the framework, as quantified by tetrahedral tilts, changes.

### 373 **4.3 Applications to Aggregate Elasticity**

#### 374 **4.3.1 Isotropic Average Bulk and Shear Moduli:**

375 Isotropic estimates for the bulk and shear moduli, the Voigt, Reuss, Hill, (V-R-H) and Hashin-  
376 Shtrikman (H-S) bounds [Brown 2013] of the seven samples are listed in Table S3 of the  
377 Auxiliary Materials. In Figure 5 (left side) these isotropic parameters are plotted as a function of

378 composition. Experimental uncertainties for individual moduli are appropriately propagated and  
379 are shown with error bars given only for the Hill average.

380 The X-ray diffraction measurements were performed under uniform stress (hydrostatic  
381 compression) and so yield an isothermal bulk modulus that is equal to the Reuss bound (as  
382 shown in Figure 5). The conversion factor between the adiabatic and isothermal bulk moduli is  
383  $(1+\alpha\gamma T)$ . For plagioclase, the room-temperature volume thermal expansion coefficient  $\alpha$  ranges  
384 from  $2.89 \times 10^{-5} \text{ K}^{-1}$  for albite to  $1.53 \times 10^{-5} \text{ K}^{-1}$  for anorthite [Tribaudino *et al.*, 2010], while the  
385 Grüneisen parameter  $\gamma$  remains approximately constant at  $0.45 \pm 0.05$  [Tribaudino *et al.*, 2011].  
386 The ratio between the isothermal and adiabatic bulk moduli of plagioclase thus ranges from 0.4%  
387 to 0.2%, and is therefore smaller than the experimental uncertainties and is neglected.

388 The bulk modulus has a strong compositional dependence that is associated with the increasing  
389 stiffness along the  $a^*$  direction. In detail, the small offset at the  $C\bar{1}$  to  $\bar{1}\bar{1}$  phase boundary noted  
390 by Angel [2004] is supported by the new data. In contrast, the shear modulus is relatively  
391 insensitive to composition. The Voigt bound is essentially independent of composition, while  
392 the Reuss bound has a slight positive slope. Albite is unusually anisotropic and anorthite, while  
393 still strongly anisotropic, has significantly narrower V-R bounds. The H-S bounds are  
394 consistently narrower than the V-R bounds. The Hill averages consistently lie within the H-S  
395 bounds for all compositions studied.

### 396 **4.3.2 Isotropic and Anisotropic Anorthosite Velocities**

397 In Figure 5 middle panels, one-bar rock velocities corrected from 1 GPa measurements (these are  
398 small correction; see Table S4 and notes in Auxiliary Materials) are compared with velocities  
399 calculated using the current isotropic moduli. Nominal uncertainties of 1% (compressional) and  
400 2% (shear) are shown for reference. The trends in rock velocities with composition are well  
401 predicted by the current moduli. Compressional velocities increase from about 6.4 km/s for albite  
402 to about 7.2 km/s for anorthite. Shear wave velocities change by about 0.1 km/s. A detailed  
403 comparison of data with the calculated bounds is difficult in the face of experimental scatter and  
404 limited documentation. The Voigt-Reuss bounds are particularly wide for feldspars. Although  
405 the H-S bounds provide better constraints (narrowed bounds), nearly all rock velocities agree  
406 within uncertainty (grey bands) with the simple average of the V-R bounds, the Hill average.  
407 Distinguishing between H-S bounds and the Hill estimate will require rock velocity

408 measurements with significantly smaller uncertainties. However, the current work demonstrates  
409 that a correct description of intrinsic mineral elasticity allows calculation of aggregate properties  
410 that agree within mutual uncertainties with measurement.

411 Deformed rocks containing plagioclase feldspars frequently exhibit LPO with a strong alignment  
412 of the *b*-axes and girdles of *a*- and *c*-axes [Xie *et al.* 2003]. Such a fabric leads to pseudo-  
413 hexagonal symmetry (transverse anisotropy) that requires just five elastic moduli to describe. In  
414 the work of Seront *et al.* [1993] on an anorthosite of An<sub>68</sub> composition with about 10% by  
415 volume olivine, the orientations of plagioclase crystals within the rock were determined and  
416 velocities were measured at high pressure in specified directions with controlled polarizations  
417 relative to the measured LPO. Their rock had highly (but not perfectly) aligned plagioclase *b*-  
418 axes with equatorial girdles of *a*- and *c*-axes. The olivine had a distinctly different LPO.  
419 Velocities at 0.8 GPa were taken to represent the crack-free intrinsic response of the constituent  
420 minerals. They found that velocities based on their measured fabric best matched the Voigt  
421 average calculated from the elastic data of Ryzhova [1964]. As noted above, this suggests a  
422 fundamental problem with either the elastic moduli or the measurements on the rock sample.

423 We re-estimate properties for the anorthosite of Seront *et al.* [1993] using elastic moduli based  
424 on the current measurements. A large set of about 4000 crystal orientations that share the  
425 statistical properties similar to those measured in the rock were generated. The combination of a  
426 variance of 25° from complete alignment of *b*-axes and a randomization of the orientations of the  
427 *a*- and *c*-axes relative to the symmetry axis generates pole figures that visually match the  
428 distributions shown in Figure 5 of Seront *et al.* Since we found by calculation that the degree of  
429 LPO of the minority phase (olivine) has nearly negligible impact on the overall anisotropy of the  
430 rock, isotropic one-bar values from Abramson *et al.* [1997] are used in the results given here.  
431 The elastic moduli for the ensemble of 3600 An<sub>68</sub> (moduli interpolated from our measurements)  
432 and 360 Fo<sub>89</sub> crystals were averaged to determine aggregate Voigt, Reuss, and Hill bounds.  
433 Velocities were calculated as a function of angle from the transverse anisotropy axis. Based on  
434 the pressure dependence for isotropic compressional wave velocities (small) and shear wave  
435 velocities (nearly negligible), an isotropic correction of 0.08 km/s was added to calculated  
436 compressional velocities. Shear velocities of plagioclase in this compositional and pressure  
437 range are presumed to have essentially no pressure dependence.

438 Velocities as a function of angle relative to the transverse axis as reported in *Seront et al.* [1993]  
439 and those predicted using the current Hill-averaged elastic moduli are shown on the right side in  
440 Figure 5. Measured velocities along the *b*-axis cluster (the hexagonal symmetry axis) and in the  
441 symmetry plane (equatorial girdle) are reasonably matched by the predictions. The deviations  
442 between prediction and measurement found in the intermediate directions trend to velocities  
443 slightly below the prediction. A distribution of low aspect cracks that were not fully closed at  
444 the highest pressures may contribute to the velocities bias. However, general trends of velocities  
445 with direction are appropriately matched. Measured shear wave velocities in the intermediate  
446 directions, although biased low relative to the predictions, show appropriate polarization-  
447 dependent splitting. In contrast to the findings of *Seront et al.* who used elastic moduli based on  
448 results of *Ryzhova* [1964] the current Hill-averaged elastic moduli give an adequate accounting  
449 of the rock properties, and thus the non-physical situation represented by the previous match to  
450 Voigt moduli (Figure 16 in [*Seront et al.*, 1993]) is resolved. The bias (about 0.1-0.2 km/s) in  
451 intermediate directions of the measured compressional and shear velocities may include a  
452 contribution associated with a distribution of crystal orientations that was not, in detail, perfectly  
453 transversely anisotropic; the isovelocity contours (Figures 11 and 12 in [*Seront et al.*, 1993])  
454 suggest deviations from pseudo-hexagonal symmetry.

455 The range of pressure in the crust (1 GPa in continental crust at a depth of 35 km) changes  
456 compressional velocities by  $\sim 0.1$ - $0.2$  km/s. Since the pressure-induced change of the shear  
457 modulus is almost cancelled by the increase in density, shear wave velocities are essentially  
458 pressure independent within the crust. Although the detailed temperature dependence of feldspar  
459 elastic properties remains to be determined, [*Christensen and Mooney*, 1995] suggest that  
460 intrinsic temperature effects within the crust are fairly small. *Christensen and Money* [1995]  
461 compared compressional velocities of common rocks with average crust and upper mantle  
462 seismic structure. Although the average anisotropy of feldspar-rich rock in their suite of samples  
463 was less than 10%, it is noteworthy that the compressional anisotropy in the anorthosite of *Seront*  
464 *et al.* [1993] is greater. A large body of anorthosite with a consistent LPO, as might be created in  
465 regional deformation events, could be interpreted as crustal ( $V_p < 7.5$ ) or mantle ( $V_p \approx 8$  km/s)  
466 depending on its orientation in the crust relative to seismic wave propagation directions.

## 467 **5. Conclusions**



468 Elastic properties are reported for seven plagioclase feldspars that span the compositions from  
469 albite ( $\text{NaSi}_3\text{AlO}_8$ ) to anorthite ( $\text{CaSi}_2\text{Al}_2\text{O}_8$ ). Surface acoustic wave velocities measured using  
470 Impulsively Stimulated Light Scattering and compliance sums from high-pressure X-ray  
471 compression studies accurately determine all 21 components of the elasticity tensor for these  
472 triclinic minerals for the first time. The overall pattern of elasticity and compressibility can be  
473 explained in terms of the structural response of all feldspars to applied stress being dominated by  
474 the tilting of effectively rigid  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra that comprise the corner-linked  
475 framework of the crystal structure of feldspars. In particular, the flexibility of the framework  
476 results in strong anisotropy in both compressibilities and compliances, with the  $a^*$  direction in  
477 albite being softer by a factor of three than the perpendicular directions. The trends in the  
478 elasticity components can be rationalized on the basis of changes in crystal structure and  
479 chemistry across this solid-solution join. From albite to anorthite the stiffness in the  $a^*$  direction  
480 undergoes the greatest change, increasing two-fold, and represents the stiffening of the dominant  
481 mechanism of elastic response of the tetrahedral framework. Small discontinuities in the elastic  
482 components, inferred at boundaries between the three phases ( $C\bar{1}$ ,  $I\bar{1}$ , and  $P\bar{1}$ ), appear  
483 consistent with the nature of the underlying conformation of the framework-linked tetrahedra and  
484 the associated structural changes. Although Al,Si ordering is expected to have a relatively small  
485 impact on the elastic properties, ordering increases in both directions from the  $C\bar{1}$  -  $I\bar{1}$  transition  
486 and changes in slope at the boundary is probably an effect of the change in the pattern of  
487 ordering.

488 The current results provide greater assurance that the seismic structure of the mid and lower crust  
489 can be accurately estimated on the basis of specified mineral modes, chemistry, and fabric. Body  
490 wave velocities measured in nearly isotropic plagioclase-rich rocks, reported over the last five  
491 decades, are consistent with calculated Hill-averaged velocities using the current moduli.  
492 Velocities and their trends with composition are accurately predicted. This confirms  
493 longstanding speculation that previously reported elastic moduli for plagioclase feldspars are  
494 systematically in error. Velocities calculated using the new moduli document a high degree of  
495 anisotropy that moderately decreases with increasing anorthite content. Typical patterns of  
496 deformation-induced fabric (LPO) in feldspar-rich rocks lead to anisotropic velocities that can  
497 range from those typical for the lower crust to values associated with the upper mantle depending

498 on the direction of seismic wave propagation relative to the fabric. Thus, variable chemistry and  
499 variable anisotropy can control the seismic structure of feldspar-rich crustal rocks.

500 **Acknowledgments:** Partial support was provided by the National Science Foundation through  
501 grant EAR-0711591 (JMB) and EAR-1118691 (NLR and RJA). The following undergraduate  
502 students contributed to this project: A. Teel, S. Pendleton, E. Chang, A. Pitts, H. West-Foyle.  
503 We thank S. Kuehner for microprobe analyses and W. Kaminsky for assistance in aligning  
504 crystals. We are grateful for E. Abramson's efforts in maintaining the ISLS laboratory and in  
505 solving experimental problems. High-pressure single-crystal diffraction data were collected at  
506 the Virginia Tech Crystallography Laboratory by Eleda Johnson. We thank Huifang Xu  
507 (Wisconsin) for the high-resolution TEM examination of the An<sub>48</sub> sample. B. Evans (Seattle), R.  
508 Downs (Arizona), J. Selverstone (Albuquerque), G. Rossman (CIT), M. Carpenter (Cambridge)  
509 and the National Museum of Natural History at the Smithsonian Institution are thanked for the  
510 donation of samples for this project. We are grateful for discussions with Mario Tribaudino  
511 (Parma) and R. Liebermann (Stonybrook). R.L. Carlson (TAMU) and N.I. Christensen  
512 (Wisconsin) are acknowledged for their long-standing inspirational enthusiasm for the subject.

513

514 **References**

- 515 Abramson, E. H., L. J. Slutsky, and J. M. Brown (1994), Elastic constants, interatomic forces and  
516 equation of state of  $\beta$ -oxygen at high pressure, *J. Chem. Phys.*, 100, 4518-4526.
- 517 Abramson, E. H., J. M. Brown, L. J. Slutsky, and J. Zaugg (1997), The elastic constants of San  
518 Carlos olivine to 17 GPa, *J. Geophys. Res.*, 102, 12,253-12,263.
- 519 Abramson, E. H., J. M. Brown, and L. J. Slutsky (1999), Applications of impulsive stimulated  
520 scattering in the earth and planetary sciences, *Ann. Rev. Phys. Chem.*, 50, 279–313.
- 521 Angel R.J., R. M. Hazen, T. C. McCormick, C. T. Prewitt, J. R. Smyth (1988), Comparative  
522 compressibility of end-member feldspars. *Phys. Chem. Minerals*, 15, 313-318.
- 523 Angel, R. J., M. A. Carpenter, and L. W. Finger (1990), Structural variation associated with  
524 compositional variation and order-disorder behavior in anorthite-rich feldspars, *Amer. Mineral.*,  
525 75(1-2), 150-162.
- 526 Angel, R. J., D. R. Allan, R. Miletich, and L. W. Finger (1997), The use of quartz as an internal  
527 pressure standard in high-pressure crystallography, *J. Appl. Cryst.*, 30, 461-466.
- 528 Angel, R. J., C. S. J. Shaw, and G. V. Gibbs (2003), Compression mechanisms of coesite, *Phys.*  
529 *Chem. Minerals*, 30, 167-176.
- 530 Angel, R.J. (2004), Equations of state of plagioclase feldspars, *Contrib. Mineral. Petrol.* 146,  
531 506–512, doi:10.1007/s00410-003-0515-5.
- 532 Angel, R. J., J. M. Jackson, H. J. Reichmann, and S. Speziale (2009), Elasticity measurements on  
533 minerals: a review, *Eur. J. Mineral.*, 21, 525-550.
- 534 Angel R.J., and L.W. Finger (2011): SINGLE: a program to control single-crystal  
535 diffractometers. *J. Appl. Cryst.*, 44, 247-251.
- 536 Angel R.J., L.M. Sochalski-Kolbus, and M. Tribaudino (2012), Tilts and tetrahedra: the origin of  
537 anisotropy of feldspars. *Amer. Mineral.*, 97, 765-778.
- 538 Angel R. J., N. L. Ross , J. Zhao, L. M. Sochalski-Kolbus, H. Krüger, and B. C. Schmidt (2013),  
539 Structural controls on the anisotropy of tetrahedral frameworks: the example of monoclinic  
540 feldspars. *Eur. J. Mineral.*, in press
- 541 Benusa, M., R. J. Angel, and N. L. Ross (2005), Compression of albite,  $\text{NaAlSi}_3\text{O}_8$ , *Amer.*  
542 *Mineral.*, 90, 1115-1120.
- 543 Birch, F. (1961), The velocity of compressional waves in rocks to 10 kilobars, part 2, *J.*  
544 *Geophys. Res.*, 66, 2199-2224.
- 545 Bown, M.G., and P. Gay (1958), The reciprocal lattice geometry of the plagioclase feldspar  
546 structures. *Z. Kristallogr.* 111, 1-14.
- 547 Brown, J. M., L. J. Slutsky, K.A. Nelson, and L-T. Cheng (1989), Single crystal elastic constants  
548 for San Carlos Peridot: An application of impulsive stimulated scattering, *J. Geophys. Res.*, 94,  
549 9485-9492.
- 550 Brown, J. M., E. H. Abramson, and R. J. Angel (2006), Triclinic elastic constants for low albite,  
551 *Phys. Chem. Minerals*, doi: 10.1007/s00269-006-0074-1.

- 552 Brown, J. M., Determination of Hashin-Shtrikman bounds on the effective elastic moduli of  
553 polycrystals of any Symmetry, Computers and Geosciences, submitted 2013.
- 554 Carpenter, M.A. (1986), Experimental delineation of the “e”=  $I\bar{1}$  and “e” =  $C\bar{1}$  transformations  
555 in intermediate plagioclase feldspars. *Phys. Chem. Minerals* 13,119-139.
- 556 Carpenter, M.A., J.D.C. McConnell, A. Navrotsky (1985), Enthalpies of ordering in the  
557 plagioclase feldspar solid solution. *Contribs. Min. Pet.* 87, 138-148.
- 558 Carpenter M.A., Salje E.K.H. (1998): Elastic anomalies in minerals due to structural phase  
559 transitions. *Eur. J. Mineral.*, 10, 693-812.
- 560 Christensen, N. I. (1966), Compressional wave velocities in single crystals of alkali feldspar at  
561 pressures to 10 kilobars, *J. Geophys. Res.*, 71, 3113-3116.
- 562 Christensen, N. I., W. D. Mooney (1995), Seismic velocity structure and composition of the  
563 continental crust: A global view, *J. Geophys. Res.*, 100, 9761-9788.
- 564 Coleman, T. F., and Y. Li (1994), On the convergence of interior-reflective Newton methods for  
565 nonlinear minimization subject to bounds, *Math. Progr.*, 67, 189-224.
- 566 Coleman, T. F., and Y. Li (1996), An interior trust region approach for nonlinear minimization  
567 subject to bounds, *SIAM J. Optimization*, 6(2), 418-445.
- 568 Crowhurst, J. C., and J. M. Zaugg (2004), Surface acoustic waves in germanium single crystals,  
569 *Phys Rev B*, 69, 52301-52304.
- 570 Every, A. G., K. Y. Kim, and A. A. Maznev (1998), Surface dynamic response functions of  
571 anisotropic solids, *Ultrasonics*, 36, 349–353.
- 572 Farnell, G. W. (1970), Properties of elastic surface waves, in *Physical Acoustics*, edited by W. P.  
573 Mason and R. N. Thurston, Academic, New York.
- 574 Hill R. (1963) Elastic properties of reinforced solids: some theoretical principles. *J Mech Phys.*  
575 *Solids* 11, 357-372
- 576 Kroll, H., and P.H. Ribbe (1980), Determinative diagrams for Al,Si order in plagioclases. *Amer.*  
577 *Mineral.*, 65, 449-457.
- 578 Kroll, H., and P.H. Ribbe (1983), Lattice parameters, composition and Al, Si order in alkali  
579 feldspars. *Mineral. Soc. Am. Rev. Mineral*, 2, 57-99.
- 580 Liebermann, R. C., and A. E. Ringwood (1976), Elastic properties of anorthite and nature of  
581 lunar crust, *Earth Planet. Sci. Lett.*, 31, 69–74.
- 582
- 583 Mainprice, D., R. Hielscher, and Schaeben, H. (2011), Calculating anisotropic physical  
584 properties from texture data using the MTEX open-source package. From: Prior, D. J., Rutter, E.  
585 H. & Tatham, D. J. (eds) Deformation Mechanisms, Rheology and Tectonics:  
586 Microstructures, Mechanics and Anisotropy. Geological Society, London, Special Publications,  
587 360, 175–192. DOI: 10.1144/SP360.10
- 588 Megaw, H.D. (1970), Structural relationship between coesite and felspar. *Acta Cryst. B*, 26, 261-  
589 265.
- 590 Maznev, A. A., A. Akthakul, and K. A. Nelson (1999), Surface acoustic modes in thin films on  
591 anisotropic substrates, *J. Appl. Phys.*, 86, 2818–2824.

592 Mueller, H. J., J. Lauterjung, F. R. Schilling, C. Lathe, and G. Nover (2002), Symmetric and  
593 asymmetric interferometric method for ultrasonic compressional and shear wave velocity  
594 measurements in piston-cylinder and multi-anvil high-pressure apparatus, *Eur. J. Mineral.*, *14*,  
595 581–589. doi: 10.1127/0935-1221.

596 Nye, J. F. (1957), *Physical Properties of Crystals: Their Representation by Tensors and*  
597 *Matrixes*, Oxford, Clarendon Press.

598 Press, W. H., S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery (2007), *Numerical Recipes:*  
599 *The Art of Scientific Computing, Third Edition*, Cambridge University Press, New York.

600 Ribbe, P.H. (1983), Chemistry, structure, and nomenclature of feldspars. *Mineral. Soc. Am. Rev.*  
601 *Mineral*, *2*, 1-19.

602 Ryzhova, T. V. (1964), Elastic properties of plagioclases, *Akad. SSSR Izv. Ser. Geofiz.*, *7*, 1049–  
603 1051.

604 Salje, E.K.H. (1985), Thermodynamics of sodium Feldspar. I: order parameter treatment and  
605 strain induced coupling effects. *Phys. Chem. Minerals*, *12*, 93-98 .

606 Seront, B., D. Mainprice, and N. I. Christensen (1993), A determination of the 3-dimensional  
607 seismic properties of anorthosite—comparison between values calculated from the petrofabric  
608 and direct laboratory measurements, *J. Geophys. Res.*, *98*, 2209–2221.

609 Simmons, G. (1964), Velocity of shear waves in rocks to 10 kilobars, *J. Geophys. Res.*, *69*, 1123-  
610 1130.

611 Sochalski-Kolbus, L., R. J. Angel, and F. Nestola (2010), The effect of Al,Si disorder on the bulk  
612 moduli of plagioclase feldspars, *Mineralogical Magazine*, *74*, 943-950.

613 Smith, J. V., W. L. Brown (1988) *Feldspar Minerals I: crystal structures, physical, chemical,*  
614 *and microtextural properties*, Springer Verlage, New York.

615 Tribaudino M., R. J. Angel, F. Camara, F. Nestola, D. Pasqual, and I. Margiolaki (2010),  
616 Thermal expansion of plagioclase feldspars, *Contrib. Min. Petr.*, **160**, 899-908.

617 Tribaudino, M., M. Bruno, F. Nestola, D. Pasqual, and R. J. Angel (2011), Thermoelastic and  
618 thermodynamic properties of plagioclase feldspars from thermal expansion measurements. *Amer.*  
619 *Mineral.*, **96**, 992-1002.

620 Watt, J. P., G. F. Davies, and R. J. O’Connell (1976), The elastic properties of composite  
621 materials, *Rev. Geophys. Space Phys.*, *14*, 541-563.

622 Weidner, D. J., and H. R. Carleton (1977), Elasticity of coesite, *J. Geophys. Res.*, *82*, 1334–1346

623 Xie, Y., H.-R. Wenk, S. Matthies (2003), Plagioclase preferred orientation by TOF neutron  
624 diffraction and SEM-EBSD, *Tectonophysics*, *370*, 269–286, doi:10.1016/S0040-1951(03)00191-  
625 4.  
626

627 Table 1: Sample chemistry, unit cell parameters and densities determined from volume and  
 628 chemical analyses. Data for  $An_0$  are from *Brown et al.* [2006]. Uncertainties in last digit are  
 629 given in parentheses.

	$a$ : Å	$b$ : Å	$c$ : Å	$\alpha$ : deg.	$\beta$ : deg.	$\gamma$ : deg.	Å <sup>3</sup>	Density (g/cc)
$An_0$	8.1366(2)	12.7857(2)	7.1582(3)	94.253(2)	116.605(2)	87.756(2)	663.98(3)	2.623(3)
$An_{25}$	8.1605(15)	12.8391(6)	7.1288(3)	93.833(13)	116.440(5)	89.124(5)	667.20(13)	2.653(3)
$An_{37}$	8.16577(9)	12.85623(11)	7.11418(9)	93.622(1)	116.278(1)	89.679(1)	668.123(12)	2.666(3)
$An_{48}$	8.1744(2)	12.8638(3)	7.1102(2)	93.525(3)	116.236(1)	89.915(3)	669.10(3)	2.683(3)
$An_{60}$	8.1717(2)	12.8752(2)	14.2074(3)	93.4530(11)	116.078(1)	91.4250(11)	1337.98(5)	2.702(3)
$An_{78}$	8.1798(3)	12.8761(3)	14.1974(6)	93.423(3)	116.054(3)	90.705(3)	1339.74(8)	2.725(3)
$An_{96}$	8.1789(3)	12.8717(6)	14.1765(7)	93.194(5)	115.893(3)	91.195(3)	1338.84(10)	2.757(3)

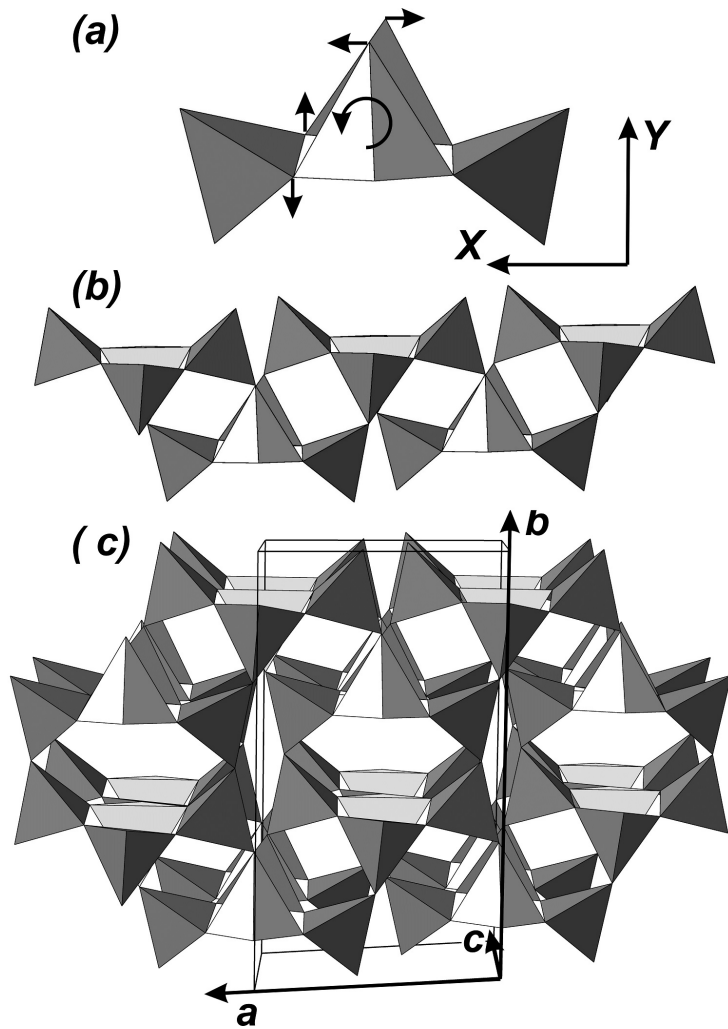
630

631 Table 2. Elastic Moduli (GPa units) for Plagioclase Feldspars. Uncertainties in parentheses are  
632  $2\sigma$  estimates. The first nine entries in each column are moduli that are non-zero for orthorhombic  
633 symmetry. The next four ( $C_{15}$ ,  $C_{25}$ ,  $C_{35}$ ,  $C_{46}$ ) are non-zero for monoclinic symmetry and all  
634 moduli are non-zero for triclinic symmetry.

GPa	An <sub>0</sub>	An <sub>25</sub>	An <sub>37</sub>	An <sub>48</sub>	An <sub>60</sub>	An <sub>78</sub>	An <sub>96</sub>
"orthorhombic" moduli							
C <sub>11</sub>	68.3 (0.8)	87.1 (1.3)	96.2 (1.6)	104.6 (1.9)	109.3 (1.7)	120.4 (2.6)	132.2 (3.0)
C <sub>22</sub>	184.3 (4.9)	174.9 (5.2)	189.4 (4.9)	201.4 (6.6)	185.5 (2.3)	191.6 (6.3)	200.2 (5.4)
C <sub>33</sub>	180.0 (3.0)	166.1 (4.7)	171.9 (4.5)	172.8 (5.1)	164.1 (1.9)	163.7 (5.0)	163.9 (4.1)
C <sub>44</sub>	25.0 (0.1)	22.9 (0.2)	23.6 (0.1)	22.9 (0.1)	22.2 (0.1)	23.3 (0.1)	24.6 (0.1)
C <sub>55</sub>	26.9 (0.1)	29.0 (0.2)	33.1 (0.3)	33.0 (0.3)	33.1 (0.2)	32.8 (0.3)	36.6 (0.2)
C <sub>66</sub>	33.6 (0.2)	35.0 (0.3)	35.5 (0.3)	35.6 (0.2)	36.8 (0.3)	35.0 (0.5)	36.0 (0.3)
C <sub>12</sub>	32.2 (1.6)	43.9 (2.0)	46.1 (2.5)	51.5 (2.8)	53.1 (1.1)	56.6 (3.4)	64.0 (3.5)
C <sub>13</sub>	30.4 (1.5)	35.4 (1.9)	38.4 (2.2)	43.9 (2.4)	42.1 (2.1)	49.9 (2.9)	55.3 (2.8)
C <sub>23</sub>	5.0 (2.6)	18.0 (3.7)	15.4 (4.0)	14.5 (4.5)	21.9 (2.8)	26.3 (4.5)	31.9 (3.7)
remaining off-diagonal moduli							
C <sub>15</sub>	-2.3 (0.3)	-0.4 (0.4)	-0.2 (0.4)	0.1 (0.5)	1.2 (0.4)	3.2 (0.6)	5.1 (0.6)
C <sub>25</sub>	-7.8 (0.7)	-2.9 (0.8)	-5.1 (1.1)	-4.8 (1.2)	0.7 (0.8)	5.4 (1.0)	3.5 (0.9)
C <sub>35</sub>	7.5 (0.6)	4.6 (0.8)	7.2 (1.1)	6.9 (1.0)	2.5 (0.8)	1.7 (0.9)	0.5 (0.9)
C <sub>46</sub>	-7.2 (0.1)	-5.2 (0.2)	-4.8 (0.2)	-3.8 (0.2)	1.4 (0.1)	0.9 (0.2)	-2.2 (0.1)
C <sub>14</sub>	4.9 (0.2)	6.1 (0.3)	5.9 (0.3)	6.5 (0.4)	7.6 (0.3)	9.0 (0.5)	9.5 (0.5)
C <sub>16</sub>	-0.9 (0.3)	-0.6 (0.4)	-0.4 (0.5)	-0.8 (0.5)	-7.7 (0.5)	-3.0 (0.6)	-10.8 (0.7)
C <sub>24</sub>	-4.4 (0.6)	-5.9 (0.6)	-7.0 (0.6)	-2.4 (0.6)	-2.9 (0.5)	2.1 (0.9)	7.5 (0.6)
C <sub>26</sub>	-6.4 (0.9)	-6.5 (0.9)	-6.8 (1.2)	-9.9 (1.2)	-6.8 (1.1)	-9.9 (1.3)	-7.2 (1.3)
C <sub>34</sub>	-9.2 (0.4)	-2.9 (0.5)	2.2 (0.7)	-0.4 (0.5)	0.2 (0.5)	1.7 (0.9)	6.6 (0.6)
C <sub>36</sub>	-9.4 (0.6)	-10.7 (0.9)	-9.8 (0.9)	-5.7 (1.0)	0.7 (0.8)	-8.1 (1.1)	1.6 (1.0)
C <sub>45</sub>	-2.4 (0.1)	-1.3 (0.1)	-1.1 (0.2)	-1.0 (0.2)	0.2 (0.1)	0.8 (0.1)	3.0 (0.1)
C <sub>56</sub>	0.6 (0.1)	0.8 (0.2)	1.4 (0.2)	2.1 (0.3)	2.8 (0.2)	4.5 (0.3)	5.2 (0.2)

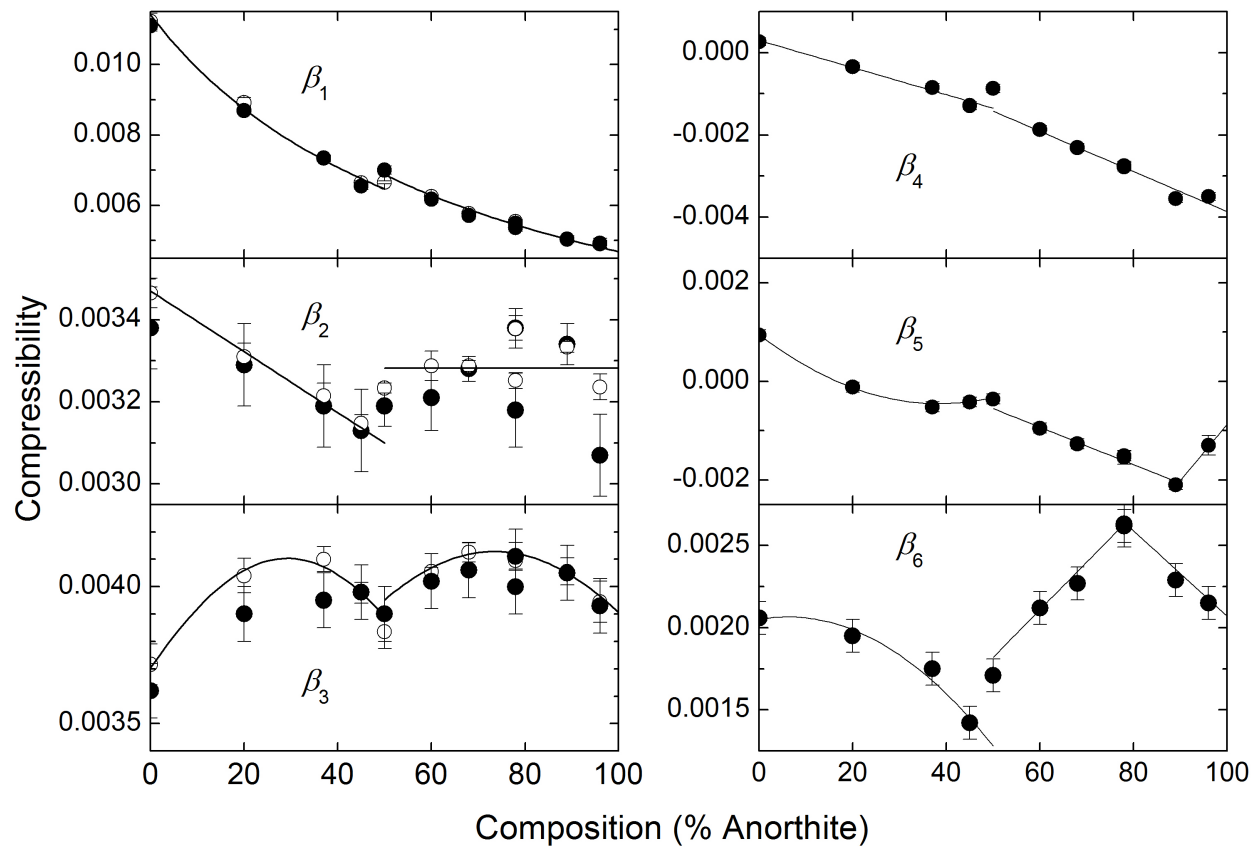
635





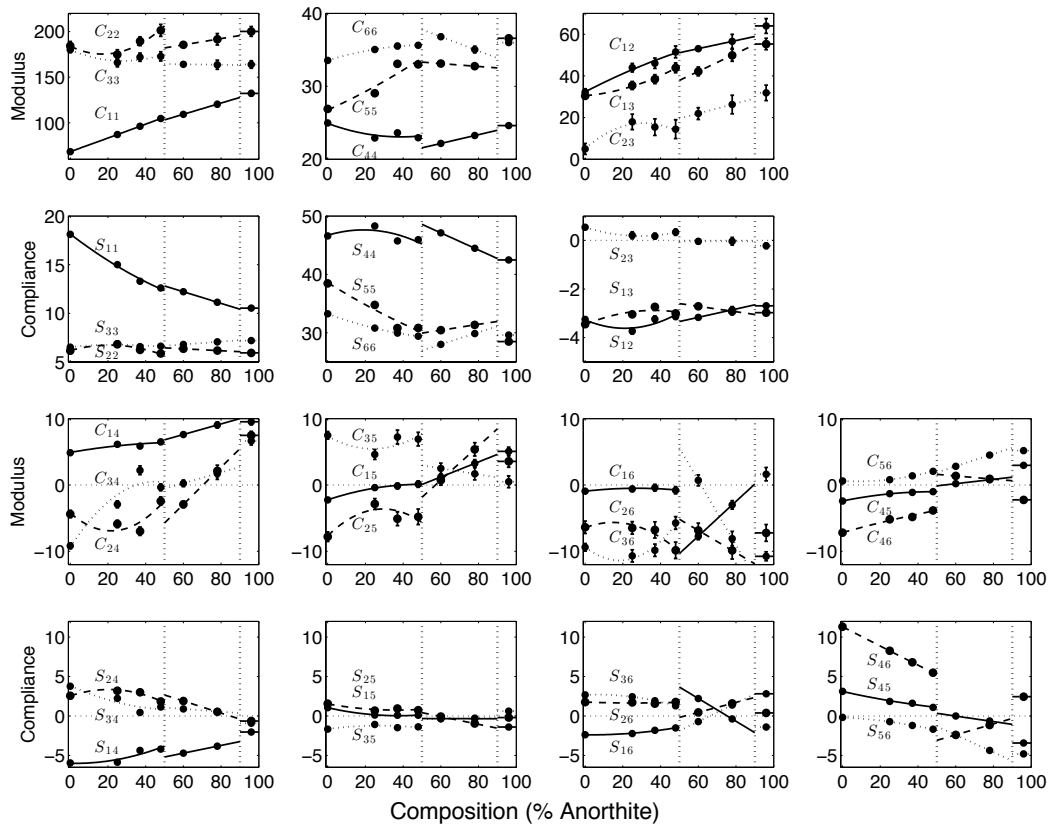
636

637 Figure 1: A polyhedral representation of the components of the aluminosilicate  
 638 framework of plagioclase feldspars, as illustrated by the structure of albite. Each  
 639 tetrahedron represents a  $\text{SiO}_4$  or  $\text{AlO}_4$  unit with an O atom at each tetrahedral corner.  
 640 All oxygen atoms are shared between two tetrahedra. The framework is built from 4-  
 641 rings of tetrahedra (a) which are free to rotate around their inner edges. The rings can  
 642 also shear, and exhibit a torsional tilt with atom motions indicated by the arrows. The  
 643 rings are combined to form the crankshaft chain (b). Changes in the torsional tilt of the  
 644 rings results in large changes in length of this chain. The chains are assembled to form  
 645 the entire 3-dimensional framework (c). The directions of both the crystallographic  
 646 axes and the Cartesian axes X and Y are indicated.



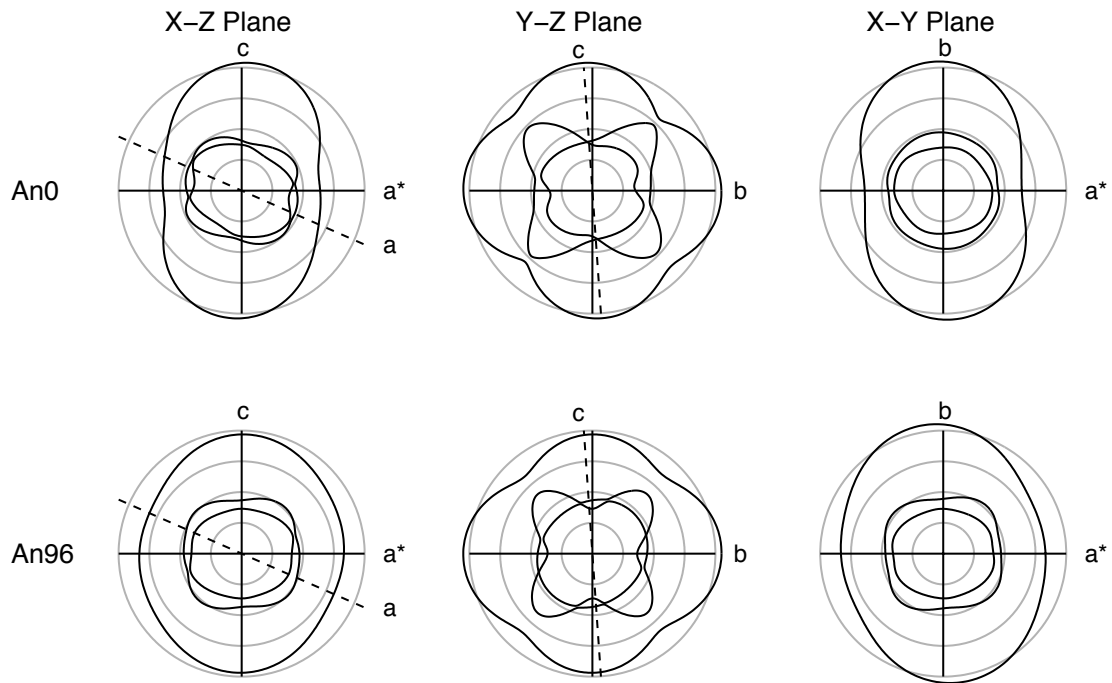
647

648 Figure 2 Variation of room-pressure compressibilities ( $\text{GPa}^{-1}$ ) with composition, as  
 649 determined by high-pressure single-crystal X-ray diffraction measurements of the unit-  
 650 cell parameter variation with pressure as determined in this work and by *Angel* [2004].  
 651 Closed symbols represent fits to incremental strain data. Open symbols are from fits of  
 652 Birch-Murngahan equations of state to the variations with pressure of the cubes of the  
 653 unit-cell dimensions corresponding to the X, Y, and Z Cartesian axial directions. Lines  
 654 are polynomial fits through the data.



655

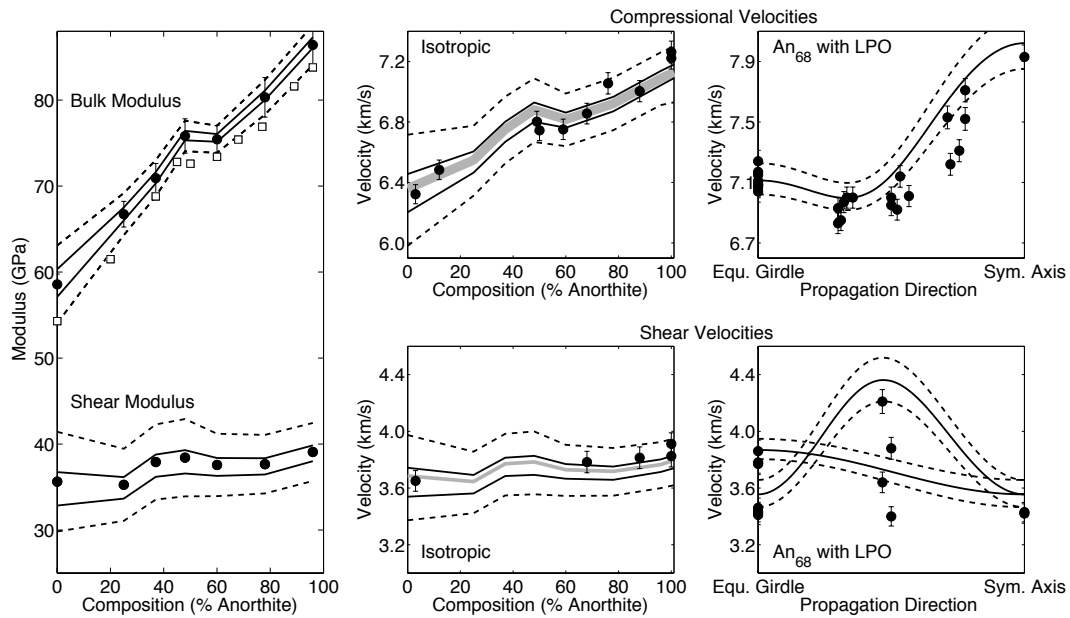
656 Figure 3. Elastic moduli (GPa) and compliances ( $\text{TPa}^{-1}$ ) for plagioclase series feldspars. Top two  
 657 rows: the “orthorhombic” moduli/compliances versus composition. Bottom two rows: The  
 658 remaining (off-diagonal) moduli/compliances versus composition. Vertical dashed lines at  $\text{An}_{50}$   
 659 and  $\text{An}_{90}$  show boundaries between  $C\bar{1}$ ,  $I\bar{1}$ , and  $P\bar{1}$  phases. Elastic matrix elements are labeled  
 660 in each panel and a (solid-dashed-dotted) curve follows each element across the compositional  
 661 space. Error bars (when larger than symbol size) are  $2\sigma$  estimates.



663

664 Figure 4. Elastic wave velocities in three orthogonal planes for (near) endmember plagioclase  
 665 compositions. Grey circles are iso-velocity lines at 2, 4, 6, and 8 km/s. Crystallographic axes (or  
 666 their projections on the plane) are indicated. Velocities are plotted in radial coordinates using  
 667 solid lines. The inner curves are the quasi-shear branches and the outer curve in each figure is  
 668 the quasi-compressional branch.

669



672 Figure 5. Orientational averaged properties for plagioclase feldspars. Left side: Isotropic elastic  
 673 moduli as a function of plagioclase composition. Hill average points are plotted as filled circles  
 674 (uncertainties are  $2\sigma$ , those for the shear modulus are within symbol size). Voigt (upper) and  
 675 Reuss (lower) bounds are plotted with dashed lines. Hashin-Shtrikman upper and lower bounds  
 676 are plotted as solid lines connecting the points. Open squares are the bulk moduli determined by  
 677 single-crystal high-pressure X-ray diffraction measurements. Middle: Isotropic body-wave  
 678 velocities for plagioclase as a function of composition. Symbols: Literature values for  
 679 compression and shear wave velocities measured at a nominal pressure of 1 GPa and corrected to  
 680 one bar (Auxiliary Data Table S4). Dashed lines are Voigt and Reuss bounds based on the  
 681 current data. Solid lines are the Hashin-Shtrikman bounds, The grey line is the Hill average with  
 682 propagated uncertainties indicated by the line width. Right: Compressional and shear wave  
 683 velocities for an anorthosite (90%  $An_{68}$  10%  $Fo_{90}$ ) with LPO. Circles- data of *Seront et al.*  
 684 [1993] at 0.8 GPa projected onto transverse anisotropy coordinates. Dashed lines are Voigt and  
 685 Reuss bounds, and the solid line is the Hill average using a statistical ensemble of orientations  
 686 for  $An_{68}$  crystals that has a variance of  $25^\circ$  in alignment of  $b$ -axes. 10% isotropic olivine is  
 687 included in the average. All calculated compressional velocities are shifted up by 0.08 km/s to  
 688 account for the pressure dependence from measured one-bar elastic moduli. No pressure  
 689 correction is applied to the shear wave velocities.