ORIGINAL PAPER

High-pressure single-crystal X-ray diffraction study of jadeite and kosmochlor

Esther S. Posner · Przemyslaw Dera · Robert T. Downs · John D. Lazarz · Peyton Irmen

Abstract The crystal structures of natural jadeite, $NaAlSi_2O_6$, and synthetic kosmochlor, $NaCrSi_2O_6$, were studied at room temperature, under hydrostatic conditions, up to pressures of 30.4 (1) and 40.2 (1) GPa, respectively, using single-crystal synchrotron X-ray diffraction. Pressure–volume data have been fit to a third-order Birch–Murnaghan equation of state yielding $V_0 = 402.5$ (4) $Å^3$, $K_0 = 136$ (3) GPa, and $K_0' = 3.3$ (2) for jadeite and $V_0 = 420.0$ (3) $Å^3$, $K_0 = 123$ (2) GPa and $K_0' = 3.61$ (9) for kosmochlor. Both phases exhibit anisotropic compression with unit-strain axial ratios of 1.00:1.95:2.09 for jadeite at 30.4 (1) GPa and 1:00:2.15:2.43 for kosmochlor at 40.2 (1) GPa. Analysis of procrystal electron density distribution shows that the coordination of Na changes from 6 to 8 between 9.28 (Origlieri et al. in Am Mineral 88:1025–1032, 2003) and 18.5 (1) GPa in kosmochlor, which is also marked by a decrease in unit-strain anisotropy. Na in jadeite remains six-coordinated at 21.5 (1) GPa. Structure refinements indicate a change in the compression mechanism of kosmochlor at about 31 GPa in both the kinking of SiO_4 tetrahedral chains and rate of tetrahedral compression. Below 31 GPa, the O3–O3–O3 chain extension angle and Si tetrahedral volume in kosmochlor decrease linearly with pressure, whereas above 31 GPa the kinking ceases and the rate of Si tetrahedral compression increases by greater than a factor of two. No evidence of phase transitions was observed over the studied pressure ranges.

Keywords Jadeite · Kosmochlor · Crystal structure · Single-crystal X-ray diffraction · Clinopyroxene · Bulk modulus

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Introduction

Pyroxenes are a major component of the Earth's upper mantle, second only to olivine in volumetric distribution. Orthopyroxene transforms to monoclinic symmetry at pressures equivalent to ~225 km depth making clinopyroxene an important phase for storing Si, O, Mg, Fe, Na, Ca, Al, and Cr (Hugh-Jones et al. 1996; Woodland 1998). A recent study by Plonka et al. (2012) reported a high-pressure polymorph of diopside ($CaMgSi_2O_6$) with a 5 % increase in density above 50 GPa and ambient temperature. Due to their large modal abundance, the elastic properties of clinopyroxene end members are necessary to appropriately model the structure of the mantle in accord with seismic observations. The crystal chemistry of pyroxenes at high pressures and temperatures has been summarized by Yang and Prewitt (2000). Structural refinements from

high-pressure in situ X-ray diffraction experiments on jadeite up to 9.17 GPa were reported by McCarthy et al. (2008a, b) and kosmochlor up to 9.28 by Origlieri et al. (2003). Additional studies have investigated the high-pressure behavior along the jadeite–aegirine join up to 8.31 GPa (Nestola et al. 2006), jadeite–hedenbergite join up to 8.31 GPa (Nestola et al. 2008), and the diopside–kosmochlor join up to 6.80 GPa (Boffa Ballaran et al. 2009).

Oceanic and continental crust are both enriched in Na_2O relative to the upper mantle (Taylor and McLennan 1985). The stability and elasticity of Na-bearing phases at high P–T conditions therefore serve as an important tracer of subducted material into the Earth's interior. Albite (NaAlSi$_3$O$_8$) transforms to jadeite + quartz near the crust-mantle boundary at 2–3 GPa and 1,000 °C (Birch and LeCompte 1960; Newton and Smith 1967; Bell and Roseboom 1969; Holland 1980). Experimental studies at higher P–T conditions reveal that jadeite dissociates to a post-spinel calcium ferrite (CF)-type $NaAlSiO_4$ phase + stishovite at ~23 GPa and 1,000–1,200 °C (Liu 1978; Yagi et al. 1994; Akaogi et al. 2002). First principles computations suggest a significant increase in seismic wave velocities and density associated with jadeite dissociation that may be seismically detectable (Kawai and Tsuchiya 2012). Kosmochlor is a common component of clinopyroxene and, therefore, hosts a significant amount of Cr in the Earth's interior. Extensive kosmochlor–jadeite and kosmochlor–diopside solid solutions have been studied in terrestrial samples (Harlow and Olds 1987; Secco et al. 2002); the latter of which has also been used as a geobarometer (Nimis and Taylor 2000; Nimis 2002). In this study, we report new high-pressure X-ray diffraction data for jadeite up to 30.4 (1) GPa and kosmochlor up to 40.2 (1) GPa at 298 K.

The jadeite and kosmochlor structures are based on an ABAC closest packed arrangement of O atoms and are characterized by chains of corner-linked SiO_4 tetrahedra that run parallel to **c** (Thompson and Downs 2003). Si chains are linked laterally by two distinct M sites; edge-sharing M1-octahedra and larger M2-polyhedra. Na in the M2-site has traditionally been considered to be eight-coordinated based on bond lengths (Clark et al. 1969; Cameron et al. 1973), but electron density and bond-valence sum calculations have also found Na to be in a highly distorted octahedral coordination (Downs 2003). Thompson and Downs (2004) showed that the compressibility of $C2/c$ pyroxenes depends primarily on the occupancy of the M1-site. SiO_4 tetrahedra typically undergo very little compression due to strong and short Si–O bonds while the tetrahedral chains themselves are relatively flexible and can rotate to change their chain length along **c**, O3–O3–O3 angle, and Si–Si distance. In this study, we report differences in structural observations and compressibility trends

between jadeite and kosmochlor, which bear Al^{3+} and Cr^{3+} in M1, respectively.

Experimental methods

A natural jadeite sample from Clear Creek, San Benito County, California, USA, supplied by Hatt Yoder and numbered R050220 in the RRUFF mineralogical database was used in this study. Jadeite crystals from the same sample were used in the original description of the jadeite structure (Prewitt and Burnham 1966) and high-pressure experimental refinements up to 9.17 GPa (McCarthy et al. 2008a, b). The composition of a jadeite crystal from the same hand specimen was determined by the average of 20 microprobe analyses to be $Na_{1.002(8)}Al_{1.000(10)}[Si_{1.979(8)}Al_{0.024}]_{\sum 2.003(8)}O_6$. The kosmochlor crystal used in the diamond anvil cell experiments was numbered R120015 in the RRUFF database and was synthesized by Harlow (1997) from a powdered Na–Cr silicate glass in a muffle furnace at 800 °C for 96 h. Kosmochlor crystals from the same sample were used in high-pressure experimental refinements up to 9.28 GPa (Origlieri et al. 2003). The composition of the synthetic kosmochlor was determined by microprobe to be $(Na_{0.994}Ca_{0.002})(Cr_{0.992}Fe_{.004}Ti_{.002})Si_{2.001}O_6$. Information on these analyses can be found at www.rruff.info. Both samples were treated as fully ordered $NaAlSi_2O_6$ and $NaCrSi_2O_6$, respectively.

Single crystals of jadeite and kosmochlor were loaded into a symmetric piston-cylinder Princeton-type diamond anvil cell. Diamond anvils with culets of 0.300 mm were mounted on asymmetric backing plates. A rhenium metal gasket pre-indented to 0.040 mm was used for sample containment. The DAC was loaded with a neon pressure medium using the GSECARS/COMPRES gas loading system (Rivers et al. 2008). Pressure was estimated based on the fluorescence spectrum of ruby collected at each pressure point (Mao et al. 1986). Single-crystal X-ray diffraction data were collected at the experimental station 13-ID-D of the GeoSoilEnviroCARS facility at the Advanced Photon Source, Argonne National Laboratory. A monochromatic beam with incident energy of 37 keV, focused with a pair of Kirkpatrick–Baez mirrors to a spot of 0.003 by 0.005 mm was used. Diffraction images were collected using MAR165 charge coupled device (CCD) detector, placed at a sample-to-detector distance of approximately 200 mm. Data collection procedure was the same as described by Dera et al. (2011). Diffraction images were analyzed using the GSE_ADA/RSV software package (Dera et al. 2013).

Table 1 Summary of crystal data and refinement results

Jadeite

	0.0001[a]	1.9 (1)	5.6 (1)	8.2 (1)	11.8 (1)	12.4 (1)	18.3 (1)	21.5 (1)	30.4 (1)
P (GPa)	0.0001[a]	1.9 (1)	5.6 (1)	8.2 (1)	11.8 (1)	12.4 (1)	18.3 (1)	21.5 (1)	30.4 (1)
a (Å)	9.4242 (2)	9.368 (3)	9.300 (2)	9.243 (3)	9.174 (2)	9.163 (2)	9.082 (3)	9.034 (2)	8.941 (3)
b (Å)	8.5657 (2)	8.539 (4)	8.447 (3)	8.407 (3)	8.353 (3)	8.340 (4)	8.200 (4)	8.184 (3)	8.025 (4)
c (Å)	5.2242 (2)	5.1975 (5)	5.157 (1)	5.1220 (5)	5.0850 (9)	5.0739 (5)	5.020 (4)	4.9875 (8)	4.919 (1)
β (°)	107.578 (2)	107.44 (1)	107.14 (2)	106.85 (1)	106.63 (2)	106.52 (9)	106.12 (2)	106.02 (1)	105.59 (2)
V (Å^3)	402.03 (2)	396.7 (2)	387.1 (2)	380.9 (2)	373.4 (2)	371.7 (2)	359.2 (2)	354.4 (2)	339.9 (2)
ρ_{calc} (g/cm^3)	3.385		3.468	3.525		3.612	3.739	3.789	
μ (mm^{-1})	0.602		0.617	0.627		0.642	0.665	0.674	
F (000)	400		400	400		400	400	400	
θ range for data collection	2.21–17.91		1.56–18.04	2.25–17.93		2.27–17.83	1.60–18.03	1.61–18.11	
No. of reflections collected	508		504	495		526	439	455	
No. of independent reflections	229		213	222		211	189	192	
No. of parameters refined	33		32	33		33	32	32	
Limiting indices	$-11 \leq h \leq 10$, $-6 \leq k \leq 7$, $-9 \leq l \leq 9$		$-15 \leq h \leq 15$, $-10 \leq k \leq 9$, $-7 \leq l \leq 7$	$-10 \leq h \leq 9$, $-6 \leq k \leq 7$, $-9 \leq l \leq 9$		$-12 \leq h \leq 11$, $-4 \leq k \leq 6$, $-9 \leq l \leq 9$	$-14 \leq h \leq 14$, $-9 \leq k \leq 8$, $-7 \leq l \leq 7$	$-14 \leq h \leq 14$, $-9 \leq k \leq 8$, $-7 \leq l \leq 7$	
R_{int}	0.0841		0.1184	0.1020		0.0899	0.1376	0.0905	
Final R_1 and ωR_2 (reflections $I > 2\sigma(I)$)	0.0530, 0.1427		0.0592, 0.1517	0.0485, 0.1262		0.0507, 0.1069	0.0681, 0.1778	0.0613, 0.1405	
Final R_1 and ωR_2 (all reflections)	0.0530, 0.1427		0.0635, 0.1518	0.0487, 0.1262		0.0507, 0.1069	0.0681, 0.1778	0.0626, 0.1406	
Goodness of fit	1.388		1.305	1.269		1.074	1.226	1.036	
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.467, −0.550		0.640, −0.702	0.543, −0.559		0.582, −0.522	0.640, −0.796	0.598, −1.008	

Kosmochlor

	0.0001[b]	2.1 (1)	11.3 (1)	18.5 (1)	31.3 (1)	35.3 (1)	40.2 (1)
P (GPa)	0.0001[b]	2.1 (1)	11.3 (1)	18.5 (1)	31.3 (1)	35.3 (1)	40.2 (1)
a (Å)	9.5720 (3)	9.524 (3)	9.328 (4)	9.197 (3)	9.084 (3)	9.067 (3)	9.011 (3)
b (Å)	8.7094 (2)	8.672 (3)	8.466 (4)	8.327 (3)	8.077 (3)	7.971 (4)	7.918 (4)
c (Å)	5.2678 (2)	5.2411 (5)	5.1310 (9)	5.0572 (6)	4.9544 (6)	4.9309 (7)	4.8955 (8)
β (°)	107.498 (3)	107.36 (1)	106.55 (2)	106.23 (2)	105.70 (1)	105.56 (2)	105.10 (2)
V (Å^3)	418.84 (3)	413.2 (2)	388.4 (3)	371.9 (2)	350.0 (2)	343.3 (2)	337.2 (2)
ρ_{calc} (g/cm^3)	3.652			4.058	4.312	4.395	4.474

Table 1 continued

Kosmochlor					
μ (mm^{-1})	1.753	1.948	2.07	2.110	2.148
F (000)	444	444	444	444	444
θ range for data collection	1.53–17.54	2.28–18.12	2.34–18.07	2.35–16.97	2.37–17.69
No. of reflections collected	761	529	502	477	416
No. of independent reflections	276	212	190	180	157
No. of parameters refined	35	35	35	35	35
Limiting indices	$-9 \le h \le 10$, $-9 \le k \le 8$, $-9 \le l \le 9$	$-10 \le h \le 9$, $-9 \le k \le 7$, $-9 \le l \le 9$	$-10 \le h \le 8$, $-8 \le k \le 6$, $-9 \le l \le 9$	$-10 \le h \le 9$, $-8 \le k \le 6$, $-8 \le l \le 8$	$-9 \le h \le 8$, $-7 \le k \le 6$, $-8 \le l \le 8$
R_{int}	0.1084	0.1049	0.0982	0.0768	0.1229
Final R_1 and ωR_2 (reflections $I > 2\sigma(I)$)	0.0494, 0.1225	0.0467, 0.1162	0.0436, 0.1091	0.0494, 0.1070	0.0483, 0.1150
Final R_1 and ωR_2 (all reflections)	0.0499, 0.1227	0.0484, 0.1246	0.0436, 0.1091	0.0581, 0.1095	0.0483, 0.1150
Goodness of fit	1.115	1.199	1.135	1.162	1.133
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.802, −0.793	0.804, −0.672	0.795, −0.836	0.787, −0.827	0.659, −0.661

Space group = $C2/c$

[a] Data at ambient pressure are from McCarthy et al. (2008a, b)

[b] Origlieri et al. (2003)

Table 2 Structural parameters of jadeite and kosmochlor as a function of pressure

Sample	Jadeite						Kosmochlor				
	1.9 (1)	5.6 (1)	8.2 (1)	12.4 (1)	18.3 (1)	21.5 (1)	2.1 (1)	18.5 (1)	31.3 (1)	35.3 (1)	40.2 (1)
M2											
x	0	0	0	0	0	0	0	0	0	0	0
y	0.3014 (6)	0.3025 (7)	0.3052 (5)	0.3063 (4)	0.3097 (8)	0.3099 (7)	0.3018 (5)	0.3098 (7)	0.3128 (7)	0.3125 (9)	0.3164 (11)
z	¼	¼	¼	¼	¼	¼	¼	¼	¼	¼	¼
U_{eq}	0.014 (1)	0.015 (1)	0.012 (1)	0.015 (1)	0.011 (11)	0.011 (1)	0.014 (2)	0.009 (2)	0.011 (2)	0.008 (2)	0.007 (3)
M1											
x	0	0	0	0	0	0	0	0	0	0	0
y	0.0937 (4)	0.0923 (4)	0.0921 (3)	0.0905 (3)	0.0903 (6)	0.0902 (5)	0.0921 (2)	0.0888 (2)	0.0876 (2)	0.0873 (3)	0.0859 (5)
z	¾	¾	¾	¾	¾	¾	¾	¾	¾	¾	¾
U_{eq}	0.007 (1)	0.007 (1)	0.007 (1)	0.010 (1)	0.008 (1)	0.006 (1)	0.005 (1)	0.005 (1)	0.005 (1)	0.006 (1)	0.007 (1)
Si											
x	0.2907 (2)	0.2909 (2)	0.2908 (2)	0.2914 (1)	0.2916 (3)	0.2916 (2)	0.2925 (2)	0.2944 (3)	0.2940 (2)	0.2943 (3)	0.2938 (3)
y	0.0942 (2)	0.0946 (3)	0.0953 (2)	0.0956 (2)	0.0965 (3)	0.0966 (3)	0.0921 (2)	0.0953 (3)	0.0973 (3)	0.0976 (5)	0.0978 (5)
z	0.2283 (2)	0.2284 (4)	0.2293 (2)	0.2300 (1)	0.2319 (5)	0.2327 (4)	0.2342 (2)	0.2368 (3)	0.2412 (3)	0.2437 (4)	0.2459 (4)
U_{eq}	0.008 (1)	0.008 (1)	0.007 (1)	0.010 (1)	0.009 (1)	0.008 (1)	0.007 (1)	0.006 (1)	0.006 (1)	0.008 (1)	0.005 (2)
O1											
x	0.1095 (6)	0.1093 (4)	0.1095 (5)	0.1090 (4)	0.1082 (6)	0.1081 (5)	0.1145 (5)	0.1146 (7)	0.1120 (7)	0.1130 (8)	0.1125 (10)
y	0.0765 (6)	0.0767 (6)	0.0788 (5)	0.0796 (4)	0.0803 (8)	0.0820 (7)	0.0793 (6)	0.0852 (7)	0.0903 (7)	0.0909 (9)	0.0931 (11)
z	0.1289 (6)	0.1292 (8)	0.1306 (5)	0.1307 (4)	0.1318 (12)	0.1314 (10)	0.1374 (7)	0.1390 (9)	0.1380 (9)	0.1373 (11)	0.1380 (12)
U_{eq}	0.007 (1)	0.006 (1)	0.007 (1)	0.008 (1)	0.008 (1)	0.006 (1)	0.008 (1)	0.006 (1)	0.009 (1)	0.006 (1)	0.006 (2)
O2											
x	0.3598 (6)	0.3609 (5)	0.3587 (5)	0.3600 (3)	0.3594 (7)	0.3596 (5)	0.3595 (5)	0.3588 (8)	0.3578 (1)	0.3556 (8)	0.3535 (10)
y	0.2648 (7)	0.2669 (7)	0.2677 (5)	0.2694 (6)	0.2731 (10)	0.2717 (8)	0.2596 (6)	0.2674 (9)	0.2710 (8)	0.2734 (11)	0.2760 (14)
z	0.2952 (7)	0.3021 (11)	0.3020 (5)	0.3077 (3)	0.3150 (12)	0.3189 (10)	0.3065 (6)	0.3276 (9)	0.3417 (9)	0.3447 (12)	0.3468 (13)
U_{eq}	0.010 (1)	0.012 (1)	0.009 (1)	0.009 (1)	0.010 (1)	0.008 (1)	0.010 (1)	0.008 (1)	0.010 (1)	0.010 (1)	0.010 (2)
O3											
x	0.1453 (6)	0.1439 (5)	0.1423 (5)	0.1412 (3)	0.1407 (6)	0.1396 (5)	0.1457 (4)	0.1378 (6)	0.1368 (5)	0.1364 (8)	0.1394 (10)
y	0.4913 (6)	0.4884 (7)	0.4861 (6)	0.4833 (5)	0.4799 (10)	0.4760 (8)	0.4890 (7)	0.4745 (8)	0.4653 (8)	0.4648 (11)	0.4663 (13)
z	−0.0052 (6)	−0.0018 (10)	−0.0013 (5)	0.0023 (3)	0.0063 (13)	0.0067 (10)	−0.0075 (6)	0.0043 (9)	0.0057 (8)	0.0049 (11)	0.0068 (12)
U_{eq}	0.007 (1)	0.009 (1)	0.007 (1)	0.008 (1)	0.008 (1)	0.007 (1)	0.008 (1)	0.007 (1)	0.008 (1)	0.008 (1)	0.009 (2)

Table 3 Atomic displacement parameters (Å^2) of jadeite and kosmochlor at P

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Jadeite						
1.9 (1) GPa						
Na	0.016 (4)	0.014 (5)	0.010 (1)	0	0.002 (2)	0
Al	0.006 (3)	0.011 (4)	0.005 (1)	0	0.002 (1)	0
Si	0.007 (2)	0.011 (2)	0.005 (1)	0 (1)	0.002 (1)	1 (1)
5.6 (1) GPa						
Na	0.015 (3)	0.014 (5)	0.015 (3)	0	0.002 (2)	0
Al	0.007 (2)	0.007 (3)	0.009 (2)	0	0.003 (1)	0
Si	0.004 (1)	0.012 (2)	0.009 (1)	0 (1)	0.002 (1)	−0.001 (1)
8.2 (1) GPa						
Na	0.011 (3)	0.014 (4)	0.008 (1)	0	0.001 (1)	0
Al	0.008 (3)	0.010 (3)	0.005 (1)	0	0.003 (1)	0
Si	0.008 (2)	0.010 (2)	0.004 (1)	1 (1)	0.002 (1)	1 (1)
12.4 (1) GPa						
Na	0.016 (2)	0.019 (4)	0.008 (1)	0	0.002 (1)	0
Al	0.007 (2)	0.019 (3)	0.005 (1)	0	0.002 (1)	0
Si	0.008 (1)	0.015 (2)	0.006 (1)	0 (1)	0.002 (1)	0 (1)
18.3 (1) GPa						
Na	0.014 (3)	0.005 (7)	0.011 (3)	0	0.001 (2)	0
Al	0.008 (2)	0.009 (5)	0.008 (2)	0	0.002 (2)	0
Si	0.005 (2)	0.012 (3)	0.011 (2)	0 (1)	0.003 (1)	0 (1)
21.5 (1) GPa						
Na	0.013 (3)	0.008 (6)	0.011 (2)	0	0.003 (2)	0
Al	0.007 (2)	0.004 (4)	0.007 (2)	0	0.002 (1)	0
Si	0.006 (1)	0.008 (2)	0.010 (1)	−0.001 (1)	0.005 (1)	0 (1)
Kosmochlor						
2.1 (1) GPa						
Na	0.020 (3)	0.008 (4)	0.010 (1)	0	0.001 (1)	0
Cr	0.007 (1)	0.005 (1)	0.004 (1)	0	0.001 (1)	0
Si	0.006 (2)	0.010 (2)	0.006 (1)	−0.001 (1)	0.002 (1)	0 (1)
18.5 (1) GPa						
Na	0.015 (4)	0.004 (5)	0.007 (2)	0	−0.001 (2)	0
Cr	0.003 (2)	0.008 (2)	0.004 (1)	0	0.001 (1)	0
Si	0.004 (2)	0.010 (2)	0.004 (1)	0 (1)	0.001 (1)	0.002 (12)
31.3 (1) GPa						
Na	0.007 (3)	0.016 (5)	0.009 (2)	0	0 (2)	0
Cr	0.007 (1)	0.006 (2)	0.003 (1)	0	0.002 (1)	0
Si	0.006 (2)	0.009 (2)	0.004 (1)	0 (1)	0.001 (1)	0.002 (1)
35.3 (1) GPa						
Na	0.007 (4)	0.008 (6)	0.008 (3)	0	0.001 (2)	0
Cr	0.004 (2)	0.011 (2)	0.002 (1)	0	0.001 (1)	0
Si	0.007 (2)	0.011 (3)	0.004 (1)	−0.002 (1)	0.001 (1)	0.001 (1)
40.2 (1) GPa						
Na	0.013 (6)	0.008 (9)	0.001 (2)	0	0.002 (2)	0
Cr	0.003 (2)	0.015 (3)	0.002 (1)	0	0.001 (1)	0
Si	0.009 (3)	0.001 (4)	0.006 (1)	0.001 (1)	0.001 (1)	0.002 (1)

The initial models for the crystal structure determination were the ambient pressure structures of jadeite (Prewitt and Burnham 1966) and kosmochlor (Clark et al. 1969). The models were optimized using conventional least squares crystal structure refinement implemented in SHELXL program (Sheldrick 2008). Crystallographic parameters

Table 4 Selected bond lengths (Å), volumes (Å^3), distortion parameters, and angles (°) from structure refinements

Sample	Jadeite						Kosmochlor				
P (GPa)	1.9 (1)	5.6 (1)	8.2 (1)	12.4 (1)	18.3 (1)	21.5 (1)	2.1 (1)	18.5 (1)	31.3 (1)	35.3 (1)	40.2 (1)
R (SiO1)	1.626 (6)	1.621 (5)	1.610 (5)	1.609 (4)	1.606 (6)	1.599 (5)	1.622 (5)	1.590 (7)	1.593 (6)	1.587 (7)	1.581 (9)
R (SiO2)	1.590 (6)	1.594 (6)	1.580 (5)	1.584 (5)	1.584 (8)	1.571 (6)	1.586 (5)	1.569 (7)	1.548 (6)	1.540 (8)	1.545 (11)
R (SiO3a)	1.638 (4)	1.630 (5)	1.633 (4)	1.620 (3)	1.603 (7)	1.613 (6)	1.641 (5)	1.631 (6)	1.636 (6)	1.622 (8)	1.591 (9)
R (SiO3b)	1.630 (4)	1.626 (5)	1.623 (3)	1.618 (3)	1.615 (6)	1.604 (5)	1.634 (4)	1.625 (5)	1.602 (5)	1.599 (6)	1.593 (7)
R <SiO>	1.621	1.618	1.612	1.608	1.602	1.597	1.621	1.604	1.595	1.587	1.578
V (SiO$_4$)	2.1696	2.1484	2.1335	2.1186	2.0957	2.0770	2.1746	2.108	2.0724	2.0434	2.006
TAV[a]	21.7965	24.8537	19.5272	19.6644	19.0149	18.6246	15.1407	12.325	12.5376	12.3924	12.0975
MTQE[b]	1.0051	1.0069	1.0046	1.0047	1.0046	1.0045	1.0036	1.0029	1.0034	1.0033	1.0031
R (NaO1)	2.350 (7)	2.331 (6)	2.319 (5)	2.298 (4)	2.276 (8)	2.259 (7)	2.376 (6)	2.292 (8)	2.208 (8)	2.187 (9)	2.179 (11)
R (NaO2)	2.402 (4)	2.365 (6)	2.369 (4)	2.334 (4)	2.305 (7)	2.274 (5)	2.371 (4)	2.261 (6)	2.192 (5)	2.185 (7)	2.195 (8)
R (NaO3c)	2.706 (5)	2.693 (6)	2.585 (5)	2.522 (4)	2.439 (7)	2.400 (6)	2.739 (5)	2.431 (6)	2.311 (6)	2.295 (8)	2.276 (10)
R (NaO3d)	2.359 (6)	2.354 (7)	2.337 (5)	2.333 (3)	2.314 (9)	2.326 (7)	2.404 (6)	2.361 (7)	2.348 (8)	2.329 (9)	2.301 (11)
Diff[c]	0.356	0.308	0.266	0.224	0.163	0.141	0.368	0.170	0.156	0.144	0.122
R <NaO>	2.454	2.428	2.402	2.372	2.333	2.314	2.473	2.336	2.265	2.249	2.238
V (NaO$_8$)	24.2091	23.5761	22.8774	22.0160	21.0849	20.6186	24.9231	21.3278	19.6649	19.3497	19.135
R (M1O1a)	1.934 (4)	1.924 (4)	1.922 (3)	1.908 (2)	1.897 (6)	1.885 (5)	2.001 (3)	1.955 (5)	1.916 (5)	1.910 (5)	1.907 (6)
R (M1O1b)	1.987 (5)	1.957 (5)	1.954 (4)	1.929 (4)	1.898 (7)	1.900 (6)	2.031 (5)	1.964 (6)	1.928 (6)	1.919 (7)	1.904 (9)
R (M1O2)	1.851 (6)	1.835 (6)	1.835 (5)	1.819 (4)	1.795 (7)	1.801 (5)	1.942 (5)	1.886 (7)	1.870 (6)	1.869 (7)	1.858 (9)
R <M1O>	1.924	1.905	1.904	1.885	1.864	1.862	1.991	1.935	1.905	1.899	1.893
V (M1O$_6$)	9.2999	9.0418	9.0229	8.7684	8.4449	8.4352	10.4042	9.5425	9.0466	8.9474	8.8388
OAV[a]	47.2915	45.2320	44.3271	42.0083	47.4905	45.1854	27.7456	28.8548	42.0251	49.2869	54.4445
MOQE[b]	1.0148	1.0142	1.0138	1.0131	1.0148	1.0139	1.0084	1.0087	1.0122	1.0141	1.0155
Si–O3–Si	138.5 (3)	137.4 (3)	136.2 (3)	135.45 (17)	134.4 (4)	133.1 (3)	139.1 (3)	133.0 (4)	129.9 (3)	129.6 (5)	130.9 (6)
O3–O3–O3	173.5 (1)	171.3 (3)	169.6 (1)	167.5 (1)	165.0 (3)	162.1 (4)	171.7 (3)	160.9 (3)	154.5 (4)	154.4 (4)	155.4 (5)

[a] *TAV/OAV tetrahedral/octahedral angle variances*

[b] *MTQE/MOQE mean tetrahedral/octahedral quadratic elongation*

[c] *Diff length differences between the longest and shorted reported Na–O bonds*
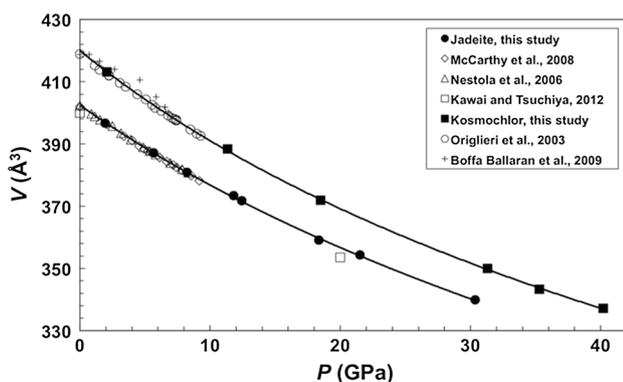
Fig. 1 Unit-cell volume as a function of pressure for jadeite and kosmochlor. Data are fit with a third-order Birch–Murnaghan equation. Kosmochlor has a larger cell than jadeite because Cr^{3+} in the octahedral M1 site has a larger ionic radius than Al^{3+}

for structure refinements are summarized in Table 1, final atomic coordinates and isotropic displacement parameters in Table 2, anisotropic displacement parameters in Table 3, and selected bond distances, angles, and distortion parameters in Table 4.

Results and discussion

Pressure–volume equations of state for jadeite and kosmochlor were obtained by fitting a third-order Birch–Murnaghan equation of state to data from Table 1, resulting in $V_0 = 402.5$ (4) Å^3, $K_0 = 136$ (3) GPa, and $K_0' = 3.3$ (2) for jadeite and $V_0 = 420.0$ (3) Å^3, $K_0 = 123$ (2) GPa, and $K_0' = 3.61$ (9) for kosmochlor. Our jadeite values match those reported by McCarthy et al. (2008a, b)

$[V_0 = 402.03\ (2)\ Å^3$, $K_0 = 136.5\ (14)$ GPa, and $K_0' = 3.4$ (4)] and Nestola et al. (2006) $[V_0 = 402.26\ (2)\ Å^3$, $K_0 = 134.0\ (7)$ GPa, and $K_0' = 4.4\ (1)$]. The kosmochlor
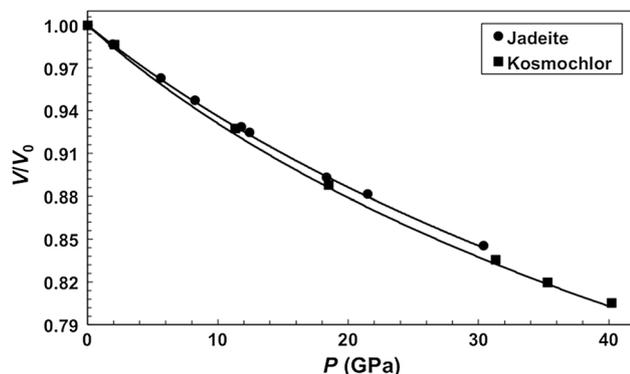
Fig. 2 Normalized unit-cell volumes versus pressure for jadeite and kosmochlor. Kosmochlor, with a larger cell volume $[V_0 = 420.0\ (3)\ Å^3]$ and smaller bulk modulus $[K_0 = 123\ (2)$ GPa, $K_0' = 3.61\ (9)]$, is more compressible than jadeite $[V_0 = 402.5\ (4), K_0 = 136\ (3),$ GPa, $K_0' = 3.61\ (9)]$, which is consistent with previous studies (Thompson and Downs 2004; McCarthy et al. 2008a, b) that clinopyroxene compressibility is primarily controlled by the occupancy of M1

K_0 value that we obtained is a little lower than the values reported by Origlieri et al. (2003) $[V_0 = 418.84\ (3)\ Å^3$, $K_0 = 134.0\ (7)$ GPa, and $K_0' = 3.7\ (6)]$ and Boffa Ballaran et al. (2009) $[V_0 = 418.76\ (2)\ Å^3$, $K_0 = 130.2\ (7)$ GPa, and $K_0' = 4.1\ (2)]$. P–V data and fitted curves are plotted in Fig. 1. The compressibility of jadeite and kosmochlor, expressed as V/V_0, is shown in Fig. 2. Unit-cell parameters for both minerals decrease with significant nonlinearity, with the exception of **b**, which, while decreasing the most rapidly of the three axes, exhibits the most linear trend (Fig. 3a–c). Unit-cell parameters **a** and **c** decrease at nearly identical rates for jadeite and kosmochlor, while **b** is more sensitive to composition with the rate of shortening, $d(x/x_0)/dP$, in kosmochlor decreasing approximately 1.1 times greater than in jadeite.

Unit-strain ellipsoids were constructed using cell parameters and STRAIN software (Ohashi 1982) to assess the degree of anisotropy between principal stress directions. In the pressure range of 0–30.4 (1) GPa, the unit-strain axial ratios for jadeite are 1.00:1.95:2.09. In the pressure range of 0–40.2 (1) GPa, the unit-strain axial ratios for kosmochlor are 1.00:2.15:2.43. The middle values represent strain symmetrically constrained to lie parallel to **b**. Strain
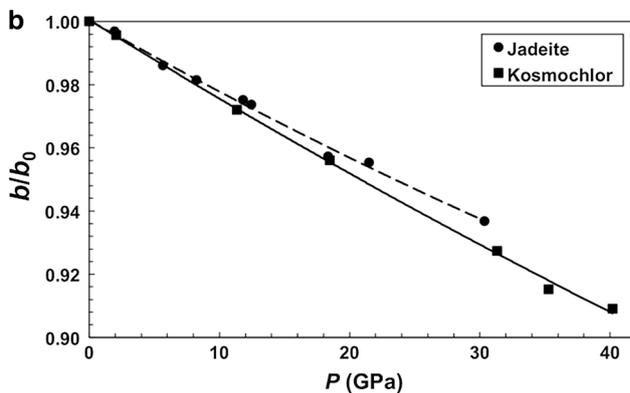
Fig. 3 Normalized axial lengths versus pressure. Trendlines are *dashed* for jadeite and *solid* for kosmochlor. Jadeite and kosmochlor compressibilities are essentially identical along **a** and **c**, while kosmochlor compresses more rapidly along **b**. This is consistent with previ-

ous suggestions that the compressibility of the entire unit cell and *b* axis is primarily controlled by the compressive strength of the $M1O_6$ chains (Thompson and Downs 2004; McCarthy et al. 2008a, b)

a

b
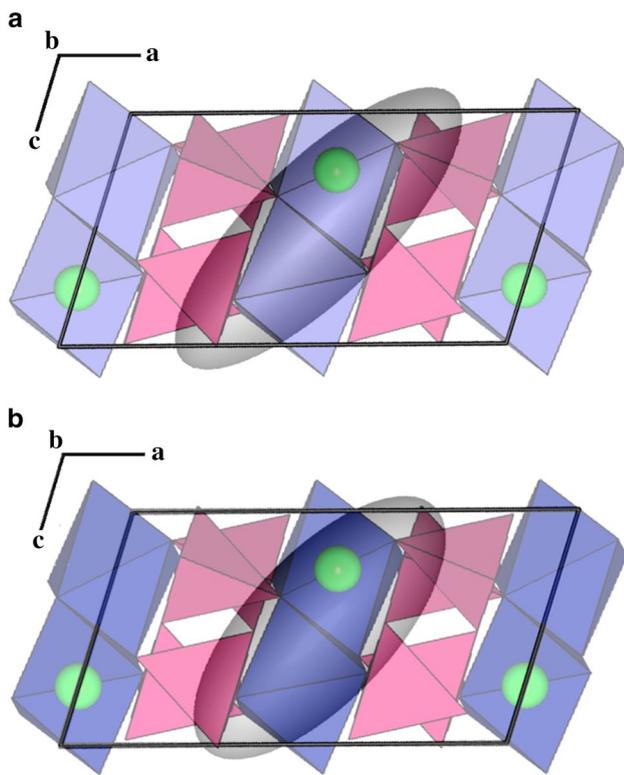
Fig. 4 Oriented unit-strain ellipsoid superimposed on the **a** kosmochlor and **b** jadeite structures at ambient pressure viewed down **b**. M2 (Na) is illustrated as a sphere

Table 5 Unit-strain ellipsoid parameters for jadeite and kosmochlor

Sample	ΔP (GPa)	Axes (GPa^{-1})($\times 10^2$)			Orientation
		ϵ_1	ϵ_2//b	ϵ_3	$\angle(\epsilon_3{}^\wedge c)$ (°)
Jadeite	30.4 (1)	0.107 (9)	0.208 (16)	0.222 (7)	30.5 (3)
Kosmo-chlor	40.2 (1)	0.093 (7)	0.200 (5)	0.226 (11)	28.3 (2)

ellipsoids are shown with respect to the ambient pressure crystal structure for both phases in Fig. 4. The axial values of the unit-strain ellipsoid and orientation of maximum strain directions are listed in Table 5. We compare our strain data with previous studies of jadeite to 8.31 GPa (Nestola et al. 2006) and 9.17 GPa (McCarthy et al. 2008a, b) and of kosmochlor to 6.80 GPa (Boffa Ballaran et al. 2009) and 9.28 GPa (Origlieri et al. 2003). Our results indicate that strain anisotropy in kosmochlor remains tri-axial (i.e. $\epsilon_3 > \epsilon_2 > \epsilon_1$) throughout the pressure range of study but undergoes an abrupt reduction from 1.00:1.88:2.15 at 11.3 (1) GPa to 1.00:1.74:1.89 at 18.5 (1) GPa, which may be associated with an M2-coordination change, as described in the next section. Strain in jadeite approaches oblate uniaxial ($\epsilon_3 \approx \epsilon_2 > \epsilon_1$) with a projected intersection of ϵ_2 and

ϵ_3 at ~40 GPa. Figure 5 illustrates the degree of anisotropy of the middle and maximum shortening directions, ϵ_2 and ϵ_3, respectively, normalized to ϵ_1, as a function of pressure.

Procrystal electron density distribution analysis indicates six Na–O bonds in both minerals at ambient conditions (Origlieri et al. 2003; McCarthy et al. 2008a, b). Sodium resides on a twofold symmetry axis, which constrains its coordination to an even number. At ambient conditions, Na is bonded to two O1, two O2, and two bridging O3 and symmetrically equivalent atoms, $O3_2$ and $O3_3$, following the nomenclature of Downs (2003). Compression data from previous studies (Origlieri et al. 2003; McCarthy et al. 2008a, b) were used to predict a $C2/c \rightarrow C2/c$ bonding transition at pressures of approximately 20 GPa when extrapolated $Na–O3_{1,4}$ and $Na–O3_{2,3}$ bonds shortened to the same length. Procrystal electron density analysis based on the data from the current study shows that Na in jadeite remains six-coordinated at 21.5 (1) GPa, while kosmochlor assumes eightfold coordination in between 9.28 (Origlieri et al. 2003) and 18.5 (1) GPa (Fig. 6). The longest Na–O "bonds" in kosmochlor at ambient conditions ($Na–O3_{1,4}$) appear to decrease with slight nonlinearity. At pressures greater than 31.3 (1) GPa, the longest Na–O bonds are, in fact, $Na–O3_{2,3}$. This crossover has also been observed in M2 (Ca–O) bonds in hedenbergite at ~4.5 GPa (Zhang et al. 1997). Although the large spacing of our pressure steps limits the resolution of this coordination change and compression trend in kosmochlor, an abrupt decrease in strain anisotropy between 11.3(1) and 18.5(1) GPa, as shown in Fig. 5a, suggests the transition occurs within this pressure region. Extrapolation of Na–O3 bond lengths in jadeite suggests that Na will assume eightfold coordination by at least 27.5 GPa, at which point $r(Na–O3_{1,4}) = r(Na–O3_{2,3})$. This is most likely an overestimate; however, as procrystal electron density analysis reveals that the coordination change in kosmochlor occurs while $Na–O3_{1-4}$ bonds are still longer than $Na–O3_{2,3}$.

The Al atom in jadeite and Cr atom in kosmochlor resides in an octahedral M1-site that remains six-coordinated with oxygen in both minerals throughout the pressure range of this study. A twofold symmetry axis runs through the M1 atoms maintaining three sets of two equivalent oxygen atoms. Polyhedral distortion is indexed using quadratic elongation, and bond angle variance measurements such that regular polyhedra have quadratic elongation values of 1, bond angle variance values of zero, and distorted polyhedra have quadratic elongation values greater than 1 and positive bond angle variance (Robinson et al. 1971). The distortion of the Al octahedra in jadeite remains relatively constant with pressure and shows little variation in the aforementioned distortion indices (Fig. 7). The Cr octahedron, however, becomes increasingly irregular with pressure above 18.5 (1) GPa. The mean octahedral angle
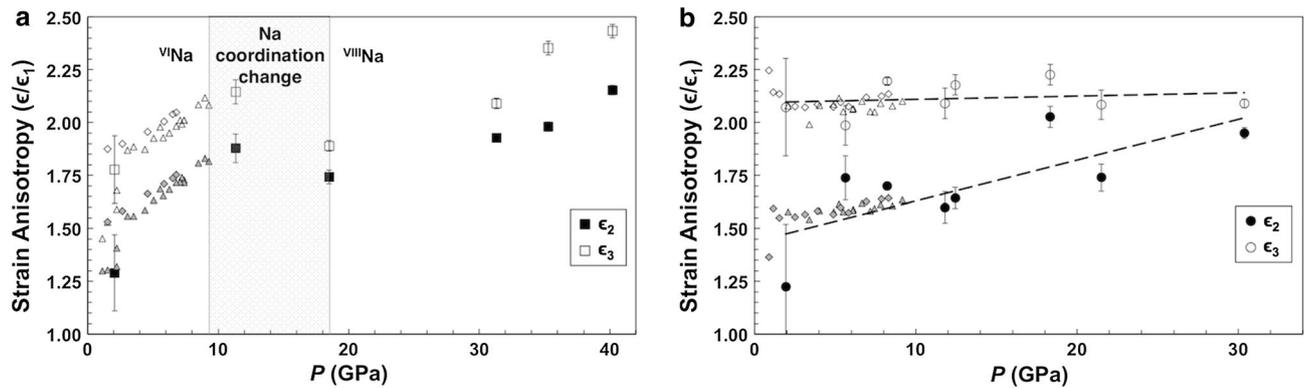
Fig. 5 Degree of anisotropic strain as a function of pressure in **a** kosmochlor and **b** jadeite. The kosmochlor strain ellipsoid is tri-axial to 40.2 (1) GPa with an abrupt decrease in anisotropy between approximately 11–18 GPa, which corresponds with the pressure interval that Na changes from six to eight coordination, as verified through procrystal electron density distribution analysis. The maximum strain direction, ϵ_3, in jadeite does not undergo additional compression

throughout the pressure range of study, relative to ϵ_1, while the intermediate (ϵ_2) continues to decrease. The jadeite strain ellipsoid is predicted to become oblate uniaxial ($\epsilon_2 = \epsilon_3$) at ~40 GPa. Large filled (ϵ_2/ϵ_1) and unfilled (ϵ_3/ϵ_1) data points are from this study, *small triangles* are from Origlieri et al. ([2003](#)) (kosmochlor) and McCarthy et al. ([2008a](#), [b](#)) (jadeite), *small diamonds* are from Boffa Ballaran et al. ([2009](#)) (kosmochlor) and Nestola et al. ([2006](#)) (jadeite)
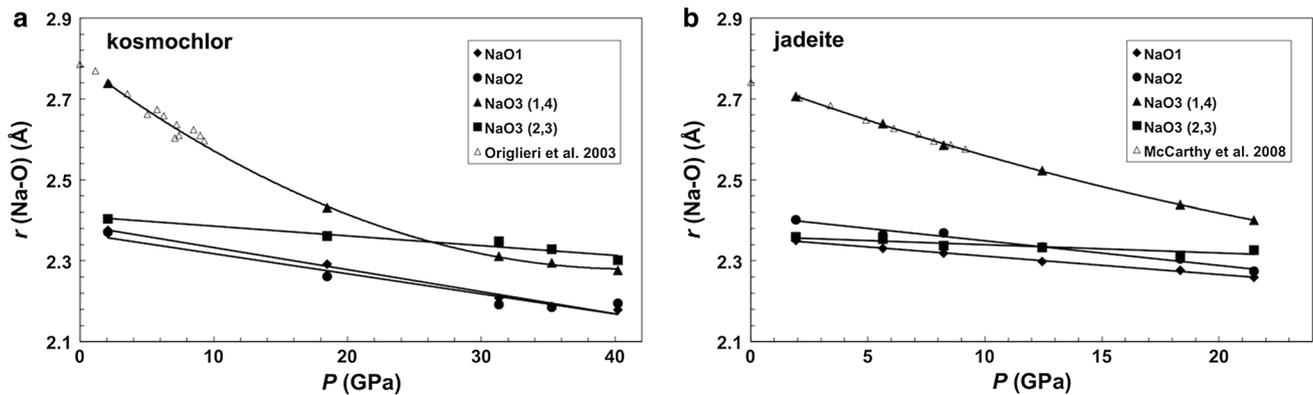
Fig. 6 Variation of Na(M2)–O bond lengths in **a** kosmochlor and **b** jadeite with pressure at 298 K. Na coordination in kosmochlor changes from 6 to 8 in between 9.28 (Origlieri et al. [2003](#)) and 18.5

(1) GPa. Na coordination in jadeite likely changes from six to eight between 24 and 28 GPa
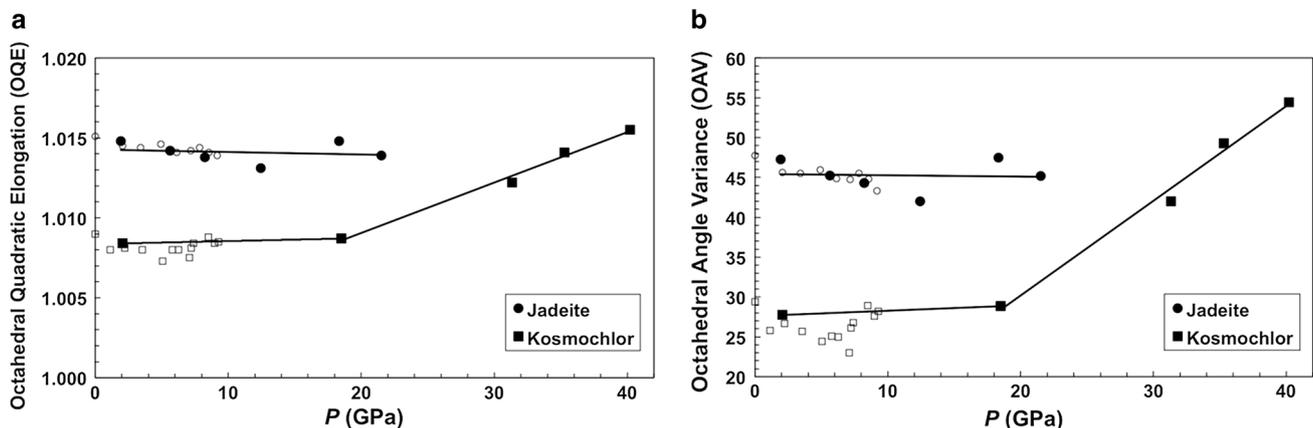
Fig. 7 M1 polyhedral distortion indices in jadeite and kosmochlor as a function of pressure: **a** octahedral quadratic elongation, **b** octahedral angle variance. M1 in kosmochlor becomes increasingly dis-

torted above 18.5 (1) GPa, while M1 distortion in jadeite remains constant. *White-filled circle* and *square* data points are from McCarthy et al. ([2008a](#), [b](#)) and Origlieri et al. ([2003](#)), respectively
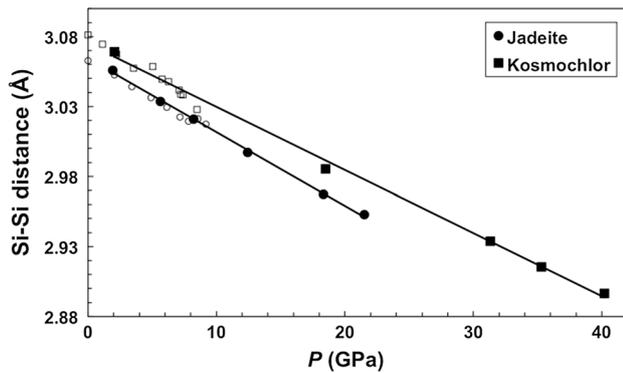
Fig. 8 Si–Si distance in a Si–O–Si linkage in jadeite and kosmochlor as a function of pressure. *White-filled circle* and *square* data points are from McCarthy et al. (2008a, b) and Origlieri et al. (2003), respectively

Fig. 10 SiO₄ tetrahedral volume in jadeite and kosmochlor as a function of pressure. Tetrahedral volume in kosmochlor decreases by approximately -3.5 (10^{-3}) Å³/GPa below approximately 32 GPa and increases to approximately -7.5 (10^{-3}) Å³/GPa above 32 GPa. Tetrahedral volume in jadeite decreases at a more consistent rate of approximately -4.4 (10^{-3}) Å³/GPa. *White-filled circle* and *square* data points are from McCarthy et al. (2008a, b) and Origlieri et al. (2003), respectively

Fig. 9 Tetrahedral chain kinking as measured by the O3–O3–O3 angle in jadeite and kosmochlor as a function of pressure. Tetrahedra reach a rotational limit at approximately 31 GPa while Si–Si distance (Fig. 8) decreases continuously. *White-filled circle* and *square* data points are from McCarthy et al. (2008a, b) and Origlieri et al. (2003), respectively

variance (OAV) in kosmochlor increases by a factor of 1.96, from 27.7456 at 2.1 (1) GPa to 54.4445 at 40.2 (1) GPa while the OAV in jadeite remains essentially unchanged at ~46.0 (Fig. 7b). This difference is likely due to Cr's electronic configuration involving *d*-orbitals such that the CrO₆ polyhedra are more easily deformed than AlO₆ polyhedra, in addition to the observation that the M2-bonding transition at pressures lower than 18.5 (1) GPa may result in a more rapid deformation of the M1-octahedron.

The distance between Si atoms decreases linearly as a function of pressure in both minerals, as shown in Fig. 8. In jadeite, this strain is complimented by a linear decrease in the ∠O3–O3–O3 of approximately $-0.56°$/GPa (Fig. 9). Rotation of SiO₄ tetrahedra in kosmochlor follows a similar trend (~$-0.59°$/GPa) to pressures of 31.3 (1) GPa at which point, increased chain kinking appears to become

energetically unfavorable, and the O3–O3–O3 angle remains constant at ~154.8° from 31.3 (1) to 40.2 (1) GPa (Fig. 9). These findings are consistent with the Webb and Jackson (1993) study on the pressure dependence on the elastic moduli of orthopyroxene, $(Mg_{0.8}Fe_{0.2})SiO_3$, in which they proposed that tetrahedral rotation would serve as the dominant compression mechanism in pyroxene only under a limited pressure range. Interestingly, the ceasing of tetrahedral chain kinking in kosmochlor is accompanied by a rapid increase in the rate of Si-tetrahedral compression from -3.5 (10^{-3}) Å³/GPa up to 31.3 (1) GPa to -7.5 (10^{-3}) Å³/GPa above 31.3 (1) GPa (Fig. 10). A similar discontinuity in both O3–O3–O3 angle and tetrahedral volume with increasing pressure was reported in orthoenstatite at lower pressure (~4 GPa) (Hugh-Jones and Angel 1994); however, this finding was refuted by Periotto et al. (2012) who re-investigated the crystal structure up to 9.4 GPa and did not measure the discontinuity, therefore attributing large refinement uncertainties to inaccurate conclusions regarding a change in compression mechanism. Nevertheless, the high-precision kosmochlor data of the present study exhibit a clear discontinuity in the rate of chain kinking and an increase by greater than a factor of two in the rate of Si-tetrahedral compression above 31 GPa. This "gridlock" of O3–O3–O3 angle and associated increase in tetrahedral compression may trigger a change in Si coordination from four to six at higher pressures, as observed in previous studies of high-pressure synthetic Na-clinopyroxenes which revealed Si to partially substitute into the octahedral M1-site (Angel et al. 1988; Konzett et al. 2005; Yang and Konzett 2005; Yang et al. 2009; Posner et al. 2012), or to transform to the *β*-phase with a conversion of

half of the corner-sharing SiO_4 tetrahedral chains into layers of edge-sharing SiO_6 octahedra as observed in natural diopside above 56.1 (1) GPa (Plonka et al. 2012).

Summary

We report a series of high-pressure crystal structure refinements on natural jadeite and synthetic kosmochlor at ambient temperature. Our results are consistent with previous studies that propose clinopyroxene compression to be primarily controlled by the occupancy of the M1-site (Thompson and Downs 2004; McCarthy et al. 2008a, b). An M2-coordination change from 6 to 8 occurs between 9.28 (Origlieri et al. 2003) and 18.5 (1) GPa in kosmochlor, while Na remains in octahedral coordination in jadeite up to 21.5 (1) GPa. Kosmochlor undergoes a change in compression mechanism at ~31 GPa indicated by discontinuities in both the rate of the Si tetrahedral chain rotation and tetrahedral compression. Below 31 GPa, O3–O3–O3 angle and tetrahedral volume in kosmochlor decrease linearly with pressure, whereas above 31 GPa chain kinking ceases and the rate of Si tetrahedral compression with pressure increases by more than a factor of two. Such structural measurements were not observed in jadeite most likely because the M2-coordination change did not occur within the pressure range of the present study. Additional high-pressure crystal structure refinements on jadeite at higher pressure, or other Na-pyroxenes such as aegirine, namansilite, or natalyite with Fe^{3+}, Mn^{3+}, and V^{3+} in M1, respectively, may reveal similar compression behavior and could be used to model pyroxene stability at transition zone pressures.

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