A silica-rich sodium pyroxene phase with six-coordinated silicon

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Phase transitions in minerals and melts that involve a change in the coordination of silicon from fourfold to sixfold are generally accompanied by large changes in material properties such as density, bulk modulus and elastic moduli. When such transformations occur within the Earth, these large changes in material properties can result in seismic discontinuities. The presence of six-coordinated silicon in minerals such as majorite garnet at upper-mantle pressures is therefore of crucial importance to an understanding of the properties of this region of the Earth. The silicate pyroxenes are also believed to comprise a significant portion of the upper mantle[1], and to provide a host for large cations such as sodium and calcium. It has long been assumed that silicon is restricted to the tetrahedral sites within the pyroxene structure. Here, however, we report the high-pressure synthesis and characterization of single crystals of a pyroxene of nominal stoichiometry $Na(Mg_{0.5}Si_{0.5})Si_2O_6$, which is the first pyroxene known to contain both tetrahedrally and octahedrally coordinated silicon.

The synthesis of $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene and its unit-cell parameters based upon X-ray powder diffraction were reported by Gasparik[2]. Single crystals were synthesized from a stoichiometric mix of high-purity SiO_2, MgO and $Na_2Si_2O_5$ at 1,600 °C and 150 kbar using a split-sphere anvil apparatus (USSA-2000). The run products consisted of more than 90% by volume of a silicon-rich pyroxene, together with a small quantity of stishovite (SiO_2) and glass. Electron microprobe analysis of the pyroxene showed it to be homogeneous with a composition of 98–99% $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ plus 1–2 mol% of an enstatite component ($Mg_2Si_2O_6$). As we were unable to detect any evidence of exsolution of clinoenstatite either optically or by X-ray diffraction we conclude that this component exists in solid solution.

A single crystal of the pyroxene with approximate dimensions $100 \times 50 \times 25$ µm was used for X-ray diffraction. Unit-cell parameters (Table 1) were determined from the positions of 20 centred reflections in the range $50° < 2\theta < 60°$ with Mo Kα radiation. They are consistent with those refined from powder diffraction data[2], and indicate a monoclinic unit cell similar to
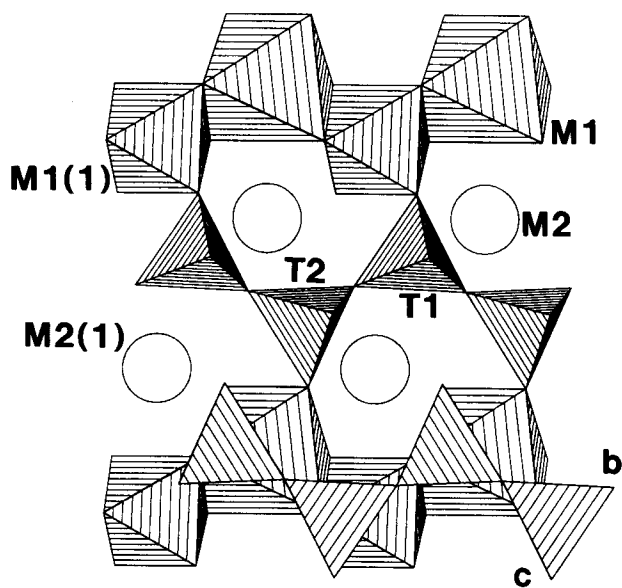

Fig. 1 A polyhedral representation[14] of a portion of the structure of $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ clinopyroxene viewed approximately normal to (100).

that of jadeite[3]. A hemisphere of intensity data was collected out to $\sin \theta / \lambda = 0.7$, corresponding to two asymmetric units of reciprocal space. Reflections of class $h0l$ with $h + l = 2n + 1$ were the only systematic absences, indicating that the space group of this pyroxene is either $P2/n$ or Pn; intensity statistics indicated a centrosymmetric space group, and thus $P2/n$. The 2,408 symmetry-allowed reflections that were measured were reduced to structure factors and averaged in Laue group $2/m$ with $R_{int} = 2.4\%$ to give 1,137 symmetry-independent reflections, of which 913 with $F > 3\sigma_F$ were included in the refinements. No absorption correction was made as $\mu_{calc} = 11.2$ cm^{-1}.

Least-squares refinements were carried out with RFINE4[4]. The atomic coordinates of an omphacite[5] refined in space group $P2/n$ were used as a starting model, with Na assigned to both the M2 and M2(1) sites, Mg to M1, and Si to M1(1) and the tetrahedral sites. Complex scattering factors for neutral atoms were taken from International Tables[6]. Initial refinements carried out with these site assignments converged smoothly to $Ru \equiv \Sigma ||F_0| - |F_c|| / \Sigma |F_0| = 0.045$, $Rw \equiv \Sigma \sigma_F^{-2} ||F_0| - |F_c||^2 / \Sigma \sigma_F^{-2} |F_0| = 0.039$, goodness of fit = 1.55 with isotropic temperature factors, and to $Ru = 0.036$, $Rw = 0.036$, goodness of fit = 1.34 with anisotropic thermal parameters for all atoms. Attempts to refine the site distribution subject to the chemistry indicated by the probe analysis (that is, with 2 mol% $Mg_2Si_2O_6$)

Table 1 Crystallographic data for $NaMg_{0.5}Si_{0.5}Si_2O_6$ pyroxene

	Occ.	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
M1	Mg	0.7500	0.6549(2)	0.2500	0.0017(2)	0.0022(2)	0.0041(6)		0.0005(3)		0.56
M1(1)	Si	0.7500	0.8469(2)	0.7500	0.0015(1)	0.0013(2)	0.0036(5)		0.0009(2)		0.40
M2	Na	0.7500	0.0513(2)	0.2500	0.0034(2)	0.0023(3)	0.0060(7)		0.0006(4)		0.83
M2(1)	Na	0.7500	0.4567(3)	0.7500	0.0056(3)	0.0025(3)	0.0091(8)		-0.0011(4)		1.30
T1	Si	0.0447(1)	0.8486(1)	0.2270(2)	0.0012(1)	0.0014(1)	0.0035(3)	-0.0001(1)	0.0006(1)	-0.0002(2)	0.39
T2	Si	0.0372(1)	0.6652(1)	0.7355(2)	0.0012(1)	0.0016(1)	0.0039(3)	-0.0000(1)	0.0010(1)	0.0001(2)	0.40
O1(1)		0.8620(3)	0.8443(3)	0.1017(4)	0.0012(3)	0.0025(3)	0.0038(8)	-0.0001(2)	0.0007(4)	0.0002(4)	0.50
O1(2)		0.8567(3)	0.6934(3)	0.6562(5)	0.0012(3)	0.0021(3)	0.0030(8)	0.0002(2)	0.0001(4)	-0.0001(4)	0.46
O2(1)		0.1234(3)	0.0146(3)	0.3077(5)	0.0020(3)	0.0018(3)	0.0053(9)	-0.0005(2)	0.0010(4)	-0.0004(4)	0.57
O2(2)		0.0982(3)	0.4950(3)	0.7911(5)	0.0022(3)	0.0019(3)	0.0073(9)	0.0005(2)	0.0012(4)	0.0001(4)	0.68
O3(1)		0.1128(3)	0.7665(3)	0.0119(5)	0.0015(3)	0.0026(3)	0.0050(9)	-0.0001(2)	0.0009(4)	-0.0012(4)	0.58
O3(2)		0.0930(3)	0.7527(3)	0.5070(5)	0.0016(3)	0.0025(3)	0.0043(9)	-0.0002(3)	0.0006(4)	0.0007(4)	0.57

Diffraction experiments with Rigaku AFC-5 diffractometer, rotating anode generator, Mo Kα_1 radiation, graphite monochromator, $\lambda = 0.7093$ Å, scan mode $\omega - 2\theta$, ambient temperature and pressure. $a = 9.418$ (1)* Å; $b = 8.647$ (1) Å; $c = 5.274$ (1) Å; $\beta = 108.13$ (1)°; $V_{cell} = 408.2$ (1) Å^3. Space group $P2/n$; $Z = 4$; molecular mass = 201.4 $\rho_{calc} = 3.28$ g cm^{-3}.
* Numbers in parentheses are the estimated standard deviation in the last quoted decimal place.

Table 2 Interatomic distances (Å)

M1-O1(1)	2.219 (3) [2]	M1(1)-O1(1)	1.826 (2) [2]
M1-O1(2)	2.090 (2) [2]	M1(1)-O1(2)	1.824 (2) [2]
M1-O2(2)	1.991 (3) [2]	M1(1)-O2(1)	1.782 (3) [2]
Average	2.100	Average	1.811
QE	1.035	QE	1.004
M2-O1(1)	2.333 (3) [2]	M2(1)-O1(2)	2.398 (3) [2]
M2-O2(1)	2.336 (2) [2]	M2(1)-O2(2)	2.434 (3) [2]
M2-O3(2)	2.350 (3) [2]	M2(1)-O3(1)	2.442 (3) [2]
M2-O3(1)	2.677 (3) [2]	M2(1)-O3(2)	2.923 (3) [2]
Average (6)	2.340	Average (6)	2.425
Average (8)	2.424	Average (8)	2.549
QE (6)	1.284	QE (6)	1.417
T1-O1(1)	1.641 (2) [1]	T2-O1(2)	1.637 (2) [1]
T1-O2(1)	1.611 (3) [1]	T2-O2(2)	1.573 (3) [1]
T1-O3(1)	1.629 (2) [1]	T2-O3(1)	1.660 (2) [1]
T1-O3(2)	1.630 (2) [1]	T2-O3(2)	1.642 (2) [1]
Average	1.628	Average	1.628
QE	1.005	QE	1.006

QE is the quadratic elongation as defined by Robinson et al.[13]. Figures in square brackets indicate bond multiplicities.

did not result in any significant deviation from the fixed unit site occupancies used in the final refinement reported here.

The pyroxene structure consists of single tetrahedral chains that cross-link bands of octahedrally coordinated cation sites (Fig. 1). Between these bands are eight-coordinated sites which normally accommodate larger cations such as Ca and Na in the monoclinic pyroxenes. End-member sodium pyroxenes, $NaM^{3+}Si_2O_6$, crystallize in space group $C2/c$, in which all of the octahedral sites (M1) are symmetrically equivalent and all of the Na sites (M2) are also equivalent to one another. The major novel features of the structure of $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene are due to to the presence of silicon in octahedral coordination. The differences in size and charge between Si and Mg result in ordering of these two cations within the M1 sites, while M2 remains occupied by Na. As in omphacitic pyroxenes, cation ordering causes a reduction of the symmetry of the structure from $C2/c$ to $P2/n$. In contrast to omphacites, the size difference between the cations in the M1 sites (Mg and Si) is so great as to result in total, rather than partial, ordering, as indicated by the different sizes of the M1 and M1(1) sites. The average M1-O bond distance of 2.100 Å is fairly typical of that found for the Mg octahedra in other pyroxene structures[7], while the M1(1)-O mean distance of 1.811 Å is similar to that found for octahedrally coordinated silicon in structures such as stishovite[8], $K_2Si_4O_9$ (ref. 9) and $MgSiO_3$ ilmenite[10] and perovskite[11]. However, severe distortions of the coordination polyhedra around all of the other cations are required in order for the pyroxene structure to accommodate such a small octahedral cation as Si. For example, the O1(1)-O1(2) edge which is common to both Mg and Si octahedra is only 2.460 Å, compared with a mean O-O edge length around the remainder of the Mg coordination polyhedron of 3.056 Å. This distortion is also reflected in the large quadratic elongation of this octahedron,

1.035, which is comparable with typical values of around 1.01 for Mg in M1 octahedra in other pyroxenes[7]. The sodium coordination polyhedra are also distorted compared to other Na end-member pyroxenes, with the mean M2-O bond being the smallest ever reported, and the mean M2(1)-O distance being longer than that in any of the naturally occurring Na-pyroxenes.

This structure refinement shows that, despite the severe distortions placed on the structure, silicon can be accommodated in substantial amounts in the octahedral sites of clinopyroxenes. There are several possible consequences of this result. The first is that the existence of pyroxenes with a silicon content in excess of 2.00 atoms per six oxygens cannot be excluded on crystal-chemical grounds, especially in those pyroxenes that already contain small cations such as Al and Mg on their M1 sites. Indeed, preliminary experiments indicate significant solubilities of a $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ component within enstatite, diopside and jadeite at mantle pressures. These substitutions would be expected to change the material properties such as the densities and elasticities of these mantle pyroxenes.

The end-member pyroxene itself was synthesized at 100 and 150 kbar and is likely to be stable to at least 200 kbar. Were the excess of silicon and the presence of sodium the only necessary conditions for the formation of $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene it would therefore replace stishovite as the most likely candidate for the silica-rich phase in the Earth's upper mantle. However, it appears that the most important condition for the stability of this silica-rich sodium pyroxene is the excess of sodium with respect to aluminium, a situation rarely found in nature. An exception may occur at the high-pressure limit of pyroxene stability, where pyroxene transforms to garnet. The incorporation of excess silica could stabilize the pyroxene and expand its stability field to higher pressures. Such behaviour would be analogous to the increase in stability of Ca-Tschermak pyroxene $(CaAl_2SiO_6)$ caused by incorporation of a Ca-Eskola component $(Ca_{0.5}AlSi_2O_6)$ in solution, which incidentally results in a pyroxene with a relative silica excess due to vacancies in the M2 site[12].

The synthesis of single crystals of $Na(Mg_{0.5}Si_{0.5})Si_2O_6$ pyroxene was performed in the Stony Brook High-Pressure Laboratory which is jointly supported by NSF and the State University of New York, and X-ray diffraction work at the Geophysical Laboratory was supported by NSF and by the Carnegie Institution of Washington.

1. Takahashi, E. & Ito, E. in *High-Pressure Research in Mineral Physics* (eds Manghnani, M. H. & Syono, Y.) (American Geophysical Union, Washington DC, 1987).
2. Gasparik, T. *Eos* **69**, 500 (1988).
3. Prewitt, C. T. & Burnham, C. W. *Am. Miner.* **51**, 956-975 (1966).
4. Finger, L. W. & Prince, E. *Natn. Bur. Stand. Tech. Note* 854 (1974).
5. Curtis, L. *et al. Can. Mineralogist* **13**, 62-67 (1975).
6. *International Tables for X-ray Crystallography* Vol. 4 (Kynoch, Birmingham, 1974).
7. Smyth, J. R. & Bish, D. L. *Crystal Structures and Cation Sites of the Rock-Forming Minerals* (Allen and Unwin, Boston, 1988).
8. Sinclair, W. & Ringwood, E. A. *Nature* **272**, 714 (1978).
9. Swanson, D. K. & Prewitt, C. T. *Am. Miner.* **68**, 581-585 (1983).
10. Horiuchi, H., Hirano, M., Ito, E. & Matsui, Y. *Am. Miner.* **67**, 788-793 (1982).
11. Horiuchi, H., Ito, E. & Weidner, D. J. *Am. Miner.* **72**, 357-360 (1987).
12. Gasparik, T. *Geochim. cosmochim. Acta* **48**, 2537-2545 (1984).
13. Robinson, K., Gibbs, G. V. & Ribbe, P. H. *Science* **172**, 567-570 (1971).
14. Fisher, R. X. *J. appl. Crystallogr.* **18**, 258-262 (1984).