

March 6th 2013 Revision 2

The structure of (Ca,Co)CoSi₂O₆ pyroxenes and the Ca-M²⁺ substitution in
(Ca,M²⁺)M²⁺Si₂O₆ pyroxenes (M²⁺ = Co, Fe, Mg)

Luciana Mantovani¹, Mario Tribaudino¹, Francesco Mezzadri², Gianluca Calestani²,
Geoffrey Bromiley³

¹Dipartimento di Fisica e Scienze della Terra “Macedonio Melloni”, Parco Area delle Scienze
157/A, 43124 Parma, Italy

²Dipartimento di Chimica, Parco Area delle Scienze 17/A, 43124 Parma, Italy

³ School of GeoSciences, University of Edinburgh, Grant Institute, West Mains Road, Edinburgh
EH9 3JW, UK

Abstract

The crystal structure of three *C2/c* clinopyroxenes with composition (Ca_{0.8}Co_{0.2})CoSi₂O₆, (Ca_{0.6}Co_{0.4})CoSi₂O₆ and (Ca_{0.4}Co_{0.6})CoSi₂O₆ was refined down to R₄₆= 2.6% by single crystal X-ray diffraction. The crystals were synthesized at P = 3GPa by cooling from 1500 to 1200°C in a piston cylinder apparatus. At the end of the refinement cycles electron density residuals (up to 2.1 e⁻) were observed close to the M2 site and related to the site splitting of Ca and Co in the M2 polyhedron in the two subsites M2 and M2'. Split refinement significantly improved the agreement factor and decreased the uncertainty in the atomic coordinates. Similar features were found in (Ca, Mg)MgSi₂O₆ and (Ca, Fe)FeSi₂O₆ intermediate pyroxenes.

The average structural changes related to the cation substitution at the M2 site in (Ca, Co)CoSi₂O₆, (Ca, Mg)MgSi₂O₆ and (Ca, Fe)FeSi₂O₆ pyroxenes are similar: the T tetrahedron becomes more regular, the difference between M1-O bond lengths increases, and the M2-O3 bond lengths with the furthestmost O3 oxygens become longer. The changes in the M2-O bond distances are, however, not linear, and they are higher for more increased substitution. The largest structural deformation occurs on the (010) plane, with higher deformation at about 60° from the c axis for any composition. The orientation of the deformation ellipsoid is most related to a shift in tetrahedral chains. The scalar deformation for the cation substitution, ε_s, is linearly related to the cation radius of the average M2

38 site (IR^{M2}), i.e. the deformation is higher as the cation size decreases, following the equation: $\epsilon_s = -$
39 $0.0072(12)IR^{M2} + 0.0082(13)$, $R^2 = 0.75$. Increasing deformation with cation substitution is supported
40 as the major limiting factor for solid solution.

41 The displacement parameters for unsplit M2, O2 and O3 atoms increase up to the intermediate
42 composition, indicating a local configuration for the M2 polyhedron centered by Ca and Co.
43 However no significant change in U_{eq} of the O3 atom is observed up to 20% substitution of the
44 smaller cation in the M2 site. Comparison with Raman spectral data suggests that local chain
45 structural configurations occur only for the substitution of the smaller cation in the M2 site higher
46 than 20%, and that the substitution mechanism is different for $C2/c$ clinopyroxenes with lower and
47 higher Ca content.

48

49 Keywords: $CaCoSi_2O_6$; single crystal X-ray diffraction; high pressure single crystal synthesis;
50 pyroxene.

51

52

Introduction

53 Pyroxenes are chain silicates and are among the major constituents of the lower crust and
54 the upper mantle. Their structural and crystal chemical behavior provides a simple model to test
55 relations between structure and composition within a silicate family. Moreover it was recently
56 found that pyroxene is a new class of ferroics (Jodlauk et al. 2007), which has now opened new
57 interest in understanding the structural details of pyroxenes (Streltsov and Khomskii 2008,
58 Redhammer et al. 2008, 2009, 2011).

59 The general formula of pyroxenes is $M_2M_1Si_2O_6$. In the holotypic structure of the
60 pyroxene diopside ($CaMgSi_2O_6$) Ca occupies an 8-fold coordinated M2 polyhedron, and Mg a
61 slightly distorted M1 octahedron. The Mg for Ca substitution in the M2 site of diopside is found in
62 natural pyroxenes, but, due to the different cation radius of Ca and Mg, it is limited by a wide and
63 asymmetric miscibility gap (Gasparik 1990). Only at high pressure and temperature, over a narrow
64 hypersolvus field, extended solid solution is possible (Newton et al. 1979). The iron equivalent of
65 diopside is hedenbergite, $CaFeSi_2O_6$. Again, replacement of Fe for Ca is possible at high pressure,
66 but limited by a miscibility gap, albeit more narrow (Lindsley and Munoz 1969, Ohashi et al. 1975).
67 The solid solutions between Ca, Mg and Fe represent almost completely the composition of the
68 most abundant “quadrilateral” pyroxenes.

69 The detailed structure changes involved in the above substitutions were investigated in
70 several papers on the $(Ca, Mg)MgSi_2O_6$ and $(Ca, Fe)FeSi_2O_6$ intermediate pyroxenes (hereafter
71 respectively Ca-Mg and Ca-Fe pyroxenes) (Ohashi and Finger 1976, Bruno et al. 1982, Tribaudino

72 et al. 1989, Tribaudino et al. 2002, Tribaudino and Nestola 2002, Nestola and Tribaudino 2003,
73 Tribaudino et al. 2005a for Ca-Mg pyroxenes, Burnham 1966, Ohashi et al. 1975, Nestola et al.
74 2007 for Ca-Fe pyroxenes). It was found that the structure of the intermediate pyroxenes is different
75 from a linear combination of the end members as: 1) changes in structure with composition are not
76 linear; 2) a phase transition occurs between Ca-rich $C2/c$ to Ca poor $P2_1/c$ pyroxenes; 3)
77 displacement parameters of several atoms (M2, O2 and O3) are significantly larger in intermediate
78 solid solutions, due to positional disorder, whereas in other atoms they are not (Ohashi et al. 1975,
79 Tribaudino et al. 1989, Tribaudino and Nestola 2002, Nestola and Tribaudino 2003).

80 In spite of the wealth of experimental data, a model relating the different cation substitution
81 in the M2 site, the structural deformation and the extension of the solid solution was not provided.

82 Here the results of single crystal refinements on three (Ca, Co)CoSi₂O₆ clinopyroxene solid
83 solutions (hereafter Ca-Co) representing the Ca-Co analogues of the Ca-Fe and Ca-Mg ones will be
84 reported. The structural changes in Ca-Co pyroxenes will be examined and compared with those
85 occurring in Ca-Mg and Ca-Fe pyroxenes. Local and average structures will be discussed aiming to
86 a comprehensive model of solid solutions in pyroxenes. In broader sense this paper aims to model
87 the structural features that limit the solid solution in quadrilateral monoclinic pyroxenes, which are
88 the basis for two pyroxene thermometry (Lindsley 1983)

89

90

91

Experimental

92

Synthesis

93 Three samples of pyroxene with composition (Ca_{0.8}Co_{0.2})CoSi₂O₆, (Ca_{0.6}Co_{0.4})CoSi₂O₆ and
94 (Ca_{0.4}Co_{0.6})CoSi₂O₆ (hereafter Ca_{0.8}Co_{0.2}, Ca_{0.6}Co_{0.4} and Ca_{0.4}Co_{0.6} respectively) were synthesized
95 using as starting material a stoichiometric mixture of Co₃O₄, CaCO₃ and SiO₂. The mixtures were
96 previously annealed in an electric furnace for 12 hours at T = 1000°C and room pressure.
97 Decarbonation and reduction of the Co³⁺ in Co₃O₄ to Co²⁺ were obtained during the synthesis. An
98 assemblage of cristobalite, Co-pyroxene, Co-olivine and Co-akermanite was obtained, with
99 cristobalite and Co-akermanite as metastable phases. This assemblage, finely ground, was put in a 5
100 mm inner diameter, 10 mm long, Pt capsule with 20 wt% distilled water to aid crystal growth, and
101 welded shut. The capsules were placed into a 0.5 inch pyrex-talc piston-cylinder assembly
102 containing an internal graphite furnace. The experiments were run at P = 3 GPa; the sample was
103 first heated at 1500°C for 30 minutes and then cooled from 1500°C to 1200°C for Ca_{0.8}Co_{0.2} and
104 Ca_{0.6}Co_{0.4} and to 1350°C for Ca_{0.4}Co_{0.6}, with subsequent annealing for 6 hours. The higher
105 temperature of annealing of sample Ca_{0.4}Co_{0.6} was chosen in order to avoid exsolution. The

106 temperature was measured with a Pt-Pt10%Rh thermocouple (for more details see Bromiley et al.
107 2004). An assemblage of Co-pyroxene crystals sized up to 600 μm was obtained, among which
108 those examined for single crystal XRD were selected by sharp optical extinction. No glass was
109 found in any sample after the synthesis. XRD powder diffraction and SEM-EDS characterization
110 confirmed that pyroxene is the only phase in all samples, with stoichiometric compositions.

111

112 **X-ray single crystal refinement**

113 Single crystal X-ray diffraction was performed using a Smart-Apex CCD device, measuring
114 full reflection sphere up to $2\theta_{\text{max}} = 64^\circ$. The intensity data were corrected for absorption using the
115 SADABS program (Sheldrick 1996). The $C2/c$ space group was found for all the samples by the
116 analysis of reflection extinctions and intensities: the intensities of $h+k$ odd reflections, which would
117 indicate switch to the P lattice were always lower than 3σ . Weighted structural anisotropic
118 refinements were performed using the SHELX-97 program (Sheldrick 1997), within the WinGX
119 suite (Farrugia 1999) and the coordinates of $\text{CaCoSi}_2\text{O}_6$ by Ghose et al. (1987) as starting model.
120 Full occupancy of Co and Si in the M1 and T sites was confirmed by site refinement. In the M2 site
121 mixed occupancy of Ca and Co was present; therefore the site occupancy of the M2 for each
122 composition was determined from the EDS analysis, ascribing all Ca in the M2 site, and filling the
123 remaining with Co.

124 After the first cycles of full matrix refinements significant positive and negative peaks in
125 the Fourier difference map were found, located along the diad axis at $\approx 0.7 \text{ \AA}$ from the M2 site. In
126 the $\text{Ca}_{0.8}\text{Co}_{0.2}$ and $\text{Ca}_{0.6}\text{Co}_{0.4}$ samples the positive peaks of 2.1 and 1.9 electrons, respectively, are
127 located at 0.21 y/b. This position matches that of the residual found in $C2/c$ clinopyroxenes when
128 Fe^{2+} and/or Mg exchange for Ca (Bruno et al. 1982; Rossi et al. 1987; Tribaudino et al. 1989, Boffa
129 Ballaran et al. 1998). Similar residuals were found by Tabira et al. (1992) in a study on $C2/c$
130 clinopyroxenes in the system $\text{CaMgSi}_2\text{O}_6$ (Di)– $\text{CaCoSi}_2\text{O}_6$ (CaCoPx), and related to a small content
131 of cobalt in the M2 site, likely in excess of the $\text{CaMgSi}_2\text{O}_6$ – $\text{CaCoSi}_2\text{O}_6$ stoichiometry. In contrast,
132 in $\text{Ca}_{0.4}\text{Co}_{0.6}$ at the same position there is a negative peak of -1.9 electrons, whereas the positive
133 peak of 1.2 electrons is located at 0.33 y/b. Electron density maps near the M2 site show in our
134 samples an asymmetric distribution along the diad axis (Fig. 1); the asymmetry is inverted between
135 $\text{Ca}_{0.6}\text{Co}_{0.4}$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$.

136 The interpretation provided by previous works (Rossi et al., 1987; Tribaudino and Nestola,
137 2002) on the observed residuals can also apply to ours: Ca and the smaller cation in the M2 cavity
138 split in two different positions along the diad axis, , respectively the M2 and M2' subsites; the
139 observed residuals occur when split electron densities are refined as a single atom. If the cation

140 smaller than Ca is present in minor amounts the asymmetric electron distribution is most evident; if
141 Ca and the smaller cation are present at similar amounts, so that the electron distribution of the two
142 cations is similar, a large apparent displacement parameter is found, although, as shown in Fig. 1,
143 some asymmetry in the Fourier map is still present. Coherently, the size of the displacement
144 parameters of the M2 site is almost doubled between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.6}\text{Co}_{0.4}$ (Fig. 2) but it is
145 similar between $\text{Ca}_{0.6}\text{Co}_{0.4}$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$ (Table 2).

146 We performed then a split refinement of the M2 site, with the new M2 site occupied by Ca
147 and the M2' subsite by Co. As indicated by Rossi et al. (1987), Ca was located in a position at y/b
148 0.30, close to the center of the M2 polyhedron. This is close to the position of the M2 site after the
149 unsplit refinements in $\text{Ca}_{0.8}\text{Co}_{0.2}$ and $\text{Ca}_{0.6}\text{Co}_{0.4}$, and also to the positive maximum at y/b 0.33 for
150 $\text{Ca}_{0.4}\text{Co}_{0.6}$. The Co in M2' was located at the position of the maximum at y/b 0.21 in $\text{Ca}_{0.8}\text{Co}_{0.2}$ and
151 $\text{Ca}_{0.6}\text{Co}_{0.4}$, and at the position of the M2 site in $\text{Ca}_{0.4}\text{Co}_{0.6}$. This was done because the higher
152 electron contribution of Co in $\text{Ca}_{0.4}\text{Co}_{0.6}$, indicates that the refined M2 position in $\text{Ca}_{0.4}\text{Co}_{0.6}$ mostly
153 represents that of Co. After few refinement cycles, allowing Ca and Co to vary independently their
154 coordinate along the diad axis, two distinct atomic positions at y/b 0.30 and 0.26 were found,
155 occupied respectively by Ca and Co. In agreement with Rossi et al. (1987), we will refer to the Ca
156 site as M2 and to the Co one as M2'. The refinement was done with Ca anisotropic and Co isotropic
157 in $\text{Ca}_{0.8}\text{Co}_{0.2}$, and with Ca and Co both anisotropic in $\text{Ca}_{0.6}\text{Co}_{0.4}$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$. A significant
158 decrease in the agreement factor and in the uncertainty of other atomic positions was observed;
159 moreover residuals became featureless. Although this procedure gave better phasing and therefore
160 more reliable positions of the other atoms, the M2 and M2' peaks after the split refinements are at a
161 distance between 0.3 and 0.4 Å, lower than the resolution of the present refinement data (0.67 Å),
162 and the reliability of the M2 and M2' split positions is lower than that of the unsplit M2.

163 Tables from 1 to 4 report refinement parameters, structural coordinates, atomic distances
164 and equivalent displacement factors. For the M2-M2' sites the M2 position and M2-O bond
165 distances before the split refinement were also reported, whereas for other atoms only those
166 obtained after the split refinement model. CIF files relevant to the best refinements in the M2 split
167 and unsplit models for each composition are deposited online.

168

169

Results

170

Average structure

171

172

173

M2 polyhedron. The M2 is a distorted 8-fold coordinated polyhedron (Fig. 3; atomic
crystallographic nomenclature as in Burnham et al. 1967). On one side the M2 cation is linked to
four O3 oxygens, namely those bridging the tetrahedra within the silicate chains. On the other side

174 two O1 oxygens are shared with the M1 polyhedron, while in between there are the O2 atoms. In
175 *C2/c* pyroxenes the M2 cation is constrained by symmetry to lie on the diad axis, but can move
176 along the axis without breaking the symmetry; the M2-O2 bonds are almost normal to the diad axis.
177 The Co for Ca substitution into the M2 site increases the average distance with the O3 chain
178 bridging oxygen and decreases that with O1 and O2 (Fig. 4), changing the average coordination of
179 M2 towards a 4+2 one like it was found in augitic pyroxenes (Domeneghetti et al. 2005). The
180 polyhedral volume decreases also. The distances with O3 and O1 change for the shift of the average
181 M2 position along the diad axis, towards the O1 oxygen. The shift of the average M2 site is by as
182 much as 0.268 Å between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$ towards the O1 oxygen, and the bond distances
183 change likewise. The M2 shift occurs while the size of the polyhedron along the diad axis does not
184 decrease: the distance between the glide plane at 0.5 y/b, which corresponds to the average position
185 of the O3 oxygen, and the position of the O1 along the b axis (y/b of the O1, being the two O1
186 oxygen symmetry equivalent, and fixed to the same y/b coordinate by the diad axis in *C2/c*
187 symmetry) shows only the negligible decrease of 0.007 Å between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$.

188 The average bond lengths represent an average situation: from the results of the refinements
189 Co and Ca are split in the two subsites M2 and M2' into the M2 polyhedron, each with its own
190 bond distances, but both lying on the diad axis. As shown in Fig. 5, M2-O and M2'-O distances
191 change little with composition, with the exception of the M2-O2 and M2'-O2 distances that
192 decrease both by the same extent. The M2 configuration is always eight fold, but in the M2' the O3
193 distances are out of coordination, and a strongly asymmetric fourfold like configuration is found
194 (Rossi et al. 1987). The positions and the y/b coordinate of the M2 and M2' site, at approximately
195 y/b 0.30 and 0.26, correspond to those of the M2 site in diopside and clinoenstatite for the Ca-Mg
196 (Cameron et al. 1973, Ohashi and Finger 1976), or in hedenbergite and clinoferrosilite for the Ca-
197 Mg pyroxenes (respectively Nestola et al. 2007 and Burnham 1966), and can be here interpreted as
198 local configurations for the Ca (M2) and Co (M2') atoms.

199 Changes in the position of the M2 cation along the diad axis do not account for the decrease
200 in the M2-O2 distance, being the bond almost normal to the axis. An approach of the O2 atom
201 towards the M2 site takes place (Table 4), and is related to a tetrahedral tilting, as it has been
202 observed in diopside-enstatite pyroxenes (Bruno et al. 1982). The decrease in the M2-O2 distance
203 accounts for the significant decrease in the M2 polyhedral volume, by 1.3 Å³ (5 %) between
204 $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$: a linear change between M2-O2 and volume is observed in Fig. 6. To
205 note, volume changes less in the first part of the series, but more with higher Co content, and the
206 same trend, albeit shifted by the difference in end members occurs in Ca-Mg and Ca-Fe pyroxenes.
207 Also the changes in the M2-O distances are very similar in the three series, dictated solely by the

208 changes in the average ionic radius and position, apart from the shorter M2-O3 distance, where
209 significant differences exist already in the Ca rich end members and are increased by substitution of
210 the smaller cation (Fig. 7).

211

212 **M1 polyhedron.** In the Ca-Co series the M1 site is always occupied by Co. As expected, the
213 volume and the average bond lengths change little within the series, although in $\text{Ca}_{0.4}\text{Co}_{0.6}$ the M1-
214 O average bond length and M1 polyhedral volume are significantly higher. Individual bond lengths
215 and angles show instead a continuous change: the M1-O1A2 distance decreases with Ca, down to
216 the value of the shorter M1-O2 distance, whereas the M1-O1A1, which is the longest M1-O
217 distance, shows a further increase (Fig. 3).

218 The changes in M1-O bond distances are interpreted as a secondary effect of the shift of the
219 cation in the M2 site towards the O1A1, B1 atoms. As shown in Fig. 8, when Ca is substituted by a
220 smaller cation, the difference between the longer and shorter M1-O bonds increases at the same rate
221 in Ca-Co, Ca-Mg and Ca-Fe pyroxenes. The shift of the M2 average position along the diad axis
222 affects the distance of the M2 to the three M1 cations whose polyhedron shares an edge with the
223 M2 polyhedron (Figs. 3 and 4). One of the above M1 cations faces M2 along the diad axis, at a
224 distance of about 3.5 Å, the two others, M1(1) in Burnham et al. (1967) nomenclature, are
225 symmetry equivalent at a distance of about 3.2 Å with M2 (Fig. 3). As a consequence of the
226 approach of the average M2 position with decreasing Ca, the O1A1-O2D2 and O1B1-O2C2 edges
227 shared with the M2 polyhedron by the symmetry equivalent M1(1) decrease their length, and the
228 O1 atoms shifts towards the O2. The shift of the O1A1 and O1B1 towards O2D2 and O2C2 opens
229 the edge O1A1-O1B1, shared between M2 and the M1 polyhedron along the diad axis, from 2.79 in
230 $\text{CaCoSi}_2\text{O}_6$ to 2.84 Å in $\text{Ca}_{0.4}\text{Co}_{0.6}$ (Fig. 3), causing lower electrostatic shielding between M2 and
231 M1 along the diad axis, when the two cations approach with decreasing Ca. As a consequence the
232 M1 cation moves off M2 along the diad axis, increasing the bond distance with the O1 atoms. The
233 O1A1-Co-O1B1 angle maintains its value of 81° throughout the series, significantly deviated from
234 the expected 90° of a regular octahedron due to the combined shift of Co in M1 away from the M2
235 and the increase of the O1A1-O1B1 shared edge.

236 Furthermore, angular distortion changes little up to $\text{Ca}_{0.6}\text{Co}_{0.4}$, but $\text{Ca}_{0.4}\text{Co}_{0.6}$ is significantly
237 more distorted. The changes in the O-M1-O angles with composition are continuous and small,
238 apart from the two O1-M1-O2 couples that change by 5°, crossing the value of 90° at $\text{Ca}_{0.6}\text{Co}_{0.4}$
239 (Table 4).

240

241 **T polyhedron.** As the M1 octahedron, the tetrahedral site, which is always filled with Si, is
242 also affected by cation substitution in the M2 polyhedron. The polyhedral volume does not change,
243 but the average bond distances decrease between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$. This is due to a
244 decrease in bond lengths of Si with the oxygen shared by two tetrahedra, i.e the T-O3 bridging,
245 while the distances with other oxygen (T-O non bridging) increase. Also the tetrahedral angle with
246 the two bridging oxygen becomes closer to the 109.4° ideal value with a strong increase in the O3-
247 M1-O3 angle (from 104.3 to 106.9) and a decreased tetrahedral distortion (Fig. 3).

248 The decrease in the difference between bridging and non bridging oxygen is related to the
249 cation substitution in the M2 site (Fig. 9). The increased average M2-O3 bond distance decreases
250 the nominal charge on the O3 atom, whereas the electrostatic contribution of the M2 cation to O2
251 and O1A increases. The lower contribution to the bridging O3 from the M2 site is compensated by
252 a decrease in the distance of the bridging oxygen with tetrahedral Si. Also the O3-O3 distance,
253 which is a shared edge with the M2 polyhedron, increases, and as a consequence the polyhedral
254 angle opens.

255

256 **Cell parameters and structure.** The substitution of a smaller cation like Co for the larger
257 Ca decreases, as expected, the size of the unit cell. The decrease is comparable to that of the sum of
258 the volumes of the 4 eight coordinated M2 polyhedra in the unit cell (-5.4 vs -5.1 \AA^3) for the cell
259 parameters between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}$. The cell volume decreases mostly as a consequence
260 of contraction along a^* (d_{100}), whereas the b axis increases its size, and the c axis is unchanged. The
261 present data do not show a deviation from the linear behavior in volume, but the axial changes are
262 not linear (Fig. 10).

263 Along the b axis the increase is by about 0.3 \AA . As discussed in Tribaudino et al. (2005b),
264 the length of the b axis in $C2/c$ pyroxenes is determined by the sum of the contributions along the
265 M2 polyhedron, and the M1 octahedral and T tetrahedral chains (Fig. 11). The contribution of the
266 M2 polyhedron is determined by the distance along the diad axis between the O1 atoms and the
267 glide plane at $0.5 y/b$, i.e the average y/b of the O3 oxygen (Fig. 11). It changes little along the
268 series: as discussed above the cation substitution in the M2 site occurs with little change in the
269 positions of the surrounding oxygen, apart from the O2 atoms, and, as it will be discussed later, a
270 shift in the O3 oxygen. The change in the M2-O2 distance and the O3 shift do not affect the size of
271 the b axis, being almost normal to the diad axis. Likewise the tetrahedral chain contribution is very
272 small. The increase along b is due to an increase in the size of the M1 polyhedron, in turn due to the
273 increase in the M2-O1A1 distances (Figs. 3 and 4).

274 The size of the *c* axis is related to the tetrahedral chain size (Cameron et al. 1973). It may
275 change by a kinking of the O3-O3-O3 tetrahedral angle, or by a variation in the O3C1-O3C2
276 distance, which is oriented almost along the *c* axis. In *C2/c* Co-pyroxenes the *c* axis changes little
277 along the series, like previously found in Ca-Mg pyroxenes (Tribaudino 2000): a balance occurs
278 between the small chain kinking along the series, which would decrease, and the O3C1-O3C2
279 distances, which would increase the *c* axis.

280 The parameters that change the most along the series are the *a* axis and the β angle, both
281 lying on the (010) plane. The deformation on the (010) plane mostly accounts for the deformation
282 due to chemical substitution, as shown by an analysis of the strain tensor.

283 The changes in cell parameters with composition give rise to a macroscopic compositional
284 strain whose tensor is calculated from the cell parameters of the different compositions; it is
285 geometrically represented by a strain ellipsoid, whose axes are the diagonal components of the
286 strain tensor (Ohashi and Burnham 1973). In monoclinic pyroxenes the strain ellipsoid is
287 constrained by symmetry to have two axes lying onto the (010) plane and the third coincident with
288 the **b** axis. The relevant variables are the size of the axes and the orientation onto the (010) plane
289 respect to the crystallographic **a** and **c** axes. The usefulness of the strain analysis is to relate atomic
290 changes to the macroscopic cell shape deformation, and to compare such effect within isostructural
291 series.

292 The strain for the substitution of a smaller cation for Ca in the M2 site was therefore
293 calculated comparing cell parameters of different composition, in our Co-pyroxenes and the related
294 Ca-Mg and Ca-Fe pyroxenes. An Eulerian strain formalism, with the orientation of the reference
295 Cartesian with crystallographic axes as $x \parallel a^*$, $y \parallel b$ and $z \parallel c$, was used. The compliance tensor
296 sums were calculated from the unit-cell parameter variation with pressure using the WinStrain
297 program, a modified version of the Strain program by Ohashi (1972), kindly provided by R.J. Angel
298 (University of Padova). The results are reported in Table 5.

299 As shown in Table 5 the two strain axes showing higher deformation lie both on the (010)
300 plane: one shows a compression at 60° from the *c* axis, the other a smaller expansion normal to that
301 direction. Instead the strain along the *b* axis is the smallest. The orientation of the strain ellipsoid is
302 almost the same in the three series, indicating a similar mechanism of deformation.

303 The highest deformation direction (ϵ_1) is almost coincident to the projection onto the (010)
304 of the M2-O3C1,D1 bonds, i.e. the distance O3C1-O3D1 (Fig. 12). This distance decreases
305 strongly along the series, from 3.404 to 3.219 Å, i.e. by about 6%. The expansion normal to the ϵ_1 ,
306 along the ϵ_3 axis, occurs very close to the O3C2-O3D2 distance, along the projection of the longest
307 M2-O3 bonds onto (010): again the changes along this distance, with increases from 4.369 to 4.483

308 \dot{A} account for the deformation. This pattern of deformation is present in Ca-Co, Ca-Fe and Ca-Mg
309 pyroxenes, but the degree of deformation varies: the deformation increases with increasing
310 substitution in Ca-Co and Ca-Mg pyroxenes, much less in Ca-Fe pyroxenes. It looks that the same
311 substitution has a more profound effect with larger ionic radius difference.

312 The structural mechanism involved in this deformation is that of a shift of the tetrahedral
313 chains (Fig. 12). Tetrahedral chain shift was described in detail in several papers (Benna et al. 1988,
314 Tribaudino 1996, Tribaudino and Nestola 2002), to describe the change in position of the O3
315 bridging atoms on facing tetrahedral chains. Such shift in *C2/c* clinopyroxenes enables to decrease
316 the average coordination for the M2 site with increasing substitution of a smaller cation for a larger
317 one.

318

319 **Local structure**

320 The displacement parameters of this work pyroxenes increase their size from $\text{Ca}_{0.8}\text{Co}_{0.2}$ to
321 $\text{Ca}_{0.6}\text{Co}_{0.4}$, whereas in $\text{Ca}_{0.4}\text{Co}_{0.6}$ they are similar to $\text{Ca}_{0.6}\text{Co}_{0.4}$ (Tab. 2, Figs 2 and 13). A plot of the
322 displacement parameters for the M2 site (unsplit) in the Ca-Co, Ca-Mg and Ca-Fe series shows that,
323 in spite of the different experimental setup and collection methods, the displacement parameters
324 follow a well defined trend: an increase up to the intermediate composition, and a symmetric
325 decrease towards end members, so that in intermediate compositions the vibration ellipsoid is much
326 larger than in end members. The *C2/c* to *P2₁/c* transition at ~ 0.60 and 0.30 atoms p.f.u. in Ca-Mg
327 and Ca-Fe pyroxenes (Ohashi et al 1975, Tribaudino 2000) does not affect this trend.

328 The U_{eq} of all atoms increase from the end members towards the intermediate solid
329 solutions, but the increase is higher in the M2, O2 and O3 atoms. Also the orientation of the
330 displacement parameters changes significantly with composition, best seen on the M2 site, which in
331 intermediate samples has a displacement ellipsoid elongated with the diad axis, whereas in end
332 members it has the major axis normal to the diad axis (Fig. 2).

333 The results in Fig. 13 are simply interpreted as an effect of positional disorder overlapping
334 to thermal vibration. The positional disorder is higher in some atoms, like M2, O2 and O3. The
335 coexistence of local configurations centered by Ca and Co in the M2 site, affecting also the O2 and
336 O3 atoms is the most obvious interpretation: disorder disappears in end members, where only one
337 configuration is present.

338 The position of split O2 and O3 atoms was previously refined in *C2/c* and *P2₁/c*, Ca-Mg
339 pyroxenes, collected with high resolution, and full configuration of Ca and Mg centered M2
340 polyhedra could be obtained (Tribaudino et al. 1989, Tribaudino and Nestola 2002). It was observed
341 that the split M2 polyhedral configurations are quite similar to those in end member structures.

342 However, the behavior of the M2 and O2 atoms is different from that of the O3 atom: the former
343 increase continuously from the Ca-rich end member, whereas the O3 has a non-linear increase,
344 smaller at first, and higher then (Fig. 13).

345

346

Discussion

347 The above results detail the structural changes resulting from the substitution of a smaller
348 cation for Ca in the M2 site of *C2/c* pyroxenes. The solid solution involves M2 site splitting, a shift
349 in the average M2 position off the O3 atoms along the diad axis, and a shift in the tetrahedral chain,
350 normal to the diad axis (Fig. 14). The chain shift and the related change of interchain O3-O3
351 distances accommodate most of the compositional macroscopic strain. During this process the M2
352 polyhedron does not change its size along the b axis, but normal to this axis the O2 atom
353 approaches the M2 cation. The approach of the O2 atom is obtained by a tilt of the tetrahedral
354 chain, which does not affect the cell deformation. This is found when Ca is substituted by either Co,
355 Mg or Fe (Figs. 3, 6, 7, 8, 9, 14), for any degree of cation substitution; changes in M2-O bond
356 lengths, in the deformation of the M2 polyhedron, in chain shift, and, in general, in the
357 compositional strain are higher as Ca content decreases. The substitution of a smaller cation in M2
358 (like Mg) also promotes higher deformation than that of a larger one (like Fe): higher chain
359 deformation is obtained with less substitution in Ca-Mg, in respect to Ca-Co and Ca-Fe pyroxenes
360 (Ohashi et al. 1975, Tribaudino 2000).

361 The proposed mechanism of solid solution appears limited to a critical composition when
362 the *C2/c* phase is no more stable at room conditions, and the transition to *P2₁/c* occurs. In Ca-Co
363 pyroxenes the transition occurs between $\text{Ca}_{0.4}\text{Co}_{0.6}\text{CoSi}_2\text{O}_6$ and $\text{Ca}_{0.3}\text{Co}_{0.7}\text{CoSi}_2\text{O}_6$ (Mantovani et al.
364 2012), and in Ca-Mg ones at $\text{Ca}_{0.6}\text{Mg}_{0.4}\text{MgSi}_2\text{O}_6$ (Tribaudino 2000), i.e. at a composition where the
365 chain shift approaches 0.9 Angstrom, which is near a limiting value (Fig. 14).

366 In Ca-Fe the transition was observed at $\text{Ca}_{0.3}\text{Fe}_{0.7}\text{FeSi}_2\text{O}_6$, by the appearance of symmetry
367 violating reflections (Ohashi et al. 1975). Although at this composition the shift is lower than in Ca-
368 Mg and Ca-Co pyroxenes, the same non-linear mechanism applies.

369 The above data indicate that substitution in the M2 site strongly affects the tetrahedral chain
370 shift, in a non linear way, accounting for the compositional strain. In *C2/c* pyroxenes the
371 substitution may occur maintaining the equivalence in facing chains by a shift of the tetrahedral
372 chains. As the substitution of a smaller cation for Ca goes on, the compositional deformation
373 increases, and at a given composition, the equivalence of facing chains is lost, and a transition to the
374 *P2₁/c* symmetry occurs.

375 The M2-O bond distances, chain shift, O3-O3-O3 angle and compositional strain show that
376 small degrees of substitution of a smaller cation for Ca has a smaller effect on the tetrahedral chain
377 than when the substitution occurs to a greater extent.

378 An analytical representation of the increased deformation of the unit cell with the decreased
379 size of the average cation radius in the M2 site is shown in Fig. 15. The axial compositional strain
380 was calculated for several intervals in Ca-Fe, Ca-Co and Ca-Mg pyroxenes (deposited, partially
381 reported in Table 5). To obtain a single scalar value a unit scalar strain ϵ_s was also calculated from
382 the three ϵ_1 , ϵ_2 and ϵ_3 axes of the strain ellipsoid as :

$$383 \quad \epsilon_s = \sqrt{\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2}$$

384 It is observed that the unit strain ϵ_s is linearly related to the average M2 ionic radius (IR^{M2} ,
385 Fig 15); it appears that some difference exists between Ca-Co and Ca-Mg pyroxenes, the latter
386 showing higher strain, but an overall general trend can be all the same fitted as:

$$387 \quad \epsilon_s = -0.0072(12)IR^{M2} + 0.0082(13), R^2 = 0.75.$$

388 To note, the strain is very close to zero at the ionic radius of Ca (1.12Å). The deformation
389 needed to accommodate the same amount of the smaller cation in the M2 polyhedron increases
390 therefore with substitution, up to a point where solid solution is no more possible: a higher
391 deformation increases the energetic demand for a further substitution, thus increasing the free
392 energy of the solid solutions. This explains the presence of a miscibility gap in quadrilateral
393 pyroxenes. Further investigation is in progress to constrain the presence of a miscibility gap also in
394 Ca, Co pyroxenes.

395 At the level of the local structure the same is apparent also from the displacement
396 parameters of the O3 atoms: the U_{eq} of the O3 atoms do not increase significantly their size up to
397 20% substitution of the smaller cation (Fig. 13), whereas M2 and O2 do. The O3 atoms are tightly
398 bonded to the tetrahedral chain, from which they receive most of their formal charge, whereas the
399 displacement of the O2 atoms is most sensitive to local M2-O2 distances. The suggestion is that
400 small substitution does not affect local chain configurations. An independent confirmation comes
401 from the analysis of the Raman peaks in Ca-Mg pyroxenes. The strong peak at 670 cm^{-1} , which by
402 quantum-mechanical simulation was ascribed mostly to the tetrahedral chain bending (Prencipe et
403 al. 2012), does not increase its linewidth from diopside up to $(Ca_{0.8}Mg_{0.2})MgSi_2O_6$, whereas the
404 linewidth of peak at 340 cm^{-1} , which was instead related to bending and stretching of the M2-O
405 bonds, increases significantly (Tribaudino et al. 2012).

406 With higher substitution also the tetrahedral chains are deformed differently for the
407 different substituting cations in the M2 polyhedron, and local chain configurations occur. As the

408 tetrahedral chain is more and more affected by cation substitution, higher strain occurs, eventually
409 hindering further solid solution.

410

411

412

Acknowledgements

413 The present work benefited from financial support of the Italian PRIN2008 “SPIN GEOTECH”.

414 GB acknowledges the support of the University of Edinburgh Moray Endowment Fund. The

415 authors thank Fabrizio Nestola and an anonymous reviewer for the constructive comments.

416

417

References

418

419 Benna, P., Tribaudino, M., and Bruno, E. (1988) Crystal structure of $Di_{50}CaTs_{50}$ synthetic
420 clinopyroxene ($CaMg_{0.5}AlSi_{1.5}O_6$). Crystal chemistry along the Di-CaTs join. *Mineralogy*
421 *and Petrology*, 38, 189-200.

422

423 Boffa Ballaran, T., Carpenter, M., Domeneghetti, M.C., and Tazzoli, V. (1998) Structural
424 mechanisms of solid solution and cation ordering in augite-jadeite pyroxenes: I. A
425 macroscopic perspective. *American Mineralogist*, 83, 419-433.

426

427 Bruno, E., Carbonin, S., and Molin, G.M. (1982) Crystal structure of Ca-rich clinopyroxenes on
428 the $CaMgSi_2O_6$ - $Mg_2Si_2O_6$ join. *Tschermaks Mineralogische und Petrographische*
429 *Mitteilungen*, 29, 223-240.

430

431 Bromiley, G.D., Keppler, H., McCammon, C., Bromiley, F.A. and Jacobsen, S.D. (2004) Hydrogen
432 solubility and speciation in natural, gem-quality chromian diopside. *American Mineralogist*,
433 89, 941-949.

434

435 Burnham, C.W. (1966) Ferrosilite. *Carnegie Inst. Washington. Year Book*, 65, 285-290.

436

437 Burnham, C.W., Clark, J.R., Papike, J.J., and Prewitt, C.T. (1967). A proposed crystallographic
438 nomenclature for clinopyroxene structures. *Zeitschrift für Kristallographie*, 125, 109-119.

439

440 Cameron, M., Sueno, S., Prewitt, C.T., and Papike, J.J. (1973) High temperature crystal chemistry
441 of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. *American Mineralogist*,
442 58, 594-618.

- 443
444 Domeneghetti, M.C., Zema, M., and Tazzoli, V. (2005) Kinetics of Fe²⁺-Mg order-disorder in
445 *P2₁/c* pigeonite. American Mineralogist, 90, 1816-1823.
446
447 Farrugia, L.J. (1999) *WinGX* suite for small-molecule single-crystal crystallography. Journal of
448 Applied Crystallography, 32, 837-838.
449
450 Gasparik, T. (1990) A thermodynamic model for the enstatite-diopside join. American
451 Mineralogist, 75, 1080-1091.
452
453 Ghose, S., Wan, C., and Okamura, F. (1987) Crystal-structures of CaNiSi₂O₆ and CaCoSi₂O₆ and
454 some crystal-chemical relations in *C2/c* clinopyroxenes. American Mineralogist, 72, 375-
455 381
456
457 Jodlauk, S., Becker, P., Mydosh, J.A., Khomskii, D.I., Lorenz, T., Streltsov, S.V., Hezel, D.C., and
458 Bohatý L. (2007) Pyroxenes: A new class of multiferroics. Journal of Physics Condensed
459 Matter, 19, 432201-432210.
460
461 Lindsley, D.H. (1983) Pyroxene thermometry. American Mineralogist, 68 , 477-493.
462
463 Lindsley, D.H., and Munoz, J.L. (1969) Subsolidus relations along the join hedenbergite-ferrosilite.
464 American Journal of Science, 267A, 295-324.
465
466 Mantovani, L., Tribaudino, M., Bersani, D., Lottici, P.P., and Bromiley, G.D. (2012) Raman
467 spectroscopy in Ca,Co pyroxenes: a model for structure and composition in silicates.
468 European Mineralogical Conference, Frankfurt, ECM2012-131.
469
470 Nestola, F., and Tribaudino, M. (2003) The structure of *Pbca* orthopyroxenes along the join
471 diopside-enstatite (CaMgSi₂O₆-Mg₂Si₂O₆). European Journal of Mineralogy, 15, 365-371.
472
473 Nestola, F., Tribaudino, M., Boffa Ballaran, T., Liebske, C., and Bruno, M. (2007) The crystal
474 structure of pyroxenes along the jadeite - hedenbergite and jadeite - aegirine joins. American
475 Mineralogist, 92, 1492-1501.
476

- 477 Newton, R.C., Charlu, T.V., Anderson, P.A.M., and Kleppa, O.J. (1979) Thermochemistry of
478 synthetic clinopyroxenes on the join $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6$. *Geochimica et Cosmochimica*
479 *Acta*, 43, 55-60.
480
- 481 Ohashi, Y. (1972) Program strain. Program listing provided in Hazen and Finger (1982)
482 *Comparative crystal-chemistry*. Wiley, New York.
483
- 484 Ohashi, Y., and Burnham, C.W. (1973) Clinopyroxene lattice deformations: the roles of chemical
485 substitution and temperature. *American Mineralogist*, 58, 843-849.
486
- 487 Ohashi, Y., Burnham, C.W., and Finger, L.W. (1975) The effect of Ca-Fe substitution on the
488 clinopyroxene crystal structure. *American Mineralogist*, 60, 423-434.
489
- 490 Ohashi, Y., and Finger, L.W. (1976) The effect of Ca substitution on the structure of clinoenstatite.
491 *Carnegie Institute Washington Year Book*, 75, 743-746.
492
- Prencipe, M., Mantovani, L., Tribaudino, M., Bersani, D., and Lottici, P.P. (2012) The Raman
spectrum of diopside: a comparison between *ab initio* calculated and experimentally
measured frequencies. *European Journal of Mineralogy*, 24, 457-464.
- 493 Redhammer, G.J., Roth, G., Treutmann, W., Paulus, W., André, G., Pietzonka, C., and Amthauer,
494 G. (2008) Magnetic ordering and spin structure in Ca-bearing clinopyroxenes $\text{CaM}^{2+}(\text{Si},$
495 $\text{Ge})_2\text{O}_6$, M = Fe, Ni, Co, Mn. *Journal of Solid State Chemistry*, 181, 3163-3176.
496
- 497 Redhammer, G.J., Roth, G., Treutmann, T., Hoelzel, M., Paulus, W., André, G., Pietzonka, C., and
498 Amthauer, G. (2009) The magnetic structure of clinopyroxene-type $\text{LiFeGe}_2\text{O}_6$ and revised
499 data on multiferroic $\text{LiFeSi}_2\text{O}_6$. *Journal of Solid State Chemistry*, 182, 2374-2384.
500
- 501 Redhammer, G.J., Senyshyn, A., Tippelt, G., and Roth, G. (2011) Magnetic spin structure of
502 pyroxene-type MnGeO_3 . *Journal of Physics Condensed Matter*, 23, 254202-254212.
503
- 504 Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: A quantitative measure of
505 distortion in coordination polyhedra. *Science*, 172, 567-570.
506

- 507 Rossi, G., Oberti, R., Dal Negro, A., Molin, G.M., and Mellini, M. (1987) Residual electron
508 density of the M2 site in *C2/c* clinopyroxenes relationship with bulk chemistry and sub-
509 solidus evolution. *Physics and Chemistry of Minerals*, 14, 514-520.
510
- 511 Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances
512 in halides and chalcogenides. *Acta Crystallographica A*32, 751–767.
513
- 514 Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
515
- 516 Sheldrick, G.M. (1997) SHELXL-97, program for crystal structure solution GM Sheldrick -
517 University of Göttingen, Germany.
518
- 519 Streltsov, S.V., and Khomskii, D.I. (2008) Electronic structure and magnetic properties of
520 pyroxenes (Li,Na)TM(Si,Ge)₂O₆: Low-dimensional magnets with 90° bonds. *Physical*
521 *Review*, B77, 064405-064415..
522
- 523 Tabira, Y., Ishizawa, N., Marumo, F. (1992) Cobalt atoms at M(2) site in *C2/c* clinopyroxenes of
524 the system CaMgSi₂O₆ (Di)–CaCoSi₂O₆ (CaCoPx). *Mineralogical Journal*, 16, 225-245.
525
- 526 Tribaudino, M. (1996) High-temperature crystal chemistry of *C2/c* clinopyroxenes along the join
527 CaMgSi₂O₆-CaAl₂SiO₆. *European Journal of Mineralogy*, 8, 273-279.
- 528 Tribaudino, M. (2000) A transmission electron microscope investigation of the *C2/c* → *P2₁/c* phase
529 transition in clinopyroxenes along the diopside-enstatite (CaMgSi₂O₆-Mg₂Si₂O₆) join.
530 *American Mineralogist*, 85, 707-715.
531
- 532 Tribaudino, M., Benna, P., and Bruno, E. (1989) Average structure and M2 site configurations in
533 *C2/c* clinopyroxenes along the Di-En join. *Contributions to Mineralogy and Petrology*, 103,
534 452-456.
535
- 536 Tribaudino, M., and Nestola, F. (2002) Average and local structure in *P2₁/c* clinopyroxenes along
537 the join diopside-enstatite (CaMgSi₂O₆-Mg₂Si₂O₆). *European Journal of Mineralogy*, 14,
538 549-555.
539
- 540 Tribaudino, M., Nestola, F., Cámara, F., and Domeneghetti, M.C. (2002) The high temperature

541 *P2₁/c-C2/c* phase transition in Fe-free pyroxene (Ca_{0.15}Mg_{1.85}Si₂O₆): structural and
542 thermodynamic behavior. American Mineralogist, 87, 648-657.

543

544 Tribaudino, M., Nestola, F., and Meneghini C. (2005a) The structure behavior of intermediate
545 pyroxenes along the diopside-enstatite join. Canadian Mineralogist, 43, 1411-1421.

546

547 Tribaudino M., Nestola, F., and Ohashi, H. (2005b) High temperature single crystal investigation in
548 a clinopyroxene of composition (Na_{0.5}Ca_{0.5})(Cr_{0.5}Mg_{0.5})Si₂O₆. European Journal of
549 Mineralogy, 17, 297-304.

550

551 Tribaudino, M., Mantovani, L., Bersani, D., and Lottici P.P. (2012) Raman spectroscopy of
552 (Ca,Mg)MgSi₂O₆ clinopyroxenes. American Mineralogist, 97, 1339-1347.

553

554

555

556

557

558

559

560

561

562 **Table 1.** Cell and structure refinement parameters.

Samples	Ca _{0.8} Co _{0.2}	Ca _{0.6} Co _{0.4}	Ca _{0.4} Co _{0.6}
a (Å)	9.794(2)	9.7754(4)	9.747(6)
b (Å)	8.953(2)	8.9686(4)	8.982(5)
c (Å)	5.243(1)	5.2421(4)	5.249(3)
β (°)	105.66(3)	106.302(4)	107.46(8)
V (Å ³)	442.64	440.11	438.37
Space group	C2/c	C2/c	C2/c
Z	4	4	4
Radiation	MoK α	MoK α	MoK α
No. of indep. refl. $I > 4\sigma$	684	671	590
2 θ_{\max} (°)	64	64	64
R _{4σ} (F) (%)*	2.6	2.6	2.6
No. parameters	49	52	52
Goof	0.800	0.807	1.107

563 * split model

564

565

566 **Table 2.** Fractional atomic coordinates and isotropic displacement parameters. x and z for the M2,
 567 M2* and M2' special position are 0 and 0.25, for the M1 0 and 0.75 (both in e Wyckoff position)

		Ca _{0.8} Co _{0.2}	Ca _{0.6} Co _{0.4}	Ca _{0.4} Co _{0.6}
M2	y	0.2965(1)	0.2857(1)	0.2690(1)
	U _{eq}	0.0134(2)	0.0222(3)	0.0233(2)
M2*	y	0.3016(2)	0.3003(4)	0.2966(5)
	U _{eq}	0.0072(3)	0.0093(5)	0.0118(8)
M2'	y	0.2721(6)	0.2650(4)	0.2580(2)
	U _{eq}	0.0199(16)	0.0173(8)	0.0144(5)
M1	y	0.9072(1)	0.9063(1)	0.9052(1)
	U _{eq}	0.0056(2)	0.0068(2)	0.0098(2)
T	x	0.2881(1)	0.2903(1)	0.2940(1)
	y	0.0924(1)	0.0914(1)	0.0900(1)
	z	0.2322(2)	0.2370(2)	0.2476(2)
	U _{eq}	0.0047(2)	0.0062(2)	0.0098(2)
O1	x	0.1177(2)	0.1185(3)	0.1203(2)
	y	0.0884(2)	0.0886(3)	0.0888(2)
	z	0.1473(4)	0.1478(5)	0.1503(4)
	U _{eq}	0.0064(4)	0.0079(4)	0.0108(4)
O2	x	0.3617(2)	0.3646(3)	0.3700(3)
	y	0.2487(2)	0.2478(3)	0.2459(3)
	z	0.3239(4)	0.3329(6)	0.3475(5)
	U _{eq}	0.0096(4)	0.0144(5)	0.0185(5)
O3	x	0.3511(2)	0.3515(2)	0.3529(2)
	y	0.0198(2)	0.0221(3)	0.0232(3)
	z	0.9948(4)	0.9972(5)	1.0064(5)
	U _{eq}	0.0074(4)	0.0101(5)	0.0200(5)

568

569

570 **Table 3 (to be deposited)** Anisotropic displacement parameters.

571	$\text{Ca}_{0.8}\text{Co}_{0.2}$	$\text{Ca}_{0.6}\text{Co}_{0.4}$	$\text{Ca}_{0.4}\text{Co}_{0.6}$	
572	M2			
573	U ₁₁	0.0124(4)	0.0114(2)	0.0135(3)
574	U ₂₂	0.0177(4)	0.0450(6)	0.0410(5)
575	U ₃₃	0.0084(3)	0.0086(4)	0.0133(3)
576	U ₁₂	0	0	0
577	U ₁₃	-0.0001(2)	0.0002(3)	0.0008(3)
578	U ₂₃	0	0	0
579	M2*			
580	U ₁₁	0.0103(5)	0.0108(7)	0.0136(11)
581	U ₂₂	0.0040(5)	0.0080(11)	0.0086(22)
582	U ₃₃	0.0057(4)	0.0079(7)	0.0108(10)
583	U ₁₂	0	0	0
584	U ₁₃	-0.0012(3)	0.0005(5)	-0.0001(8)
585	U ₂₃	0	0	0
586	M1			
587	U ₁₁	0.0065(2)	0.0073(2)	0.0106(3)
588	U ₂₂	0.0054(2)	0.0070(2)	0.0083(3)
589	U ₃₃	0.0054(2)	0.0064(2)	0.0105(2)
590	U ₁₂	0	0	0
591	U ₁₃	0.0011(2)	0.0021(2)	0.0036(2)
592	U ₂₃	0	0	0
593	T			
594	U ₁₁	0.0052(3)	0.0062(3)	0.0102(4)
595	U ₂₂	0.0044(3)	0.0061 (3)	0.0071(3)
596	U ₃₃	0.0051(3)	0.0073(3)	0.0128(3)
597	U ₁₂	-0.0005(2)	-0.0011(2)	-0.0013(2)
598	U ₁₃	0.0013(2)	0.0032(2)	0.0047(2)
599	U ₂₃	-0.0004(2)	-0.0008(2)	-0.0011(2)
600	O2			
601	U ₁₁	0.0049(7)	0.0070(7)	0.0111(8)
602	U ₂₂	0.0075(7)	0.0098(7)	0.0097(8)
603	U ₃₃	0.0077(7)	0.0075(7)	0.0109(8)
604	U ₁₂	0.0005(5)	0.0009(5)	0.0009(6)
605	U ₁₃	0.0014(6)	0.0024(5)	0.0036(6)
606	U ₂₃	0.0005(5)	0.0002(5)	0.0001(6)
607	O1			
608	U ₁₁	0.0120(7)	0.0167(8)	0.0215(9)
609	U ₂₂	0.0070(7)	0.0096(8)	0.0112 (8)
610	U ₃₃	0.0114(8)	0.0206(9)	0.0290(10)
611	U ₁₂	-0.0030(6)	-0.0058(6)	-0.0074(7)
612	U ₁₃	0.0043(6)	0.0112(7)	0.0167(8)
613	U ₂₃	-0.0016(6)	-0.0048(6)	-0.0080(7)
614	O3			
615	U ₁₁	0.0071(7)	0.0063(7)	0.0102(8)
616	U ₂₂	0.0098(7)	0.0170(7)	0.0290(11)
617	U ₃₃	0.0065(7)	0.0073(7)	0.0201(9)
618	U ₁₂	0.0001(5)	0.0001(6)	0.0011 (7)
619	U ₁₃	0.0025(6)	0.0030(6)	0.0035(7)
620	U ₂₃	-0.0021(5)	-0.0033(6)	-0.0117(8)
621				
622				
623				

624 **Table 4:** atomic distances and angles.

	CaCoSi ₂ O ₆	Ca _{0.8} Co _{1.2}	Ca _{0.6} Co _{1.4}	Ca _{0.4} Co _{1.6}
M2-O1A1,B1 ×2	2.378(1)	2.329(2)	2.259(2)	2.154(2)
M2-O2C2,D2 ×2	2.332(1)	2.315(2)	2.236(3)	2.117(3)
M2-O3C1,D1 ×2	2.454(1)	2.619(2)	2.697(3)	2.793(3)
M2-O3C2,D2 ×2	2.744(1)	2.736(2)	2.796(3)	2.917(3)
<M2 – O>	2.502(1)	2.500(2)	2.497(3)	2.495(3)
M2*-O1A1,B1 ×2		2.366(2)	2.364(3)	2.347(4)
M2*-O2C2,D2 ×2		2.323(2)	2.257(2)	2.147(3)
M2*-O3C1,D1 ×2		2.585(2)	2.598(3)	2.594(4)
M2*-O3C2,D2 ×2		2.710(2)	2.716(3)	2.767(4)
<M2 – O>		2.496	2.484	2.463
M2'-O1A1,B1 ×2		2.159(4)	2.118(3)	2.082(2)
M2'-O2C2,D2 ×2		2.286(2)	2.219(2)	2.113(3)
M2'-O3C1,D1 ×2		2.790(5)	2.848(3)	2.874(3)
M2'-O3C2,D2 ×2		2.874(4)	2.913(3)	2.983(3)
<M2' – O>		2.527(4)	2.524(3)	2.513(3)
V _{M2} (Å ³)	25.85(3)	25.73(4)	25.32(4)	24.51(10)
M2 along b axis**	3.686	3.685	3.690	3.693
M2-M1	3.505(1)	3.485(1)	3.403(1)	3.268(1)
M2-M1(1)	3.208(1)	3.194(1)	3.136(1)	3.056(1)
M1-O1A2,B2 ×2	2.095(1)	2.091(2)	2.082(3)	2.077(2)
M1-O1A1,B1 ×2	2.136(1)	2.141(2)	2.157(2)	2.176(2)
M1-O2C1,D1 ×2	2.071(1)	2.069(2)	2.070(3)	2.074(2)
<M1 – O>	2.101(1)	2.100(2)	2.103(3)	2.109(2)
V _{M1} (Å ³)	12.28(1)	12.28(2)	12.32(2)	12.42(4)
OAV***	14.6	14.3	14.1	17.0
O1-M1-O2 x2	92.8(1)	92.2(1)	92.8(1)	92.9(1)
O1-M1-O2 x2	92.6(1)	92.3(1)	90.8(1)	88.3(1)
O1-M1-O2 x2	88.9(1)	89.2(1)	90.9(1)	93.8(1)
O1-M1-O1 x2	92.6(1)	92.7(1)	92.6(1)	92.4(1)
O1-M1-O1 x2	85.8(1)	85.7(1)	85.5(1)	85.3(1)
O2C1-M1-O2D1	93.3(1)	93.3(1)	93.2(1)	92.8(1)
O1A1-M1-O1B1	81.7(1)	81.6(1)	81.5(1)	81.5(1)
O1A1-O1B1	2.793(1)	2.797(2)	2.815(2)	2.840(3)
O1B1-O2C2	3.012(1)	2.999(2)	2.956(2)	2.891(3)
M1 along b axis**	3.038	3.041	3.056	3.080
M1-M1	3.100(1)	3.104(1)	3.114(1)	3.128(1)
T - O1	1.605(1)	1.606(2)	1.612(3)	1.615(3)
T - O2	1.588(1)	1.589(2)	1.595(3)	1.598(3)
T -O3A1	1.666(1)	1.663(2)	1.658(3)	1.652(3)
T-O3A2	1.684(1)	1.681(2)	1.672(3)	1.655(3)
<T – O>	2.181(1)	2.180(2)	2.179(3)	2.173(3)
V _T (Å ³)	2.23(1)	2.23(1)	2.22(1)	2.21(1)
TAV***	25.3	23.3	18.7	15.7
tilting angle****	2.8	2.8	3.4	4.5
O3A1-T-O3A2	104.3(1)	104.7(1)	105.5(1)	106.9(1)
O3-O3-O3	165.05(11)	164.5(2)	162.8(2)	161.9(2)
O3A1-O3A2	2.644(1)	2.646(1)	2.651(1)	2.657(2)
T along b axis**	2.226	2.227	2.222	2.209

625 * split model; ** M2 contribution: (0.5-y/b₀₁)*b; M1 contribution: (y/b₀₂-y/b₀₁)*b; T contribution (y/b₀₂-
 626 0.5)*b *** OAV and TAV are angle variance for tetrahedra and octahedra (Robinson et al. 1971); ****
 627 tilting angle: angle between (100) and the basal face O2-O3-O3 of a tetrahedron. Data for CaCoSi₂O₆ were
 628 taken from Ghose et al. (1987)

629
 630

631
 632

Table 5. Unit strain and axial orientation.

Compositional range	Unit strain ($\times 10^{-4}/^{\circ}\text{C}$)			angle with c ($^{\circ}$)			axial expansion ellipsoid
	ϵ_1	ϵ_2	ϵ_3	ϵ_1	ϵ_2	ϵ_3	
Di ₁₀₀ – Di ₈₀ En ₂₀	-2.5(1)	- 0.7(1)	0.1(1)	62	90	152	1:0.28:-0.03
Di ₈₀ En ₂₀ – Di ₆₆ En ₄₀	-5.6(1)	- 0.5(1)	3.1(1)	57	90	147	1:0.08:-0.55
CaCoSi ₂ O ₆ – Ca _{0.8} Co _{0.2}	-1.6(1)	0.2(1)	0.4(1)	62	90	152	1:-0.12:-0.25
Ca _{0.8} Co _{0.2} – Ca _{0.6} Co _{0.4}	-4.2(1)	0.8(1)	1.6(1)	57	90	147	1:-0.19:-0.38
Ca _{0.6} Co _{0.4} – Ca _{0.4} Co _{0.6}	-7.2(1)	0.8(1)	3.4(1)	59	90	149	1:0.11:-0.47
Hd ₁₀₀ – Hd ₇₀ Fs ₃₀	-2.8(1)	0.9(1)	-0.1(1)	56	90	146	1:-0.32:0.04
Hd ₇₀ Fs ₃₀ – Hd ₄₀ Fs ₆₀	-5.2(1)	1.1(1)	1.4(1)	58	90	148	1:-0.21:-0.27

633
 634
 635
 636
 637
 638
 639

Notes: an angle of 90° corresponds to the orientation along the **b** axis. The orientation of the other axes on (010) is measured with the **c** axis, from **c** towards **a**. The unit cell used for the calculation are taken from: (Ca, Mg)MgSi₂O₆ pyroxenes: Tribaudino et al (1989), (Ca, Co)CoSi₂O₆ pyroxenes: this work; (Ca, Fe)FeSi₂O₆ pyroxenes: Ohashi et al (1975).

640 Captions of the figures.

641

642 Figure 1: electron density map at the M2 site (x across, y down); the cation occupancy of the site is
643 reported. CaM2 and CoM2 site positions are always located respectively at the M2* and M2'
644 positions in Table 2 of $\text{Ca}_{0.4}\text{Co}_{0.6}$, to enlighten the changes in the electron density. The structure
645 factors for the calculation in the “Ca only in the M2 site” map were taken from the refinement of
646 the hedenbergite (Nestola et al. 2007).

647

648 Figure 2: atomic displacement parameters of the unsplit M2 site and surrounding oxygen at the M2
649 polyhedron.

650

651 Figure 3: main changes with composition in the M1, M2 and T (occupied by Si) polyhedra onto the
652 (100) plane. In between it is shown a sketch showing the changes discussed in the paper. The b and
653 c axes are shifted from their position. Only one chain of the two tetrahedral chains linked to M2 is
654 shown, with the fourth O1 oxygen pointing downwards, not drawn for clarity.

655

656 Figure 4: M2-O (unsplit model), M1-O and T-O bond lengths with composition. The 0 %
657 corresponds to pure $\text{Co}_2\text{Si}_2\text{O}_6$.

658

659 Figure 5: M2-O and M2'-O bond lengths with composition in the split model.

660

661 Figure 6: M2-O2 vs V_{M2} . Data from, here and in the following figures: (Ca, Mg) MgSi_2O_6
662 pyroxenes: Bruno et al. (1982), Tribaudino et al. (1989), Carbonin (Pers. comm.); (Ca, Co) CoSi_2O_6
663 pyroxenes: this work; (Ca, Fe) FeSi_2O_6 pyroxenes: Ohashi et al. (1975).

664

665 Figure 7: M2-O bond distances (unsplit model) vs ionic radius of the 8-coordinated M2 site, in
666 $(\text{Ca}_x\text{M}_{1-x})\text{MSi}_2\text{O}_6$ pyroxenes with M= Mg, Co and Fe. $\Delta\text{M2} = \text{M2-O3C2} - (\text{M2-O3C1} + \text{M2-O2} +$
667 $\text{M2-O1})/3$. Ionic radii from Shannon (1976)

668

669 Figure 8: difference between the longest and shortest distance in the M2 site, divided by the same
670 difference in the end member with Ca only in the M2 site, vs Ca content in the M2 site.

671

672 Figure 9: difference between average bridging and non bridging T-O distances vs Ca content in the
673 M2 site and average M2-O3 distance (unsplit model).

674

675 Figure 10: relative changes in cell parameters and volume in (Ca, Co) CoSi_2O_6 pyroxenes. The 0 %
676 corresponds to pure $\text{Co}_2\text{Si}_2\text{O}_6$.

677

678 Figure 11: contributions of the different polyhedra along the b axis.

679

680 Figure 12: $C2/c$ clinopyroxene structure on the (010) plane: O3-O3 distances discussed in the text,
681 the amount of deformation (exaggerated, but with relative deformation correct) and the directions of
682 compression and expansion are shown, as well as the projection of the chain shift vector.

683

684 Figure 13: U_{eq} vs composition (unsplit model).

685

686 Figure 14: chain shift vs composition. Chain shift is calculated as $2a\cos\beta(x_{\text{O3}}-0.5)+2cz_{\text{O3}}$.

687

688 Figure 15: Unit strain vs average ionic radius of the M2 cation. The unit strain was calculated in an
689 interval of 0.01 Ca atoms p.f.u. The average M2 ionic radius for the M2 site is the average ionic
690 radius of the composition in between those over which the strain was calculated.

Z-SECTION: z = 0.250





























