1   REVISION_2

2   **Solid solutions and phase transitions in $(Ca,M^{2+})M^{2+}Si_2O_6$ pyroxenes (M^{2+} = Co, Fe, Mg)**

3

4   **Luciana Mantovani[1], Mario Tribaudino[1], Giovanni Bertoni[2], Giancarlo Salviati[2] and Geoffrey**

5   **Bromiley[3]**

6   [1]Dipartimento di Fisica e Scienze della Terra "Macedonio Melloni", Parco Area delle Scienze

7   157/A, 43124 Parma, Italy

8

9   [2]IMEM–CNR, Istituto dei Materiali per l'Elettronica e il Magnetismo, Parco Area delle Scienze

10   37/A, 43124 Parma, Italy

11

12   [3] School of GeoSciences and Centre for Science at Extreme Conditions, University of Edinburgh,

13   Grant Institute, West Mains Road, Edinburgh EH9 3JW, UK

14

15   **Abstract**

16   The effect of the substitution of Ca with Co, on the phase transition and on the extension of

17 the miscibility gap, was studied in order to model the general mechanism of phase transitions and

18 solid solutions in $(Ca, M^{2+})M^{2+}Si_2O_6$ pyroxenes .

19   Eleven pyroxenes with composition $Ca_{1-x}Co_{1+x}Si_2O_6$, $(0 \leq x \leq 1)$ were therefore synthesized

20 by piston cylinder at P = 3 GPa, and T between 1100 °C and 1350 °C. The samples were

21 characterized by SEM–EDS, XRD powder diffraction, and TEM. The results were compared with

22 those of Ca–Fe and Ca–Mg pyroxenes.

23   The phase diagram of Ca–Co pyroxenes is similar to that of Ca–Fe and Ca–Mg ones, with a

24 wide asymmetric miscibility gap, and higher solubility in the Ca–rich side of the gap. The solubility

25 on the Ca-rich side of the gap is related to the radius of the cation substituting.

26   The cell parameters of the Ca-Co pyroxenes undergo a sudden change at the composition of

27   about 0.4 Ca atoms p.f.u., due to the $C2/c - P2_1/c$ phase transition. The change in volume with

28   composition follows an ideal trend, in the $C2/c$ phase, dictated by the ionic size of the substituting

29   cation. Deviation from the $C2/c$ behaviour are instead observed in the $P2_1/c$ field and ascribed to

30   volume strain. The same turnover was found in Ca–Mg, Ca–Fe and Ca–Mn pyroxenes. The $C2/c -$

31    $P2_1/c$ transition occurs with decreasing the M2 average cation radius, down to a critical value

32   between 0.85 Å and 0.88 Å, depending on the series. A stabilization of the $C2/c$ phase related to

33   crystal field in Ca–Fe and Ca–Co pyroxenes is suggested by the analysis of the volume strain in the

34    $P2_1/c$ field.

35

36   **Keywords:** Ca-Co pyroxenes, high pressure synthesis, phase transition, phase equilibria

37

38

39

40   **Introduction**

41   One of the most intriguing features of the pyroxene mineral family is the wide range of

42   chemical substitutions, in a relatively simple structure (Redhammer and Roth 2004; Yang and

43   Prewitt 2000). This can be appropriately studied in synthetic pyroxenes, which provide a structural

44   model to interpret the behaviour of natural pyroxenes with temperature, pressure and composition.

45   Synthetic pyroxenes, therefore, have been the subject of extensive investigation (Tribaudino 2000;

46   Tribaudino and Nestola 2002; Redhammer et al. 2012; Downs 2003), to detail the flexibility of the

47   pyroxene structure, to show new phase transitions, the effect of crystal chemical substitutions on

48   such transitions and, for pyroxenes bearing transition elements, the effect of structural changes on

49   the electronic transitions. More recently the properties of transition metal-bearing synthetic

50   pyroxenes were widely investigated in view of the discovery of multiferroic behaviour in pyroxenes

51   (Jodlauk et al. 2007; Redhammer et al. 2011a; 2011b).

52   Among transition metals, Co^{2+} is able to enter the pyroxene structure in the M1 site within

53   the little distorted M1 octahedron, and in the M2 6 to 8-fold coordinated site.

54   Most studies on Co pyroxenes were done on monoclinic $CaCoSi_2O_6$ (Navrotsky and Coons 1976;

55   Ghose et al. 1987) and orthorhombic $Co_2Si_2O_6$ (Akimoto et al. 1965; Sasaki et al. 1982) end

56   members. Moreover the magnetic properties of end member Ca-Co pyroxenes at low temperature

57   (Durand et al. 1996; Redhammer et al. 2008), and the visible absorption spectrum (White et al.

58   1971; Burns 1983), were also studied. Intermediate cobalt pyroxenes, which can be represented in

59   the series $CaCoSi_2O_6 – Co_2Si_2O_6$, were only studied in the recent single crystal structural

60   investigation (Mantovani et al. 2013). In such solid solution Co fills the M1 site, and the

61   substitution along the series occurs between Ca and Co in the M2 site. The ionic radius of Co is

62   intermediate between that of Mg and Fe (0.745 *vs* 0.72 and 0.78 Å respectively) (Shannon, 1976)

63   and the crystal chemistry of $(Ca,Co)CoSi_2O_6$ pyroxenes is expected to be similar to that of

64   quadrilateral pyroxenes diopside – enstatite (Di–En, $CaMgSi_2O_6 – Mg_2Si_2O_6$, hereafter Ca–Mg

65   pyroxenes) and hedenbergite – ferrosilite (Hd–Fs, $CaFeSi_2O_6 – Fe_2Si_2O_6$, hereafter Ca–Fe

66   pyroxenes). These series share the point that chemical changes occur only for the substitution of

67   Mg, Fe, Co for Ca, i.e. smaller for a bigger cation, in the M2 site.

68   At room pressure the only Ca-Co pyroxene phase that can be synthesized is the end member

69    $CaCoSi_2O_6$; further Co addition results in the formation of olivine and silica (Mukhopadhyay and

70   Jackobs, 1987). At high pressure, P > 3 GPa, the orthorhombic and monoclinic $Co_2Si_2O_6$ phases

71   were obtained by Akimoto et al. (1965) but no other systematic study at high pressure was

72   performed on Co pyroxenes. Phase equilibria in Ca–Co pyroxenes are similar to those in the Ca–Fe

73   pyroxenes, that at room pressure crystallize incongruently fayalite and quartz, whereas at high

74   pressure the pyroxene phases are stable through the join.

75   In Ca–Mg and Ca–Fe pyroxenes the space group at room conditions changes from $C2/c$ to $P2_1/c$

76   and then to *Pbca*, as Ca content decreases; orthorhombic pyroxenes are confined to the Ca poorer

77   composition, whereas the transition from $C2/c$ to $P2_1/c$ occurs at a Ca content of ~0.3 and ~0.6

78   a.p.f.u. respectively in Ca–Fe (Ohashi et al. 1975) and in Ca–Mg pyroxenes (Newton et al. 1979;

79   Tribaudino 2000; Tribaudino et al. 2005). It was proposed that the $C2/c$ to $P2_1/c$ phase transition

80   occurs as the average cation radius in the M2 site becomes lower than the critical value of 0.88 Å

81   (Arlt et al. 1998).

82   Moreover in both Ca–Mg and Ca–Fe pyroxenes there is a miscibility gap between Ca–rich and Ca–

83   poor compositions. It is asymmetric, with higher solubility on the Ca–richer limb, and widens with

84   increasing pressure; also, it is larger in Ca–Mg pyroxenes (Gasparik and Lindsley 1980; Linsdley

85   and Munoz 1969).

86   We expect that the same transition and miscibility gap also occurs in Ca–Co pyroxenes; a

87   comparison with Ca–Fe and Ca–Mg ones can provide the basis of a model of solid solutions in

88   pyroxenes.

89   In this work a series of $(Ca,Co)CoSi_2O_6$ pyroxenes was synthesized at high pressure, and analyzed

90   by XRD, SEM–EDS and TEM, to clarify the extension of the solid solutions and the symmetry

91   changes along the series. The results were compared with those of Ca–Fe and Ca–Mg pyroxenes to

92   model the effect of the substitution of Ca with a smaller cation, on the phase transition and on the

93   extension of the miscibility gap.

94   Single crystal refinements of $C2/c$ Ca–Co pyroxenes synthesized in the present study have been

95   instead reported in a previous paper (Mantovani et al. 2013).

96

97   **Experimental methods**

98

99   Synthesis

100   The starting materials for the high pressure experiments were obtained by annealing high

101   grade reagents of amorphous SiO_2 (Sigma–Aldrich 99.995%), $CaCO_3$ (Sigma–Aldrich 99.995%),

102   and Co_3O_4 (Sigma Aldrich >99.99%). The stoichiometric mixtures were prepared in order to obtain

103   the composition of $Ca_xCo_{1-x}CoSi_2O_6$ pyroxenes, with x varying from 0 to 1 at step of 0.1 Ca atoms

104   p.f.u. (Table 1). Slight silica excess (about 1-2 wt%) was present in all samples to avoid the

105   formation of silica sub-saturated phases. At first the samples were annealed at $P = 1$ atm and $T =$

106   1000 °C for 12 hours; XRD analysis of the annealed samples showed almost pure $CaCoSi_2O_6$

107   pyroxene, Co–akermanite ($Ca_2CoSi_2O_6$) and Co–olivine (Co_2SiO_4), in various amounts depending

108   on the Co content and, in all samples, an excess of SiO_2 in the form of trydimite, cristobalite and

109   amorphous silica. The mixture, after fine grinding, was used for the high pressure experiments. A ½

110   inch piston cylinder apparatus and a pyrex–talc assembly containing an internal graphite furnace

111   was used (Bromiley et al. 2004), and the experiments were run at $P = 3$ GPa and in a T range

112   between 1100 and 1350 °C . Pressure and temperature were maintained at this condition from 1 to 7

113   hours after which the heating system was switched off and the samples quenched. Temperature was

114   measured with a Pt–Pt10%Rh thermocouple. A small amount of water was added to enhance

115   reaction. The experimental conditions are reported in Table 1.

116   Run products were at first analyzed optically. They appeared as a tiny pink bunches of crystals of

117   the order of tens of micrometers in length (Fig. 1). Sharp optical extinction was noted.

118

119   SEM–EDS and X–ray powder diffraction

120   A few grains of the run products were embedded in epoxy and polished for SEM–EDS

121   analysis using a Jeol 6400 SEM equipped with an Oxford EDS, operated at 20 kV.

122   Electron backscattered images were taken on the same area where the microprobe analysis was

123   performed. The crystals are euhedral and compositionally homogeneous (Fig. 2).

124   At least 10 analytical spots were collected in each run product. The average results of the chemical

125   analyses were expressed in atoms per formula unit, calculated on the basis of six oxygen and four

126   cations and reported in Table 1; the standard deviation is reported in brackets and it is calculated on

127   the average of 10 analytical spots.

128   From the remaining sample powder diffraction was conducted using a Bruker–AXS D8 Advance

129   and CuKα radiation ($\lambda = 1.54178$ Å). Intensity measurements were taken in steps of 0.02° over 2θ

130   range from 10 to 80°, with a counting rate of 1.3 sec per step. Rietveld analysis was performed to

131   determine the unit cell parameters and quantify the phases present. GSAS–EXPGUI software

132   package was used (Larson and Von Dreele 1994; Toby 2001). Starting atomic parameters were

133   taken from Ghose et al. (1987) for $C2/c$, and from Sasaki et al. (1982) for $Pbca$ pyroxenes. For

134    $P2_1/c$ pyroxenes, the atomic parameters are taken from the structure of clinoferrosilite (Hugh–Jones

135   et al. 1994), but with the substitution of the iron atoms with cobalt. The site occupancy of the

136   intermediate pyroxenes was derived by the EDS results. The cell parameters and phase fractions are

137   reported in Table 1.

138

139   TEM observation

140   A sample with composition $Ca_{0.3}Co_{1.7}Si_2O_6$, labeled as Co7 in Table 1, was examined by

141   transmission electron microscopy. The sample were crushed, suspended on ispropylic alcohol and

142   deposited on a holey carbon film. A JEOL JEM-2200FS field emission electron microscope

143   operating at 200 kV equipped with double tilt holder was used. Selected area diffraction patterns

144   were collected along zone axes at different orientation, to show the changes in lattice symmetry.

145

146   **Results**

147

148   Single and two pyroxene stability field

149

150   SEM–EDS and XRD powder diffraction analysis showed in most runs a single pyroxene phase,

151   with composition very close to the expected pyroxene stoichiometry (Table 1), coexisting with a

152   slight amount of excess quartz related to the excess silica in the starting materials. In few runs, a

153   two pyroxene assemblage of Ca–rich and Ca–poor pyroxenes was found (Fig. 2). This happened in

154   syntheses at or below 1200°C, for starting materials with less Ca than 0.5 atoms p.f.u. in the

155   nominal pyroxene (Lindley and Munoz 1969; Gasparik and Lindsley 1980).

156   The coexistence of Ca–poor and Ca–rich pyroxenes was interpreted, in accordance to previous

157   findings for Ca–Fe and Ca–Mg pyroxenes, as an evidence of a miscibility gap between pyroxenes.

158   At 1350°C the Ca–Co in pyroxene solubility is almost complete, although it is likely that by

159   similarity with Ca–Mg and Ca–Fe phase diagrams, between $Ca_{0.1}Co_{1.9}Si_2O_6$ and $Ca_{0.2}Co_{1.8}Si_2O_6$ a

160   narrow miscibility gap between clino and orthopyroxenes exists also at 1350°C.

161   At 1280°C no evidence of exsolution for $Ca_{0.5}Co_{1.5}Si_2O_6$ was obtained, whereas at 1200°C and

162   1100°C a clino–orthopyroxene gap was present. Also, in the TEM observation on $Ca_{0.3}Co_{1.7}Si_2O_6$

163   at 1350°C exsolution lamellae of Ca-poorer (or richer) phases, like those reported in Domeneghetti

164   et al (1995) and Tribaudino et al (2003a) were not observed.

165   The composition of coexisting pyroxenes and of solid solutions reported in Table 1 and the analogy

166   with other pyroxenes allows to sketch the phase diagram between 1100 and 1350 °C (Fig. 3a).

167   The sketch of the diagram of Ca–Co pyroxenes is compared with that of Ca-Mg and Ca-Fe

168   pyroxenes at $P = 3$ GPa (Lindsley and Munoz 1969; Gasparik and Lindsley 1980) (Fig. 3b). Most

169   apparent is that the pyroxene solubility decreases on the Ca rich side with the substituting cation at

170   the M2 site, from Fe to Co and Mg. At about Ca content of 0.5 a.p.f.u. a single clinopyroxene phase

171   is present at $P = 3$ GPa between melting and a temperature of 1500°C for Ca – Mg, 1280°C for Ca-

172   Co and 900°C for Ca-Fe pyroxenes.

173

174   Cell parameters, TEM observations and the $C2/c – P2_1/c$ phase transition

175

176   The cell parameters of Ca–Co clinopyroxenes are shown as a function of composition in Fig. 4.

177   Axial parameters and volume change with Ca content. The trend is linear with composition between

178   1 and 0.4 Ca atoms p.f.u., but at about 0.4 Ca atoms p.f.u a turnover is observed, with a sudden

179   increase in the β angle, and a further decrease in the axial parameters, most apparent along the **a**

180   axis, and in the cell volume (**V**).

181 Similar trends were found in diopside–enstatite (Tribaudino 2000, Tribaudino et al. 2005), and in

182 $MnMgSi_2O_6$–$CaMgSi_2O_6$ pyroxenes (Arlt et al. 1998), for the Mg for Ca and Mn for Ca

183 substitutions respectively, and were all ascribed to the transformation from $C2/c$ to the $P2_1/c$ phase.

184 We expect the $C2/c$ to $P2_1/c$ transition when a smaller cation, like Co here, substitutes Ca in the M2

185 site, or when cooling from high temperature reduces the apparent size of the cation in the M2 site

186 (Arlt et al. 1998, Tribaudino et al. 2002).

187 The signature of the transition is, however, the presence of h+k odd reflections, symmetry forbidden

188 in $C2/c$ pyroxenes. Such reflections are best observed in single crystal investigations, as they are

189 present but quite weak in powder diffraction patterns. Single crystal XRD refinements recently

190 performed on pyroxenes between $CaCoSi_2O_6$ and $Ca_{0.4}Co_{1.6}Si_2O_6$, the h+k odd reflections were not

191 found, prompting for a $C2/c$ structure (Mantovani et al. 2013).

192 Synthesis of samples with lower Ca contents was attempted, but we did not manage to obtain

193 single crystals large enough. Alternatively the tiny crystals we synthesized were suitable for the

194 observation with transmission electron microscopy: due to the high scattering power of electrons,

195 single crystal electron diffraction patterns can be easily obtained from submicrometric areas.

196 As shown in Fig. 5, selected area diffraction patterns taken on some flakes of composition

197 $Ca_{0.3}Co_{1.7}Si_2O_6$, all revealed the presence of h+k odd reflections, confirming that composition has a

198 primitive lattice and assumingly a $P2_1/c$ symmetry.

199 We can therefore divide the series by the different symmetry: Ca richer samples with Ca between 1

200 and 0.4 atoms p.f.u. show a $C2/c$ symmetry, that switches to $P2_1/c$ for lower Ca.

201 This result was confirmed by subsequent careful analysis of powder diffraction patterns, that

202 revealed the presence of the weak –2–31 reflection in $Ca_{0.3}Co_{1.7}Si_2O_6$ and $Ca_{0.2}Co_{1.8}Si_2O_6$ (Fig. 6).

203

204 **Discussion**

205

206   The above data show that at $P = 3$ GPa along the $CaCoSi_2O_6$–$Co_2Si_2O_6$ series all the phases have

207   the pyroxene structure, in contrast to room pressure. The same is true in Ca–Fe and Ca–Mg

208   pyroxenes, but not in pyroxenes along the series $CaZnSi_2O_6$–$Zn_2Si_2O_6$, (Huber et al. 2012) which

209   require higher pressure to stabilize the pyroxene phases.

210   As shown in Fig. 3b there are several common features in the shape of the phase diagram for Ca vs

211   Fe, Mg and Co substitutions: 1) a large miscibility gap exists between Ca–rich and Ca–poor

212   pyroxenes; 2) the gap is asymmetric, with much wider solubility in the Ca richer side, whose

213   symmetry is monoclinic $C2/c$; 3) on the Ca–poorer side of the join an orthopyroxene phase is

214   present, with Ca up to a maximum content of 0.1 atoms per formula units (a.p.f.u.); 4) an

215   hypersolvus subsolidus field exists; 5) monoclinic pyroxenes with a low Ca content show a $P2_1/c$

216   space group.

217   The main difference between the three phase diagrams is the different solubility of Ca in the Ca–

218   rich side of the series, whereas the solubility appears quite similar on the Ca poorer orthopyroxene

219   side.

220   Such differences are due to a change in the size of the substituting cation, i.e. to an increase in the

221   difference of the ionic radius with Ca, and provide a good example of the general principle that the

222   extent of a solid solution depends on the difference in cation radius between the substituting cations.

223   The difference in cation radius between Ca and Fe, Co and Mg, is 22, 25.5 and 28% respectively of

224   the cation radius of Ca (Shannon 1976), and the solubility in the different series decreases with

225   increasing difference in the cation radius.

226   Changes in space group along the series occur because Ca–poorer samples require a more

227   deformed, less symmetric structure to accommodate smaller cations. This was observed in

228   Mantovani *et al.* (2013) showing that the deformation parameter $\Delta M2$ in $C2/c$ structure increases

229   with the decrease of Ca content up to a limiting value that triggers the transition. The difference

230   between Ca–Mg, Ca–Fe and Ca–Co here is in the composition at the transition from $C2/c$ to $P2_1/c$,

231   which was determined between 0.30 and 0.40 Ca atoms pfu in Ca–Co and Ca–Fe pyroxenes and at

232   about 0.60 Ca a p.f.u, in Ca–Mg ones (Ohashi et al.1975; Newton et al. 1979; Tribaudino 2000;

233   Tribaudino et al. 2005). This corresponds approximately to the turnover in volume vs composition

234   (Fig. 7), in agreement also with previous observation on $MnMgSi_2O_6$–$CaMnSi_2O_6$ pyroxenes (Arlt

235   et al. 1998).

236   The volume changes in the $C2/c$ Ca–richer pyroxenes can be modeled assuming that they are simple

237   and only due to the decreasing average size of the cation in the M2 site. The unit cell volume can

238   then be predicted as:

239

240    $$V_x = V_{EM} - Z*4/3 \, \pi \, (R^3_{Ca} - R^3_{Fe, Co, Mg})*(1-X_{Ca})$$

241

242   where V_x is the unit cell volume for a given Ca content, V_{EM} the volume of the Ca–rich end

243   member, i.e. diopside, hedenbergite or $CaCoSi_2O_6$, Z the number of M2 sites in the unit cell (4 in

244    $C2/c$ and $P2_1/c$), and R_{Ca} and $R_{Fe, Co, Mg}$ the ionic radii of divalent Ca and Fe, Co and Mg. This trend

245   predicts quite closely the changes in volume with composition, which can be modeled as linear in

246   the $C2/c$ field (Fig. 7), up to the compositions close to the transition, where the observed volumes

247   are lower than those predicted by the model.

248   While the above linear model is followed quite closely by Ca-richer $C2/c$ clinopyroxenes, in the

249    $P2_1/c$ field the cell volume is lower than predicted. We interpret the missing volume mostly as an

250   effect of the $C2/c$ – $P2_1/c$ transition . At high temperature the $P2_1/c$ pyroxenes undergo a displacive

251   transition to $C2/c$; in Ca–Mg clinopyroxenes the transition was observed at T ~ 950 and 550 °C, in

252    $Ca_{0.15}Mg_{1.85}Si_2O_6$ and $Ca_{0.52}Mg_{1.48}Si_2O_6$ pyroxenes, respectively (Tribaudino et al. 2002, 2003b).

253   From an extrapolation of the volume of the $C2/c$ pyroxenes above the transition temperature to

254   room conditions, we obtain the volume that these compositions would have without the P–C

255   transition. As shown in Fig. 7 the volume plots very close to the linear $C2/c$ trend obtained by the

256   above "ionic" model.

257   To note, the volume–composition trend we observe in Ca–Fe, Ca–Mg and Ca–Co pyroxenes could

258   also be interpreted as non-ideal in a continuous solid solution. Here instead it is interpreted as ideal

259   for $C2/c$ and $P2_1/c$ pyroxenes, and the apparent deviation from non-ideality is due to a negative

260   volume contribution for the phase transition.

261   The composition at the transition can then be pinpointed at the turnover in the volume with

262   composition trend, obtained by an extrapolation of the $P2_1/c$ volumes into the $C2/c$ trend.

263   The transition in Ca–Mg pyroxenes is then determined at 0.58 Ca atoms p.f.u, in agreement with

264   previous TEM, Raman and XRD observations (Tribaudino 2000; Tribaudino et al. 2005;

265   Tribaudino et al. 2012), and at about 0.39 Ca a.p.f.u. for Ca–Co and 0.38 a.p.f.u. for Ca–Fe

266   pyroxenes, as supported by single crystal X–ray diffraction results (Ohashi et al. 1975; Mantovani

267   et al. 2013). A further result can be obtained along the series $CaMgSi_2O_6$–$MnMgSi_2O_6$, where Mg

268   act as scaffolding cation in the M1 site, all Mn substitutes Ca in the M2 site, and the volume–

269   composition trend shows that the transition occurs at 0.21 Ca atoms p.f.u (Arlt and Armbruster

270   1997).

271   The average cation radius at the transition varies then between 0.88 Å for Ca–Mg, 0.86 Å for Ca–Fe

272   and Ca–Mn and 0.85 Å for Ca–Co pyroxenes, below, but not far from, the 0.89 Å critical cation

273   radius estimated by an extrapolation of the $P2_1/c - C2/c$ high temperature transition temperatures to

274   room temperature (Arlt and Angel 2000; Alvaro et al. 2011); it should be stressed however that the

275   limited data set near the transition hinders careful determination of the critical composition.

276   A plot of the volume difference between the linear "ionic" model and the actual volume shows for

277   the $P2_1/c$ pyroxenes a linear trend, with different slope and intercept for Ca–Mg and for Ca–Fe and

278   Ca–Co pyroxenes (fig. 8). The suggestion is that the $C2/c$ phase is stabilized in Ca–Fe and Ca–Co

279   pyroxenes.

280   Beyond ionic radius, a further contribution from the crystal field stabilization energy, which is

281   present in Fe and Co pyroxene, is therefore likely. An effect of the crystal field splitting was found

282   by Arlt et al. (1998) in the high pressure $P2_1/c - C2/c$ phase transition, comparing the transition

283   pressure of Mn^{2+} and Cr^{2+} with that of clinoenstatite and clinoferrosilite. It was suggested that the

284   effective ionic radii of M1 and M2 cations do not exclusively control the transition pressure: the HP

285     $C2/c$ clinopyroxenes with Cr^{2+} and Fe^{2+} gain additional stabilization energy from crystal field

286   effects.

287

288   **Implications and conclusions**

289

290   The thumb rule for solid solutions, derived by investigations on metals (Hume-Rothary 1939) is that

291   the difference in ionic radius of substituting cations is the factor limiting the occurrence and extent

292   of a solid solution. The rule was generalized by Kerrick and Darken (1975), stating that the

293   difference in the molar volume of the end members is the driving force. This is found here

294   comparing Ca-Fe and Ca-Mg pyroxenes, where the solid solution is lower in the Ca-Mg and higher

295   in the Ca-Fe series: in the two series the cation radius and the molar volume difference are higher

296   and lower respectively; pyroxenes in the Ca-Co series are in between. We see that the mere cation

297   substitution explains only a part of the volume change through the solid solution: comparing

298   clinoenstatite and diopside the deviation in the volume-composition for the phase transition in

299   clinoenstatite is higher than that for the Ca-Mg substitution only (Fig. 7). Also, without the phase

300   transition, the volume-composition behavior would be ideal. Alone, the difference in the molar

301   volume between the end members without the phase transition is similar in the three series, between

302   8 and 10 $Å^3$, and the final difference in the molar volume is due to the higher excess volume for the

303   transition in Ca-Mg vs Ca-Co and Ca-Fe (respectively ~ 14, 10 and 5 $Å^3$). The different solid

304   solution in the three series is therefore due to a different excess volume in the phase transition. It is

305   likely that also for other thermodynamic variables the deviation in the thermodynamic behavior due

306   to the phase transition is present: for instance Mg-richer $P2_1/c$ pyroxenes in the series diopside-

307   enstatite show a marked deviation from the trend shown by $C2/c$ Ca-richer ones in the formation

308   enthalpy (Newton et al., 1979). The obvious result is that when the phase transition is no more

309   present (at about 1200°C in the diopside-enstatite), but at much lower temperature in Fe-rich

310   pyroxenes (Shimobayashi and Kitamura 1991; Arlt et al. 1998; Alvaro et al. 2011), the excess

311   volume decreases significantly, and so the other thermodynamic excess parameters; the free energy

312   of the solid solution becomes comparable or even lower than that of a mixture of Ca-richer and

313   poorer clinopyroxenes, and higher solid solution is possible.

314   This was observed already by Cameron and Papike (1981), on crystal chemical grounds: the much

315   higher solid solution of pyroxenes at higher temperature could be explained by the presence of a

316    $C2/c$ structure also in Fe-Mg richer pyroxenes: in a $C2/c$ structure Ca enters more easily in solid

317   solution than in the $P2_1/c$.

318   The change from $P2_1/c$ to $C2/c$ at high temperature occurs via a first order transition (Smyth 1974;

319   Tribaudino et al. 2002), and the volume changes suddenly at the critical transition point. Therefore,

320   the transition temperature, the volume change before and after the transition should be well

321   determined in modeling the end member thermodynamics.

322   The implication is that the same should be done in modeling for petrologic calculations of any solid

323   solution involving phase transitions.

324   In general therefore a miscibility gap, of a given extent, may develop either simply by the strain

325   due to the cation substitution, within a series where all the end-members have the same structure, or

326   for the combined effect of cation substitution and phase transition, like here in pyroxenes. In the

327   latter case we have to consider the equilibria above and below the phase transition: the free energy

328   of the solid solution should incorporate explicitly also the contribution from the phase transition.

329   A suggestion for further work in solid solution involving phase transitions would be to assess the

330   energetic contributions due to the cation substitution alone and to phase transitions, where present.

331   The purpose should be to define a model clarifying how the deformations due to these two

332   mechanism compete. Also, from the petrologic point of view one should verify whether neglecting

333   the effect of phase transitions in solid solutions may lead to incorrect extrapolation of the

334   thermodynamic data base outside the experimental conditions.

342   **References cited**

343

344   Alvaro, M., Camara, F., Domeneghetti, M.C., Nestola, F., and Tazzoli, V. (2011) HT $P2_1/c$–

345     $C2/c$ phase transition and kinetics of Fe^{2+}–Mg order–disorder of an Fe-poor pigeonite: implications

346   for the cooling history of ureilites. Contributions to Mineralogy and Petrology, 162, 599-613

347

348   Akimoto, S.I., Katsura, T., Syono, Y., Fujisawa, H., and Komada, E. (1965) Polyrnorphic

349   transitions of pyroxenes $FeSiO_3$ and $CoSiO_3$ at high pressures and temperatures. Journal of

350   Geophisical Research, 70, 5269–5278

351

352   Arlt, T., Angel, R.J., Miletich, R., Armbruster, Th., and Tjerk, P. (1998) High pressure $P2_1/c$ – $C2/c$

353   phase transitions in clinopyroxenes: influence of cation size and electronic structure. American

354   Mineralogist, 83, 1176–1181

355

356   Arlt, T. and Armbruster, T. (1997) The temperature–dependent $P2_1/c$ – $C2/c$ phase transition in the

357   clinopyroxene kanoite $MnMg[Si_2O_6]$: a single crystal X–ray and optical study. European Journal of

358   Mineralogy, 9, 953–964

359

360   Arlt T. and Angel R.J. (2000) Displacive phase transitions in C-centred clinopyroxenes:

361   spodumene, $LiScSi_2O_6$ and ZnSiO. Physics and Chemistry of Minerals, 27, 719–731

362

363   Bromiley, G.D., Keppler, H., McCammon, C., Bromiley, F.A. and Jacobsen, S.D. (2004) Hydrogen

364   solubility and speciation in natural, gem–quality chromian diopside. American Mineralogist, 89,

365   941–949

366

367   Burns, R.G. (1993) Mineralogical Applications of Crystal Field Theory. Cambridge University

368   Press.

369

370   Cameron, M. and Papike, J.J., (1981) Structural and chemical variation in pyroxenes. American

371   Mineralogist, 66, 1-50

372

373   Domeneghetti M. C., Molin M., Stimpfl M., and Tribaudino M. (1995) Orthopyroxene from the

374   Serra de Magé meteorite: structure refinement and estimation of $C2/c$ pyroxene contributions to

375   apparent $Pbca$ diffraction violations. American Mineralogist, 80, 923-929.

376

377   Downs, R.T. (2003) Topology of the pyroxenes as a function of temperature, pressure, and

378   composition as determined from the procrystal electron density. American Mineralogist, 88, 556–

379   566

380

381   Durand, G., Vilminot, S., Rabu, P., Derory, A., Lambour, J.P., and Ressouche, E. (1996) Synthesis,

382   Structure, and Magnetic Properties of $CaMSi_2O_6$ ($M=$ Co, Ni) Compounds and Their Solid

383   Solutions. Journal of Solid State Chemistry, 124, 374–380

384

385   Gasparik, T. and Lindsley, D.H. (1980) Phase equilibria at high pressure of pyroxenes containing

386   monovalent and trivalent ions. Reviews in Mineralogy and Geochemistry, 7, 309–339

387

388   Ghose, S., Wan, C., and Okamura, F.P. (1987) Crystal structures of $CaNiSi_2O_6$ and $CaCoSi_2O_6$ and

389   some crystal–chemical relations in $C2/c$ clinopyroxenes. American Mineralogist, 72, 375–381

390

391   Huber, A.L., Heuss–Aßbichler, S., Fehr, K.T., and Bromiley, G. D. (2012) Petedunnite

392   ($CaZnSi_2O_6$): Stability and phase relations in the system $CaO–ZnO–SiO_2$. American Mineralogist,

393   97, 739–749

394

395   Hugh-Jones, D.A., Woodland, A.B. and Angel, R.J. (1994) The structure of high-pressure $C2/c$

396   ferrosilite and crystal chemistry of high-pressure $C2/c$ pyroxenes. American Mineralogist, 79, 1032-

397   1041

398

399   Hume-Rothery, W. (1939) The structure of metals and alloys. Chemical publishing company, Inc.,

400   Brooklyn, New York, Part III, 30–49

401

402   Jodlauk, S., Becker, P., Mydosh, J.A., Khomskii, D.I., Lorenz, T., Streltsov, S.V., Hezel, D.C., and

403   Bohatý, L. (2007) Pyroxenes: a new class of multiferroics. Journal of Physics: Condensed Matter,

404   19, 432201

405

406   Kerrick, D.M. and Darken, L.S. (1975) Statistical thermodynamic models for ideal oxide and

407   silicate solid solutions, with application to plagioclase. Geochimica et Cosmochimica Acta, 39, 10,

408   1431-1442

409

410   Larson, A.C. and Von Dreele, R.B. (1994) General Structure Analysis System (GSAS). Los

411   Alamos National Laboratory Report, LAUR, 86–748

412

413   Lindsley, D.H. and Munoz, J.L. (1969) Subsolidus relations along the join hedenbergite–ferrosilite.

414   American Journal of Science, 267, 295–324

415

416   Mantovani, L, Tribaudino, M., Mezzadri, F., Calestani, G. and Bromiley G. (2013) The structure of

417    $(Ca,Co)CoSi_2O_6$ pyroxenes and the Ca–M^{2+} substitution in $(Ca,M^{2+})M^{2+}Si_2O_6$ pyroxenes (M^{2+} =

418   Co, Fe, Mg). American Mineralogist, 98, 1241-1252

419

420   Mukhopadhyay, S. and Jacob, T. (1996) Phase equilibria in the system CaO–CoO–SiO_2 and Gibbs

421   energies of formation of the quaternary oxides $CaCoSi_2O_6$, $Ca_2CoSi_2O_7$, and $CaCoSiO_4$. American

422   Mineralogist, 81, 963–972

423

424   Navrotsky, A. and Coons, W.E. (1976) Thermochemistry of some pyroxenes and related

425   compounds. Geochimica et Cosmochimica Acta, 40, 1281–1288

426

427   Newton, R.C., Charlu, T.V., Anderson, P.A.M., and Kleppa, O.J. (1979) Thermochemistry of

428   synthetic clinopyroxenes on the join $CaMgSi_2O_6$–$Mg_2Si_2O_6$. Geochimica et Cosmochimica Acta,

429   43, 55–60

430

431   Ohashi, Y., Burnham, C.W. and Finger, L.W. (1975) The effect of Ca–Fe substitution on the

432   clinopyroxene crystal structure. American Mineralogist, 60, 423–434

433

434   Redhammer, G.J., Senyshyn, A., Tippelt, G., and G Roth, G. (2011a) Magnetic spin structure of

435   pyroxene–type $MnGeO_3$. Journal of Physics: Condensed Matter, 23, 25, 4202

436

437   Redhammer, G., Senyshyn, A., Tippelt, G., Pietzonka, C., Roth, G., and Amthauer, G. (2011b)

438   Magnetic and nuclear structure and thermal expansion of orthorhombic and monoclinic polymorphs

439   of $CoGeO_3$ pyroxene. Physics and Chemistry of Minerals, 37, 311–322

440

441   Redhammer, J.G., Roth, G., Treutmann, W., Paulus, W., André, G., Pietzonka, C., and Amthauer,

442   G. (2008) Magnetic ordering and spin structure in Ca–bearing clinopyroxenes $CaM^{2+}(Si, Ge)_2O_6$,

443   M=Fe, Ni, Co, Mn. Journal of Solid State Chemistry, 181, 3163–3176

444

445   Redhammer, G., Nestola, F., and Miletich, R. (2012) Synthetic $LiAlGe_2O_6$: The first pyroxene

446   with $P2_1/n$ symmetry. American Mineralogist, 97, 1213–1218

447

448   Redhammer, G. and Roth, G. (2004) Structural variation and crystal chemistry of $LiMe^{3+}Si_2O_6$

449   clinopyroxenes Me^{3+} = Al, Ga, Cr, V, Fe, Sc and In. Zeitschrift für Kristallographie – Crystalline

450   Materials, 219, 5, 278–294

451

452   Sasaki, Y.T., Fujino, K., and Akimoto, S. (1982) Electron–density distribution of three

453   orthopyroxenes, $Mg_2Si_2O_6$, $Co_2Si_2O_6$ and $Fe_2Si_2O_6$. Zeitschrift für Kristallographie, 158, 279–297

454

455   Shannon, R. (1976) Revised effective ionic radii and systematic studies of interatomic distances in

456   halides and chalcogenides. Acta Crystallographica A, 32, 751–767

457

458   Shimobayashi N, Kitamura M (1991) Phase transition in Ca-poor clinopyroxenes: a high-

459   temperature transmission electron microscopic study. Physics Chemistry Minerals, 18, 153–160

460

461 Smyth, J.R. (1974) The high temperature crystal chemistry of clinohypersthene. American

462 Mineralogist, 59, 1061–1082

463

464 Toby, B. H.(2001) EXPGUI, a graphical user interface for GSAS. Journal of Applied

465 Crystallography, 34, 210–213.

466

467 Tribaudino, M. (2000) A transmission electron microscope investigation of the $C2/c{\rightarrow}P2_1/c$ phase

468 transition in clinopyroxenes along the diopside–enstatite ($CaMgSi_2O_6$–$Mg_2Si_2O_6$) join. American

469 Mineralogist, 85, 707–715.

470

471 Tribaudino, M. and Nestola, F. (2002) Average and local structure in $P2_1/c$ clinopyroxenes along

472 the join diopside–enstatite ($CaMgSi_2O_6$–$Mg_2Si_2O_6$). European Journal of Mineralogy, 14, 549–555

473

474 Tribaudino M., Pasqual D., Molin G.M., and Secco L. (2003a) Microtextures and crystal chemistry

475 in $P2_1/c$ pigeonites. Mineralogy and Petrology, 77, 161-176

476

477 Tribaudino, M., Nestola, F., Meneghini, C., and Bromiley, G. D. (2003b) The high-temperature

478 $P2_1/c$–$C2/c$ phase transition in Fe-free Ca-rich $P2_1/c$ clinopyroxenes. Physics and Chemistry of

479 Minerals, 30, 527-535.

480

481 Tribaudino, M., Nestola, F. and Meneghini, C. (2005) Rietveld refinement of clinopyroxenes with

482 intermediate Ca–content along the join diopside–enstatite. The Canadian Mineralogist, 43, 1411–

483 1421.

484

485 Tribaudino, M., Mantovani, L., Bersani, D., and Lottici, P.P. (2012) Raman spectroscopy of

486 $(Ca,Mg)MgSi_2O_6$ clinopyroxenes. American Mineralogist, 97, 1339–1347.

487

488   White, B.W., McCarthy, G.J., and Scheetz, B.E. (1971) Optical spectra of chromium, nickel, and

489   cobalt–containing pyroxenes. American Mineralogist, 56, 72–89

490

491   Yang, H. and Prewitt, C.T. (2000) Chain and layer silicates at high temperatures and pressures.

492   Reviews in Mineralogy and Geochemistry, 41, 211–255

493

494   **Figure captions**

495   **Figure 1**: images of Ca-Co pyroxenes recorded by optical microscope. (**a**) parallel polars. (**b**)

496   crossed polars.

497   **Figure 2:** Backscattered electrons image. (**a**) single clinopyroxene phase in the sample

498    $Ca_{0.9}Co_{1.1}Si_2O_6$. The presence of quartz is related to the excess silica in the starting materials. (**b**)

499   cohexistence of Ca-rich (cpx) and Ca-poor (opx) phases in samples $Ca_{0.4}Co_{1.6}Si_2O_6$ (Co6, T =

500   1200°C).

501   **Figure 3:** (**a**) sketch of a phase diagram of the join $CaCoSi_2O_6 - Co_2Si_2O_6$ at $P = 3GPa$. Light blue

502   crosses represent the monoclinic single phase while deep blue circles the orthorombic phase.

503   Crosses into the miscibility gap represent the cohexistence of opx and cpx. The shape of the

504   miscibility gap is built up with reference to literature data for the Ca-Mg and Ca-Fe pyroxene and it

505   is only loosely constrained by the synthesis experiments. (**b**) sketch of a comparison at $P = 3$ GPa

506   between phase diagrams of Ca–Mg (Gasparik and Lindsley 1980), Ca–Fe (Lindsley and Munoz

507   1969) and Ca–Co pyroxenes (This work); comparative size of Ca and Fe^{2+}, Mg and Co ions and

508   ionic radius difference (Δ) are shown.

509   **Figure 4:** Cell parameters along the join $CaCoSi_2O_6 - Co_2Si_2O_6$ in the $C2/c$, red, and $P2_1/c$, blue

510   fields.

511   **Figure 5:** selected area electron diffraction pattern along [010] of $Ca_{0.3}Co_{1.7}Si_2O_6$. Note the

512   presence of reflections h+k odd, violating the C lattice and of streaking along a*, interpreted as

513   staking disorder, as in Tribaudino (2000)

514   **Figure 6:** The evolution with composition of the h+k odd -2-31 reflection between $Ca_{0.4}Co_{1.6}Si_2O_6$

515   and $Ca_{0.2}Co_{1.8}Si_2O_6$.

516   **Figure 7:** cell volume vs composition in Ca-Co, Ca-Mg and Ca-Fe pyroxenes: the blue lines

517   represent change in volume modeled by a "ionic model" (see text), red circles the experimental data

518   for $C2/c$, room and extrapolated from high temperature (arrowed), and black diamond for $P2_1/c$

519   pyroxenes [Newton et al. (1979); Tribaudino (2000); Tribaudino et al. (2005) for Ca-Mg, Ohashi et

520   al. (1975) for Ca-Fe pyroxenes]. Best fits for $C2/c$ and $P2_1/c$ are dashed.

521   **Figure 8:** difference with cation radius between experimental volume and that predicted by a "ionic

522   model". Different best fit lines for Ca-Mg, and for Ca-Co and Ca-Fe pyroxenes are shown,

523   calculated using only data from the $P2_1/c$ region.

524

525   **Tables**

526   **Table 1**: Synthesis condition, chemical analyses and cell parameters of the synthetized samples.

527   Phase percentage in the two phase assemblage are wt %, determined by Rietveld refinement.

528

Sample	Nominal Ca (a.p.f.u.)	P (GPa)	T (°C)	Time (h)	Ca (a.p.f.u.)	Co (a.p.f.u.)	Si (a.p.f.u.)	Phase	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
Co0	1	3	1200	6	0.997(11)	0.968(14)	2.023(10)	cpx	9.802(1)	8.962(1)	5.249(1)	105.40(1)	444.54(3)
Co1	0.9	3	1200	4	0.949(8)	1.058(7)	1.995(8)	cpx	9.799(1)	8.949(1)	5.246(1)	105.53(1)	442.81(3)
Co2	0.8	3	1200	6	0.860(8)	1.133(6)	2.005(5)	cpx	9.791(1)	8.954(1)	5.246(1)	105.77(1)	442.58(8)
Co3	0.7	3	1200	4	0.723(15)	1.283(17)	2.010(6)	cpx	9.777(1)	8.958(1)	5.242(1)	106.13(1)	441.05(8)
Co4	0.6	3	1200	4	0.618(19)	1.397(31)	2.005(13)	cpx	9.769(1)	8.964(1)	5.243(1)	106.46(1)	440.28(3)
Co5	0.5	3	1100	5	0.687(30)	1.319(32)	1.997(7)	cpx (65.3%)	9.798(1)	8.984(1)	5.258(1)	106.33(1)	445.21(1)
					0.106(51)	1.897(48)	2.007(11)	+ opx (34.6%)	18.357(2)	8.941(1)	5.224(1)		857.3(1)
Co5	0.5	3	1280	5	0.519(28)	1.488(33)	2.009(6)	cpx	9.751(1)	8.962(1)	5.239(1)	106.78(1)	438.28(9)
Co5	0.5	3	1350	6	0.517(14)	1.498(5)	2.018(23)	cpx	9.753(1)	8.964(1)	5.238(1)	106.83(1)	438.41(8)
Co6	0.4	3	1200	6	0.626(35)	1.376(36)	1.999(5)	cpx (66.6%) +	9.747(1)	8.955(1)	5.233(1)	106.64(1)	437.66(5)
					0.110(11)	1.891(17)	2.000(5)	opx (33.3%)	18.338(3)	8.927(2)	5.207(1)		852.48(9)
Co6	0.4	3	1350	5	0.419(23)	1.596(25)	1.991(15)	cpx	9.749(1)	8.963(1)	5.237(1)	106.82(7)	438.11(9)
Co7	0.3	3	1350	7	0.300(27)	1.691(19)	2.010(6)	cpx	9.717(1)	8.952(1)	5.245(1)	107.92(6)	434.09(8)
Co8	0.2	3	1350	4	0.209(12)	1.802(15)	2.002(4)	pig	9.707(1)	8.950(2)	5.238(1)	108.43(5)	431.7(1)
Co10	0	3	1200	6	-	2.012(123)	2.005(15)	opx	18.298(2)	8.921(2)	5.203(1)		849.4(1)
Co10	0	7	1000	1	-	2	2	cpx	9.650(5)	8.929(5)	5.222(3)	108.8(1)	424.3(3)