1   **Revision 4**

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3   **Ca-Zn solid solutions in *C*2/*c* pyroxenes: synthesis, crystal structure**

4   **and implications for Zn geochemistry**

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18   **ABSTRACT**

19   The effect of Zn substitution on a series of clinopyroxenes along the join $CaZnSi_2O_6$-

20    $Zn_2Si_2O_6$ was studied. The pyroxenes were synthesized at P = 4-5 GPa and T = 1000-1200ºC by a

21   multi anvil apparatus. SEM-EDS and XRD analysis showed complete solid solution; all of the

22   samples have the *C*2/*c* space group. No miscibility gap between clino and orthopyroxene nor phase

23   transition to the *P*2₁/*c* space group was found. Moreover, the cell volume of Ca-Zn pyroxenes

24   decreases less than expected from the decrease of the average cation size for the substitution of Zn

25   for Ca.

26   The crystal structures of three synthetic pyroxenes of composition $(Ca_{0.5}Zn_{0.5})ZnSi_2O_6$,

27    $(Ca_{0.3}Zn_{0.7})ZnSi_2O_6$ and $(Ca_{0.2}Zn_{0.8})ZnSi_2O_6$ were refined by single crystal X-ray diffraction ($R_{4\sigma}$

28   between 3 and 4.5%). It was observed that the Ca-Zn substitution occurs in the M2 polyhedron,

29   with a sub-site splitting of Zn in a position at approximately 0.7 Å from Ca. In this position, Zn

30   retains a highly distorted fourfold coordination; moreover, the tetrahedral chain configuration is

31   little changed along the series, and the M1 polyhedral size increases with Zn substitution in M2.

32   An implication of the present work is the interpretation of the partitioning of Zn between

33   clinopyroxene and melt. The distribution coefficients of Zn and Co are quite different in rocks of

34   the same composition, despite their very similar ionic radius, and the difference is related to the

35   preference of Zn for the M2 site, where Zn may find a suitable atomic coordination.

36   **Keywords:** clinopyroxene, high pressure, X-ray diffraction, trace elements, Zn.

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40   **INTRODUCTION**

41   The crystal structure of pyroxene, due to its inherent flexibility, provides an effective

42   playground for obtaining models relating the atomic structure to composition and *P-T* conditions

43   and for interpreting phase equilibria and solid solutions in minerals.

44   The formula unit of pyroxenes is $M2M1T_2O_6$, with M2 hosted in a distorted six-eightfold

45   polyhedron, M1 into a more regular octahedron and T in tetrahedral coordination (Fig. 1). In natural

46   pyroxenes, the M2 site is occupied by larger cations, such as Ca, Na, Mg, Fe^{2+}, and Li, the M1 site

47   is occupied by Mg, Fe^{2+}, Fe^{3+}, Al, and Cr, whereas the T site is occupied by only Si and Al. Further

48   substitutions are possible in synthetic pyroxenes: the M2 site can also be filled by Sr, Co, Ni, Mn

49   and Zn; the M1 site can be filled by Co, Ni, Cr, Mn, Ni, Zn, Sc, Ti, Cu, Ga and V; and Ge can fully

50   exchange with Si in the tetrahedral site (Ohashi et al. 1990; Redhammer and Roth 2004;

51   Redhammer et al. 2012; Redhammer and Tippelt 2014; Tribaudino et al. 2005a, b; Arlt and Angel

52 2000; Tribaudino et al. 2002; Heuer et al. 2005; Tribaudino et al. 2009; Thompson et al. 2005;

53 Hugh-Jones et al. 1994).

54   The above synthetic pyroxenes are a counterpart to natural ones. For instance, in a recent

55 investigation on the crystal structure, phase equilibria and phase transitions in synthetic pyroxenes

56 along the series $CaCoSi_2O_6$-$Co_2Si_2O_6$ (Mantovani et al. 2013, 2014), Co-pyroxenes were compared

57 with natural Ca-Mg and Ca-Fe pyroxenes to study the effect of cation substitutions in the M2 site. It

58 was observed that in Ca-richer pyroxenes with $C2/c$ structure, the solid solution is ideal and volume

59 changes simply due to the different cation radii of the substituting cations; the apparent deviation

60 from the ideal behavior in Ca-poorer compositions is due to the negative excess volume for the

61 transition from the $C2/c$ to the $P2_1/c$ space group.

62   Moreover, it was observed that the $C2/c$-$P2_1/c$ phase transition occurs at an average M2

63 cation radius between 0.86 to 0.88 Å.

64   A different behavior can be expected in Ca-Zn pyroxenes. Zn has a ionic radius very similar

65 to that of Co and Mg, i.e., 0.74 *vs*. 0.745 and 0.72 Å, respectively, but it enters differently in the M2

66 site. Co, Mg and Fe in the M2 site show a 4+2 sixfold coordination, whereas Zn exhibits a fourfold

67 coordination (Morimoto et al. 1975). Moreover, at room pressure and temperature, monoclinic

68 $Zn_2Si_2O_6$ has a $C2/c$ structure, whereas monoclinic $Co_2Si_2O_6$, $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$ show a $P2_1/c$

69 space group (Morimoto et al. 1975; Ohashi et al. 1975; Morimoto et al. 1960; Sasaki and Takéuki

70 1981; Ohashi 1984). The fourfold coordination of Zn in the M2 cavity was explained by the

71 preference of Zn for covalent bonding and an sp^3 tetrahedral hybrid electronic configuration

72 (Morimoto et al. 1975).

73   Experimental data on Zn substitution in pyroxenes are scarce. Zn is a relatively common

74 element, but due to its low affinity for silicates, it occurs in rock forming silicates such as

75 pyroxenes as a trace element; actually, in natural pyroxenes, it is found as a major constituent in

76 only the rare mineral petedunnite (Essene and Peacor 1987). In petedunnite, the $CaZnSi_2O_6$

77 component is present in solid solution with johansennite ($CaMnSi_2O_6$).

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78   Pure $CaZnSi_2O_6$ pyroxene was synthesized at P>0.8 GPa (Huber et al. 2012); it has a *C2/c*

79 structure under room and high pressure conditions (Ohashi et al. 1996; Nestola et al. 2010). The Ca-

80 free orthorhombic *Pbca* and monoclinic *C2/c* polymorphs of the end member $Zn_2Si_2O_6$ were

81 synthesized by Syono et al. (1971), and their crystal structure was refined by Morimoto et al.

82 (1975).

83   At high pressure, the monoclinic *C2/c* $Zn_2Si_2O_6$ polymorph shows two phase transitions

84 with pressure, one to *P2$_1$/c* at P=1.92 GPa and the other to a high pressure *C2/c* structure at P=4.9

85 GPa (Arlt and Angel 2000). The high pressure *C2/c* structure has tetrahedral chain kinking and cell

86 parameters quite different from the room pressure *C2/c* (Arlt and Angel 2000).

87   Orthorhombic Zn pyroxenes with mixed Ni, Co, Mg and Zn occupancy were synthesized

88 and refined by Syono et al. (1971) and Morimoto et al. (1975), showing that Zn partitions strongly

89 in the M2 site.

90   No data are available for intermediate compositions between $CaZnSi_2O_6$ and $Zn_2Si_2O_6$. The

91 relations between the *C2/c* structures of the end members, one with Ca in eightfold and the other

92 with Zn in fourfold coordination, are not clear, nor is the extent of mutual solid solution. A specific

93 point of interest comes from the preference of Zn in the M2 polyhedron for a tetrahedral

94 coordination dictated by covalent bonding, whereas most cations substituting in the M2 polyhedron

95 of pyroxenes obey a simple ionic mechanism.

96   An investigation of Zn entrance in the M2 site also has an implication for the petrologic

97 behavior of Zn in pyroxenes as the structural behavior can provide a rationale for the geochemical

98 behavior of Zn in pyroxenes. The partitioning of Zn between clinopyroxene and melt was recently

99 proposed as a potential tracer for mantle source and an indicator for high temperature metamorphic

100 conditions (Le Roux et al. 2010; Huber et al. 2012).

101   We have therefore synthesized at high pressure a series of pyroxenes between $CaZnSi_2O_6$

102 and $Zn_2Si_2O_6$, finding that complete solid solution may be attained. Single crystal and powder

103 diffraction analysis detailed the structural mechanism for the Ca-Zn substitution; the implications

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104   for the partitioning of Zn between pyroxene and melt, in comparison with other trace elements,

105   were eventually discussed.

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107   **EXPERIMENTAL METHODS**

108   **Synthesis**

109   A set of Ca-Zn pyroxenes with composition between $CaZnSi_2O_6$ and $Zn_2Si_2O_6$ (Table 1)

110   was synthesized under high-pressure/high-temperature (HP/HT) conditions, using as a starting

111   material a stoichiometric mixture of $CaCO_3$, ZnO and SiO_2 (Sigma-Aldrich> 99.99%). The mixtures

112   were previously annealed in an electric furnace for 12 hours at T= 1000ºC and room pressure, to

113   obtain an assemblage of willemite (Zn_2SiO_4), hardystonite ($Ca_2ZnSi_2O_7$) and quartz. This

114   assemblage, finely ground, was put in a multi-anvil Walker-type press using Pt and Au capsules.

115   The capsules (30 μm-thick Pt or Au foil) were loaded into an octahedral MgO pressure cell and then

116   into the multi-anvil apparatus, in contact with a 10% Pt/Pt-Rh thermocouple for monitoring the

117   temperature during the reaction. The experiments were run at P= 5 GPa, and the capsules were

118   heated up to T= 1200ºC at a rate of 25ºC/min for $(Ca_{0.8}Zn_{0.2})ZnSi_2O_6$, $(Ca_{0.5}Zn_{0.5})ZnSi_2O_6$,

119    $(Ca_{0.3}Zn_{0.7})ZnSi_2O_6$, and $(Ca_{0.2}Zn_{0.8})ZnSi_2O_6$ (hereafter referred to as $Ca_{0.8}Zn_{1.2}$, $Ca_{0.5}Zn_{1.5}$,

120    $Ca_{0.3}Zn_{1.7}$, and $Ca_{0.2}Zn_{1.8}$). For $CaZnSi_2O_6$ and $Zn_2Si_2O_6$ (hereafter referred to as Ca_1Zn_1, Zn_2), the

121   runs were performed at P= 4 GPa and T= 1000ºC.

122   This condition was maintained for 3 hours of solid-state reaction, and then the capsules were

123   quenched to room temperature by switching off the heater. Finally, the pressure was slowly released

124   to prevent mechanical damage.

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126   **SEM-EDS and X-ray powder diffraction**

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

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

129   backscattered images were taken, showing that most of the sample was made by a phase with

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130   pyroxene stoichiometry, with a little excess of silica. The crystal size varies from 10 to 100 μm,

131   depending on the samples.

132   At least 10 analytical spots were collected on each run product. The chemical composition

133   confirmed the expected stoichiometry.

134   Powder X-ray diffraction was performed using a Bruker D2 PHASER diffractometer and a

135   Thermo ARL X'tra powder diffractometer equipped with a solid-state thermo electron detector,

136   operating with $CuK_{\alpha 1}$ radiation (λ= 1.5406 Å).

137   Rietveld analysis was performed to determine the unit cell parameters and the phase ratio,

138   using the GSAS-EXPGUI software package (Larson and Von Dreele 1994; Toby 2001). Starting

139   atomic parameters for the Ca-Zn pyroxenes were taken from Ohashi et al. (1996) for $CaZnSi_2O_6$

140   and from Morimoto et al. (1975) for $Zn_2Si_2O_6$. Rietveld analysis of powder patterns indicates that

141   clinopyroxene is the major phase, together with a small amount of coesite, less than 10%. Rietveld

142   refinement results are reported in Table 1.

143   **X-ray single-crystal refinement**

144   Single crystal X-ray diffraction data were collected on a Bruker AXS Smart diffractometer

145   equipped with an APEX II CCD area-detector, on selected crystals chosen for sharp optical

146   extinction, for the compositions $(Ca_{0.5}Zn_{0.5})ZnSi_2O_6$, $(Ca_{0.3}Zn_{0.7})ZnSi_2O_6$ and $(Ca_{0.2}Zn_{0.8})ZnSi_2O_6$.

147   The data collection was also attempted for other compositions, but suitable single crystals were not

148   found because of the highly twinned nature of the crystals.

149   Data collection conditions and parameters are reported in Table 2. The MoK_{α} radiation was

150   used, and the intensity data were corrected for absorption using the SADBS program (Sheldrick

151   1996). The $(Ca_{0.2}Zn_{0.8})ZnSi_2O_6$ crystals turned out to be systematically twinned on (100). The

152   refinement was performed on the intensities of one of the individuals after twin correction during

153   the data reduction.

154   Preliminary analysis of the reflection extinctions and intensities indicated a $C2/c$ space

155   group for all the samples.

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156   Weighted structural anisotropic refinements were performed using the SHELX-97 program

157 (Sheldrick 1997), within the WinGX suite (Farrugia 1999) and the coordinates of $CaZnSi_2O_6$ by

158 Ohashi et al. (1996) and of $Zn_2Si_2O_6$ by Morimoto et al. (1975) as starting models. Full occupancy

159 of Zn and Si in the M1 and T sites was confirmed by site occupancy refinement. In the M2 site,

160 mixed occupancy of Zn and Ca were present and refined but without significant deviations from the

161 expected stoichiometry.

162   Similar to other pyroxenes where Ca (or Na) coexists with a smaller cation, we observed a

163 significant improvement in the agreement factor by assuming that in the M2 cavity, Ca and the

164 smaller cation (here Zn) are split between two subsites (M2 for Ca and M2' for Zn). In previous

165 works, the M2 and M2' subsites were located along the b axis, at y/b~0.30 for Ca and 0.25 for the

166 smaller cation (Rossi et al. 1987; Tribaudino et al. 1989). In our case, the position for Zn was

167 refined further away from Ca, at y/b~0.23-0.24, at the same position found for Zn in $C2/c$ $Zn_2Si_2O_6$

168 (Morimoto et al. 1975). The electron density map along the diad axis at the M2 site position clearly

169 shows the two split atoms (Fig. 1). Polyhedra volume and bond valence are calculated by IVTON

170 (Balic Zunic and Vickovic 1996).

171   Cell, data collection and refinement parameters, atomic coordinates, anisotropic

172 displacement parameters and a selection of bond lengths and angles are reported in Tables 2, 3 and

173 4.

174

175   **RESULTS**

176 **Cell parameters**

177   In Fig. 2, the cell parameters of Ca-Zn pyroxenes are shown. For comparison, the trend

178 observed in $CaCoSi_2O_6$-$Co_2Si_2O_6$ pyroxenes, with Co replacing Zn, is reported (Mantovani et al.

179 2014); because the cation radius of Co is similar to that of Zn, the cell parameters are expected to

180 vary similarly. However, this is observed in only the Ca-rich end member, with no Zn in the M2

181 site (Fig. 2). As Zn enters the M2 polyhedron, we find significant differences: the a parameter

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182   decreases little in Ca-Zn pyroxenes, much more than in Ca-Co ones; the b increases, but it is

183   constant in Ca-Co pyroxenes; c decreases in Ca-Co pyroxenes and increases in Ca-Zn ones, and the

184   β angle increases most in Ca-Zn pyroxenes. Volume changes are higher and non-linear in pyroxenes

185   of the series $CaCoSi_2O_6$-$Co_2Si_2O_6$ and smaller and linear in Ca-Zn pyroxenes.

186   Similar differences can also be observed between Ca-Zn (this work), Ca-Mg (Tribaudino et

187   al. 1989) and Ca-Fe (Ohashi et al. 1975) pyroxenes.

188   The lower volume change in Ca-Zn pyroxenes can be in part ascribed to the absence of a

189    $C2/c$-$P2_1/c$ phase transition at intermediate compositions, but the Ca-Zn and Ca-Co trends are also

190   different when both phases have $C2/c$ symmetry, i.e., when Ca is higher than 0.4 Ca atoms per

191   formula unit (a.p.f.u.).

192   The cell volume in Ca-Zn pyroxenes shows a linear change with composition, following an

193   ideal behavior (Fig. 2). The same was observed in Ca-Mg, Ca-Fe and Ca-Co $C2/c$ pyroxenes (Arlt

194   et al. 2000; Mantovani et al. 2014) where a deviation from the ideal behavior occurs for only the

195    $P2_1/c$-$C2/c$ phase transition. The phase transition occurs with a volume decrease of the $P2_1/c$

196   structure with respect to the volume that would be observed in a $C2/c$ pyroxene with the same

197   composition; in the $P2_1/c$ field we observe linear changes in cell volume.

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199   **M2 polyhedron**

200   In $CaZnSi_2O_6$ pyroxene, with only Ca in the M2 site, the M2-O bond distances (Fig. 3) are

201   very close to those observed in $CaCoSi_2O_6$ (Mantovani et al. 2013, 2014; Ghose et al. 1987), which

202   are, in turn, similar to those of diopside and hedenbergite (Bruno et al. 1982; Nestola et al. 2007)

203   indicating that the different cations in M1 have little effect on the Ca in the M2 site. However, when

204   Zn exchanges for Ca into the irregular eightfold polyhedron surrounding Ca atoms, which we can

205   call the M2 cavity (Fig. 1), the electron density map shows the coexistence of two distinct positions

206   for Ca and Zn. The two atomic positions split so much that an average structure is hardly significant

207   and, in our Zn-rich solid solution, we have to consider different distances for the Ca and the Zn

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208   environments. In agreement with previous investigations (Rossi et al. 1987), we define M2 as the

209   polyhedron for Ca and M2' as that for the smaller cation (here Zn).

210   There are suggestions that oxygen also shows atom splitting as it was observed in synthetic

211   pyroxenes along the Di-En series by the analysis of the size of the U_{eq} *vs*. composition (Fig. 4)

212   (Bruno et al. 1982; Tribaudino et al. 1989; Tribaudino et al. 2003).

213   In Ca-Zn pyroxenes, similar to other *C*2/*c* pyroxenes where Ca exchanges with a smaller

214   cation, the U_{eq} for the O2 atoms are larger in the intermediate compositions than in the end

215   members and are generally larger than for other atoms of oxygen. Positional disorder explains the

216   increased size in intermediate compositions as the displacement parameters record an average of

217   local positions, which are different if the O2 is bonded to Zn in M2' or Ca in M2.

218   The M2'-O distances with the O2 and O1 atoms are close to 2.0 Å, whereas, as Ca is

219   exchanged by Zn, the M2'-O3 interatomic distances are greater than 3.0 Å. This results in an

220   irregular fourfold coordination of O1 and O2 atoms of oxygen around Zn (in the M2' site) (Fig. 1).

221   The same was found in $Zn_2Si_2O_6$ by Morimoto et al. (1975), and here, it is also observed in the

222   intermediate compositions: it is likely that Zn enters into fourfold coordination in the M2

223   polyhedron, even if present in a small amount.

224   Zn-O1 and Zn-O2 distances do not change with composition, and Zn-O3 distances become

225   even larger as zinc increases. However, from the geometrical point of view, we are far from a

226   regular tetrahedron: for instance, in $Ca_{0.3}Zn_{1.7}$, the O2-M2'-O2 angle is 169.7º and the other angles

227   of the O1 and O2 atoms of oxygen with M2' are between 90º and 100º, to compare with the ideal

228   109.4º predicted by tetrahedral coordination.

229   The fourfold coordination of Zn in M2' is specific to C2/c clinopyroxenes: in the

230   orthopyroxene and in the high pressure $P2_1/c$ structure, Zn instead shows an asymmetric sixfold

231   coordination, with two out of four O3 oxygens in coordination (Morimoto et al. 1975; Arlt et al.

232   2000).

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233   As Ca decreases, the bond distances with the furthermost O3 atoms of oxygen (M2-

234   O3C2,D2) and those with the closer O3 (M2-O3C1,D1 distances) increase; the M2-O1 distance is

235   constant, and the M2-O2 distance decreases. Within the eightfold M2 cavity, Ca then shows a 4+2

236   sixfold coordination and Zn shows a fourfold one.

237   The contribution of the M2 cavity to the cell volume can be obtained by the volume of the

238   eightfold coordinated polyhedron, regardless of the actual coordination of the cation in the site. This

239   volume is compared in Fig. 5 with that of other pyroxenes where Ca exchanges with a smaller

240   cation. The volume of the M2 cavity changes in a way very similar to that of Ca-Co, Ca-Fe and Ca-

241   Mg pyroxenes, with the only exception in the end member $Zn_2Si_2O_6$, which has the same volume as

242    $Ca_{0.2}Zn_{1.8}Si_2O_6$.

243   This result is quite surprising and indicates that the volume of the M2 cavity changes almost

244   completely for the different cation radii of Zn and Ca,, despite the different bonding of Zn and Co

245   in the M2 cavity (Fig. 5). This change is similar to what was found between Co and Ca. The

246   suggestion is that Ca, being the larger cation, accounts for the decrease in the size of the cavity, no

247   matter for the local coordination of Zn. The volume decrease in the M2 cavity of Ca-Co pyroxenes

248   explains the cell volume decrease almost completely; however, as discussed in the following

249   paragraph, in Zn pyroxenes, a cell volume increase driven by the M1 polyhedron opposes the

250   decrease in the M2 cavity and results in a lower volume change (Fig. 5).

251   **M1 polyhedron**

252   In the Ca-Zn series, Zn fully occupies the M1 site. The M1-O bond lengths *vs*. Ca are shown

253   in Fig. 6 and compared with those of Ca-Co pyroxenes. The two longer and smaller M1-O1

254   distances (M1-O1 A1,B1 and M1-O1 A2,B2, respectively) show a strong and opposite change with

255   Ca: the shorter distances decrease whereas the longer ones increase; the intermediate M1-O2

256   distances instead change slightly. The difference between shorter and longer distances also

257   increases in Ca-Co pyroxenes, but at a lower rate (Mantovani et al. 2013). For instance, the longer

258   M1-O1 distance increases by 0.064 Å along the series $CaCoSi_2O_6$-$Co_2Si_2O_6$, but in Ca-Zn

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259   pyroxenes, it increases by 0.174 Å. As a result, in $Zn_2Si_2O_6$ a 4+2 coordination is observed, with the

260   longer M1-O1B being less bonded. We also interpret this behavior as an attempt of Zn in the M1

261   site to approach the fourfold coordination, as in the M2 cavity. However, a transition to a fourfold

262   coordination in the M1 site is hindered because the M1 polyhedron is tighter and less flexible than

263   the M2 one; in the M2 cavity, which is more flexible and enables higher deformation, Zn finds its

264   own fourfold coordination.

265   Average bond distances and M1 polyhedral volume are very similar in $CaZnSi_2O_6$ and

266    $CaCoSi_2O_6$, although individual bond lengths are somewhat different. As shown in Fig. 7, the

267   polyhedral M1 volume is related to the M1 ionic radius in pyroxenes with only Ca in the M2 site,

268   suggesting that Zn in the M1 site shows an ionic behavior. In intermediate solid solutions, the

269   average M1-O distances increase with substitution of Zn for Ca in the M2 site, which is surprising

270   as the M1 site is always filled by Zn. In fact, the average bond distances (M1-O) are almost the

271   same for the whole series in Ca-Fe, Ca-Co and Ca-Mg pyroxenes (Fig. 8), where Fe, Co and Mg fill

272   the M1 polyhedron. The contribution of the increased size of the M1 polyhedron to the cell volume

273   explains why the M2 cavity in the case of Zn-pyroxenes does not account for the change in volume

274   as observed for the Co-pyroxenes: the Ca-Zn substitution in the M2 polyhedron decreases the cell

275   volume, but the increased M1 polyhedral size opposes such a decrease.

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277   **T tetrahedron and tetrahedral chain**

278   Throughout the series, the volume and average bond distances in the Si filled tetrahedron do

279   not change significantly but the individual T-O bond distances and angles do show significant

280   changes with Ca. The bond distances of Si with the O3 atoms, i.e., the T-O bridging (T-O$_{br}$),

281   decrease with decreasing Ca, whereas the distances with O1 and O2 atoms (T-O non bridging, T-

282   O$_{nbr}$), slightly increase (Fig. 9). Moreover, the tetrahedral angle variation (TAV) decreases with

283   decreasing Ca, showing that the tetrahedron becomes more regular. The T-O$_{br}$ distances decrease

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284 for the lower electrostatic contribution from Ca and Zn as both the M2-O3 and M2'-O3 distances

285 increase with Zn, making the tetrahedral chains further from the cations.

286   The O3-O3 distance, which is a shared edge with the M2 polyhedron, increases as Ca

287 decreases, accounting for the strong increase in the c parameter. As in the M1 polyhedron, we have

288 therefore an effect of the M2-O distances on the arrangement of the tetrahedral bond distances. The

289 same rearrangement in Si-O bond lengths is also found in other pyroxenes when Ca is exchanged

290 by a smaller cation (Fig. 10a).

291   The geometry of the tetrahedral chain does not change much with Ca-Zn substitution: the

292 kinking angle decreases, following the same trend in $C2/c$ Ca-Co, Ca-Mg and Ca-Fe pyroxenes

293 (Fig. 10b). Rather than a high temperature fully extended configuration similar to that found in

294 spodumene or high temperature pigeonite (Cameron et al. 1973), in the $C2/c$ end member $Zn_2Si_2O_6$,

295 the tetrahedral chain shows intermediate kinking, close to that observed in diopside. The kinking of

296 the end member $Zn_2Si_2O_6$ is very close to that of $(Ca_{0.3}Zn_{0.7})ZnSi_2O_6$ and $(Ca_{0.2}Zn_{0.8})ZnSi_2O_6$.

297   The relationship between the kinking angle and the cell β angle (Thompson et al. 2005) is

298 not found here. The β angle increases much more in Ca-Zn than in Ca-Co pyroxenes (Fig. 2), but

299 the O3-O3-O3 kinking angle changes likewise (Fig. 10b), with the exception of the end member

300 $Zn_2Si_2O_6$. The strong increase in the β angle is described by the shift of the tetrahedral chains

301 (Benna et al. 1988; Tribaudino 1996; Mantovani et al. 2013) that accounts for the offset between

302 the two tetrahedral chains facing onto the M2 polyhedron along the c direction (Tribaudino et al.

303 1989). It was observed by Mantovani et al. (2013) that chain shift enables an increase in the bond

304 distance between M2 and the furthermost O3, maintaining the $C2/c$ symmetry; in Ca-Fe, Ca-Mg

305 and Ca-Co pyroxenes, it takes a maximum value of 0.9 Å, which was suggested to be a limiting

306 value before the transition to the $P2_1/c$ symmetry. In Ca-Zn pyroxenes, higher shift can occur in the

307 $C2/c$ symmetry, accounting for the higher values in the β angle (Fig. 10c).

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DISCUSSION

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Zn substitution and phase transition

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313   The average ionic radius for six-coordinated M2 decreases from 1.0 to 0.74 Å along the

314   series. Following the prediction of a critical cation radius at approximately 0.86-0.88 Å, a $C2/c$-

315    $P2_1/c$ phase transition should occur as Ca becomes less than 0.4-0.5 a.p.f.u., but the $C2/c$ symmetry

316   is retained for any Zn substitution.

317   This effect reflects a different interaction of the cation in the M2 site with the tetrahedral

318   chain. In Ca-Mg, Ca-Fe, Ca-Co and Mn-Mg pyroxenes, the phase transition occurs as the size of the

319   average M2 cation decreases; then, in the $P2_1/c$ structure, the cation falls out from the special

320   position along the diad axis and the tetrahedral chains are rearranged to alternatively decrease and

321   increase the bond lengths with the M2 cation. Therefore, there is an active interaction between the

322   M2 and O3 oxygen.

323   In the case of Ca-Zn pyroxenes, at least at room conditions, this interaction is not observed:

324   the tetrahedral chain kinking does not change much along the series, and for Zn richer samples, it

325   does not change at all. The tetrahedral chain kinking angle decreases only if the Ca content is large

326   enough. For higher Zn content, the cation has no interaction with the tetrahedral chain and no

327   significant kinking occurs. The reduced ionic radius for Ca-Zn exchange in M2 is compensated by

328   the tetrahedral chain shift.

329   This effect does not occur simply because Zn lies in the M2' site at a position more

330   displaced from the tetrahedral chain than Mg, Co or Fe (Tribaudino et al. 1989; Rossi et al. 1987;

331   Mantovani et al. 2013; Ohashi et al. 1975; Nestola et al. 2007) and the bond distances with the O3

332   oxygen are longer (Fig. 3). A calculation on the charge on the O3 atom, which is, apart from Si,

333   bonded by only the M2-M2' atoms (Fig. 1), shows only little difference between Ca-Co and Ca-Zn

334   pyroxenes (Fig. 11). A likely explanation lies in the covalent character and the tetrahedral

335   coordination of the Zn-O bonding, which does not involve the O3 atoms of the chains facing the

13

336   M2 polyhedron: the charge balance model, which assumes an ionic charge distribution, is not

337   correct for Zn in M2 in Zn pyroxenes. Bonding for Zn involves only the O1 and O2 atoms, and an

338   interaction with the O3 atoms is not present.

339   A switch from the above "covalent" behavior to a "ionic" one occurs at high pressure,

340   reducing the Zn-O3 distances and promoting an approach to the tetrahedral chains,. At high

341   pressure, an interaction of Zn with the O3 bridging atoms promotes the transition to the $P2_1/c$

342   symmetry, at P= 1.9 GPa in $Zn_2Si_2O_6$ (Arlt and Angel 2000). In the high pressure $P2_1/c$ structure, as

343   well as in the *Pbca* structure of the orthopyroxene, which can be described as a twin at the unit cell

344   scale of the $P2_1/c$ structure, Zn is no longer fourfold coordinated (Morimoto et al. 1975; Arlt and

345   Angel 2000). Following the same rationale, we could also predict the transition to $P2_1/c$ at low

346   temperature, as a consequence of a supposed decrease in the volume of the M2 polyhedron and

347   approach of the tetrahedral chains to M2. This prediction is indeed supported by quantum

348   mechanical calculations at 0 K on monoclinic $Zn_2Si_2O_6$ (Karazhanov et al. 2009) but not by

349   experiments. Powder XRD down to 100 K by Galkin et al. (2007) in $Zn_2Si_2O_6$ does not show any

350   evidence of a transition to $P2_1/c$, and the transition, if any, should occur at even lower temperature.

351

352   **Solid solution in *C*2/*c* pyroxenes**

353   A complete solid solution is obtained in Ca-Zn clinopyroxenes at a temperature of 1200ºC;

354   under the same conditions where the solid solution was very limited in the Ca-Co and Ca-Mg

355   pyroxenes (Lindsley and Dixon 1976; Mantovani et al. 2014). In Ca-Co, as in Ca-Mg and Ca-Fe

356   pyroxenes, we have a miscibility gap separating a wider solid solution field of Ca-rich

357   clinopyroxenes from a narrow Ca-poor orthopyroxene field. Here, the orthopyroxene is not stable

358   and the two-pyroxene assemblage does not lead to a decrease in free energy with respect to the

359   single phase pyroxene.

360   Therefore, also in view of the ideal behavior of cell volumes, as long as the symmetry is

361   *C*2/*c*, complete solid solution can be expected.

14

362   The different coordination of Zn in the M2 cavity in *C*2/*c* and *Pbca* pyroxenes accounts for

363   the above behavior. In the M2 site of the *Pbca* $Zn_2Si_2O_6$ orthopyroxene, two of the O3 atoms of

364   oxygen are in coordination, although in an asymmetric position within the M2 cavity, and the

365   coordination in the M2 site can be described as 4+2 sixfold (Domeneghetti et al. 1995). The same

366   was observed in high pressure *P*2$_1$/*c* $Zn_2Si_2O_6$ (Arlt and Angel 2000). In *C*2/*c* clinopyroxene, the

367   shorter M2-O3 distances are out of bonding (~3.03 Å, Morimoto et al. 1975) and the coordination

368   of Zn in M2 is fourfold. Given the preference of Zn for a fourfold coordination, the higher stability

369   of the *C*2/*c* phase with respect to the *P*2$_1$/*c* and orthorhombic *Pbca* is not surprising (Syono et al.

370   1971).

371

IMPLICATIONS

373   In this work on synthetic pyroxenes, we have filled the M1 site with Zn and exchanged Zn

374   for Ca in the M2 site, which was possible because Ca does not enter the M1 site and any Ca will

375   buffer the M2 site. In natural petedunnite, we also have the M2 site completely filled by Ca and Zn

376   enters only the M1 site. However, Zn can enter both the M2 and the M1 sites if Ca does not buffer

377   the M2 site, as in clinopyroxenes from basalts and mantle peridotites.

378   Intracrystalline M2-M1 site preference for trace elements can be tested by the analysis of the

379   partition coefficients of the same elements between clinopyroxene and melt. Partitioning

380   coefficients are modified by the different chemical environments, but in a given sample, for a given

381   phase and in a given chemical site, they are related to the ionic radius of the partitioning element by

382   Onuma diagrams (Onuma et al. 1981). Onuma diagrams provide a curve showing the partitioning

383   coefficient vs. cation radius for cations in each structural site. Different curves are provided for

384   different structural sites. In general, cations with very similar ionic radii and charge, confined in a

385   given structural site, have very similar mineral-melt partition coefficients. Cations in different

386   structural sites may on the contrary have different crystal-melt partitioning even if they have similar

387   ionic size.

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388   We could then expect that Zn will have a very similar partitioning coefficient to cations such

389   as Co and Mg, with the same valence and similar size if they are concentrated in the same structural

390   site. This similarity is not found.

391   In Fig. 12, the clinopyroxene-melt distribution coefficients for a series of divalent cations, as

392   reported for a Ca-poor lherzolitic clinopyroxene by Adam and Green (2006), are plotted as a

393   function of ionic radius. The six- and eight-coordinated radii were reported (Shannon 1976),

394   respectively, for the M1 and M2 polyhedra. The Onuma diagram curves reported in Adam and

395   Green (2006) for the specific case were calculated from the lattice strain model of Blundy and

396   Wood (2003). In this model, the partition coefficients can be predicted by the polyhedral Young's

397   modulus and the ideal radius that the cation should have in a given polyhedron.

398   We observe that the clinopyroxene-melt partitioning coefficients for atoms such as Ca, Pb

399   and Mn, which are completely (Ca, Pb) or almost completely (Mn) partitioned in the M2 site, fall

400   on the curve calculated for the M2 site. Those for Co and Mg fall close to the curve calculated for

401   the M1 site, showing that their distribution is fully predicted, assuming that they enter the M1 site.

402   Zn instead shows a much lower clinopyroxene-melt distribution coefficient than expected if

403   concentrated in the octahedral M1 site, whereas, assuming that Zn enters the M2 site, the observed

404   partitioning agrees with predictions (Fig. 12).

405   The suggestion from crystal-melt partitioning is that Zn enters the M2 site. Although this

406   suggestion awaits experimental confirmation by an analysis of intracrystalline site partitioning

407   between the M2 and M1 sites in natural clinopyroxene, a strong preference was shown by Zn for

408   the M2 site in a solid solution of Co, Ni, Zn orthopyroxenes and in $ZnMgSi_2O_6$ synthetic

409   orthopyroxene (Morimoto et al. 1975; Ghose et al. 1975).

410   A likely crystal chemical explanation of the preference of Zn in the M2 site, in

411   clinopyroxenes and in orthopyroxenes, is that the M2 cavity is more flexible and better suited to

412   host the Zn cation in a fourfold sub-site than is the M1 polyhedron, which is a tighter cavity.

413   Incidentally, Ghose (1975) showed that there is a strong correlation between the intracrystalline

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414   partition coefficients and ionic radii in the M1 site, and Zn is again an exception, being more

415   concentrated in the M2 site than expected by its ionic radius.

416   The crystal chemical considerations put forward by the present work may also have a

417   petrologic implication. The crystal chemical preference of Zn for the M2 site results in a different

418   (lower) partitioning of Zn in the clinopyroxene but also a higher partitioning in the melt. A melt

419   formed by clinopyroxene-rich source rocks will be then enriched in Zn. The enrichment of Zn in

420   basaltic melts resulting from partial melting of clinopyroxene-rich source rocks was used by Le

421   Roux et al. (2010, 2011) to constrain the origin of the observed magmas, to track the source rock of

422   the original magmas and to detect the mantle source heterogeneities.

423   The above petrologic implications derive from the peculiar bonding requirements of Zn in

424   pyroxenes that confine Zn to the M2 cavity, and the clinopyroxene-melt partitioning coefficient is

425   then lower than what we would have if Zn was present in the M1 octahedral coordination. The

426   empirical predictions by Onuma diagrams are respected, once it is assumed that the smaller Zn fits

427   into the larger M2 cavity.

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430   **ACKNOWLEDGMENTS**

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641   **Figure captions**

642   **Figure 1:** (**a**) Crystal structure of one of the *C*2/*c* clinopyroxenes synthesized ($Ca_{0.5}Zn_{1.5}Si_2O_6$),

643   viewed perpendicular to the *c* axis and electron density map at the M2 site (*z* section); the cation

644   occupancy of the site is reported; (**b**) CaM2 and ZnM2 site positions are always located,

645   respectively, at the M2 and M2'sites.

646

647   **Figure 2:** Unit cell parameters *vs.* composition in Ca-Zn and Ca-Co pyroxenes: the former are

648   represented by the green points, and the latter are represented by purple squares. Solid and dashed

649   lines show the trend for the *C2/c* and *P*2$_1$/*c* pyroxenes, respectively [Data for Ca-Co pyroxenes

650   from Mantovani et al. (2014)].

651

652   **Figure 3:** M2-O bond lengths *vs.* composition in Ca-Zn and in Ca-Co pyroxenes (**a**); M2'-O bond

653   lengths with composition in Ca-Zn pyroxenes and in Ca-Co pyroxenes (**b**) [Data for Ca-Co

654   pyroxenes from Mantovani et al. (2013) and Ghose et al. (1987); for Ca-Zn pyroxenes from Ohashi

655   et al. (1996), Morimoto et al. (1975) and this work].

656

657   **Figure 4:** $U_{eq}O2$ *vs.* composition [Data for Ca-Co pyroxenes from Mantovani et al. (2013) and

658   Ghose et al. (1987); for Ca-Zn pyroxenes from Ohashi et al. (1996), Morimoto et al. (1975) and this

659   work; for Ca-Mg from Bruno et al. (1982) and Tribaudino et al. (1989); for Ca-Fe from Ohashi et

660   al. (1975) and Nestola et al. (2007)].

661

662   **Figure 5:** (**a**) ΔV (Å^3) of the cell, M2 eightfold and M1 polyhedra with composition (mol %) for

663   Ca-Zn and (**b**) Ca-Co pyroxenes; (**c**) volume of the M2 eightfold polyhedron *vs.* average M2 ionic

664   radius for Ca-Co, Ca-Mg, Ca-Fe, and Ca-Zn pyroxenes [For references see Fig. 4].

665

666   **Figure 6:** M1-O bond length variation with composition in Ca-Zn and Ca-Co pyroxenes [For

667   references see Fig. 3].

668

669   **Figure 7:** M1 polyhedral volume *vs.* cation radius predicted by an "ionic model" [Data for Ca-Co

670   pyroxenes from Ghose et al. (1987); for Ca-Zn pyroxenes from Ohashi et al. (1996); for Ca-Mg

671   from Tribaudino et al. (1989); for Ca-Fe from Nestola et al. (2007)].

672

673   **Figure 8:** Average M1-O bond lengths *vs.* composition (Ca content in the M2 site) for Ca-Zn,

674   Ca-Co, Ca-Fe and Ca-Mg pyroxenes. It is assumed that polyhedral bond lengths are not different in

675   the monoclinic and orthorhombic phases for $Co_2Si_2O_6$, $Mg_2Si_2O_6$ and $Fe_2Si_2O_6$ (Ohashi et al. 1996;

676   Sasaki and Takéuki, 1981; Hugh-Jones et al. 1994, Morimoto et al. 1960) [For references see Fig.

677   4].

678

679   **Figure 9:** T-O bond lengths *vs.* composition in Ca-Zn and in Ca-Co pyroxenes. [For references see

680   Fig. 3].

681

682   **Figure 10:** (**a**) Difference between average bridging and non-bridging T-O distances *vs.* Ca content

683   in the M2 site; (**b**) O3-O3-O3 kinking angle with composition; (**c**) tetrahedral chain shift *vs.* Ca

684   content in the M2 site: tetrahedral chain shift S= $2a\cos(\beta)(x_{O3}-0.5)+2cz_{O3}$. [For references see Fig.

685   4].

686

687   **Figure 11:** Bond valence of the O3 atoms coming from M2-M2' cations [For references see Fig. 3].

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689   **Figure 12:** The ionic partitioning curves for M1(**a**) and M2 sites (**b**) and divalent cations of

690   different ionic radius calculated using the parameters reported for a Ca poor lherzolitic pyroxene by

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691   Adam and Green (2006). The distribution coefficients for the cations are taken from the same

692   paper.

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694   **Tables:**

695   **Table 1:** Synthesis conditions, cell parameters and phase abundance from Rietveld refinement of

696   the X-ray diffraction powder pattern.

697   **Table 2:** Structure refinement data and unit cell parameters for Ca-Zn pyroxenes.

698   **Table 3:** Fractional atomic coordinates and isotropic displacement parameters for Ca-Zn pyroxenes.

699   Data for $CaZnSi_2O_6$ and $Zn_2Si_2O_6$ are taken from Ohashi et al. (1996) and Morimoto et al. (1975),

700   respectively, here and in Table 4.

701   **Table 4:** Bond lengths (Å), polyhedral volumes ($Å^3$) and angles for Ca-Zn pyroxenes.

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Sample	Ca_1Zn_1	$Ca_{0.8}Zn_{1.2}$	$Ca_{0.5}Zn_{1.5}$	$Ca_{0.3}Zn_{1.7}$	$Ca_{0.2}Zn_{1.8}$	Zn_2
P (GPa)	4	5	5	5	5	4
T (°C)	1000	1200	1200	1200	1200	1000
a (Å)	9.816(1)	9.801(1)	9.787(1)	9.783(1)	9.789(2)	9.807(2)
b (Å)	8.990(1)	9.004(1)	9.079(1)	9.125(1)	9.157(1)	9.197(1)
c (Å)	5.258(1)	5.251(1)	5.2652(1)	5.273(1)	5.288(2)	5.306(2)
β (°)	105.892(1)	106.494(8)	108.223(2)	109.777(5)	110.433(3)	111.454(4)
V (Å^3)	446.34(1)	444.27(3)	444.40(7)	443.01(9)	443.93(2)	445.48(2)
Diffractometer	Bruker D2	Thermo ARL X'tra	Thermo ARL X'tra	Bruker D2	Bruker D2	Bruker D2
Scan range (°)	7-80° 2θ	10-100° 2θ	10-100° 2θ	7-80° 2θ	7-80° 2θ	7-80° 2θ
pyroxene[a]	99.8%	97.1%	99.8%	96.2%	90.9%	97.7%
coesite[a]	0.2%	2.9%	0.2%	3.8%	9.1%	2.3%

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718   [a]wt% as determined by Rietveld refinement.

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720   Table 1

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Sample	$Ca_{0.5}Zn_{1.5}$	$Ca_{0.3}Zn_{1.7}$	$Ca_{0.2}Zn_{1.8}$
Space group	$C2/c$	$C2/c$	$C2/c$
Z	4	4	4
a (Å)	9.794(6)	9.773(6)	9.779(6)
b (Å)	9.071(5)	9.116(5)	9.146(5)
c (Å)	5.264(3)	5.272(2)	5.284(3)
β (°)	108.26(8)	109.74(8)	110.47(8)
V (Å^3)	444.1(5)	442.2(5)	442.8(4)
Diffractometer	Bruker AXS Smart	Bruker AXS Smart	Bruker AXS Smart
Radiation	Mo$K\alpha$	Mo$K\alpha$	Mo$K\alpha$
No. of indep. refl. $I > 4\sigma$	712	736	724
$2\theta_{max}$ (°)	63.34	64.38	64.28
$R_{4\sigma}$ (F)%	3.3	3.6	4.4
wR$_2$ (%)	8.4	8.6	10.0

Table 2

		Ca_1Zn_1*	$Ca_{0.5}Zn_{1.5}$	$Ca_{0.3}Zn_{1.7}$	$Ca_{0.2}Zn_{1.8}$	Zn_2§
M2 (Ca)	y/b	0.30015(5)	0.2955(3)	0.2883(7)	0.2838(10)	
	U_{eq}	0.0079(1)	0.0119(6)	0.0122(14)	0.0085(3)	
M2' (Zn)	y/b		0.2439(2)	0.2394(2)	0.2377(1)	0.2361(1)
	U_{eq}		0.0118(4)	0.0092(3)	0.0085(3)	0.0067(4)
M1 (Zn)	y/b	0.90583(3)	0.90033(6)	0.89680(7)	0.8949(9)	0.8919(1)
	U_{eq}	0.00625(6)	0.0141(2)	0.0130(2)	0.0122(2)	0.0073(2)
T (Si)	x/a	0.28631(5)	0.2936(10)	0.29784(13)	0.2996(2)	0.3016(1)
	y/b	0.09265(4)	0.08905(9)	0.08692(11)	0.0858(1)	0.0849(1)
	z/c	0.22916(9)	0.2455(2)	0.2562(2)	0.2609(3)	0.2668(2)
	U_{eq}	0.00424(9)	0.0114(2)	0.0098(3)	0.0083(3)	0.0042(2)
O1	x/a	0.1164(1)	0.1195(3)	0.1212(3)	0.1228(4)	0.1241(3)
	y/b	0.0889(1)	0.0880(2)	0.0872(3)	0.0866(3)	0.0868(3)
	z/c	0.1442(2)	0.1442(5)	0.1452(6)	0.1458(7)	0.1473(6)
	U_{eq}	0.0061(3)	0.0126(5)	0.0113(6)	0.0101(7)	0.0077(5)
O2	x/a	0.3602(1)	0.3695(3)	0.3747(4)	0.3761(4)	0.3787(3)
	y/b	0.2479(1)	0.2440(3)	0.2409(3)	0.2403(4)	0.2393(3)
	z/c	0.3212(2)	0.3478(6)	0.3625(7)	0.3668(8)	0.3719(6)
	U_{eq}	0.0082(3)	0.0235(6)	0.0193(7)	0.0139(7)	0.0090(5)
O3	x/a	0.3500(1)	0.3523(2)	0.3530(3)	0.3547(4)	0.3533(3)
	y/b	0.0190(1)	0.0219(3)	0.0239(3)	0.0241(4)	0.0238(3)
	z/c	0.9932(2)	1.0077(5)	1.0173(6)	1.0226(7)	1.0273(5)
	U_{eq}	0.0066(3)	0.0152(5)	0.0150(6)	0.0125(7)	0.0084(5)

Notes: x/a and z/c for the M2 and M1 special position are 0 and 0.25. * Data from Ohashi et al. (1996).
§Data from Morimoto et al. (1975).

Table 3

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		Ca_1Zn_1*	$Ca_{0.5}Zn_{1.5}$	$Ca_{0.3}Zn_{1.7}$	$Ca_{0.2}Zn_{1.8}$	Zn_2[§]
M2	Ca-O1A1, B1× 2	2.356(1)	2.374(3)	2.347(6)	2.337(8)	
	Ca-O2C2, D2× 2	2.336(1)	2.133(4)	2.014(4)	1.975(4)	
	Ca-O3C1, D1× 2	2.601(1)	2.604(3)	2.644(6)	2.665(8)	
	Ca-O3C2, D2× 2	2.729(1)	2.812(3)	2.889(5)	2.934(7)	
	<Ca-O>	2.505	2.480	2.474	2.478	
M2'	Zn-O1A1, B1× 2		2.023(3)	2.018(3)	2.029(4)	2.031(3)
	Zn-O2C2, D2× 2		2.105(4)	2.004(4)	1.973(4)	1.933(2)
	Zn-O3C1, D1× 2		2.987(3)	3.018(4)	3.022(4)	3.027(2)
	Zn-O3C2, D2× 2		3.110(3)	3.174(3)	3.205(4)	3.255(3)
	<Zn-O>		2.556	2.554	2.557	2.561
	V_{M2} (Å^3) 8-coord.	25.91(11)	24.91(11)	24.39(13)	24.29(12)	24.27(12)
	M2 along b axis[a]	3.690	3.737	3.763	3.780	3.800
M1	Zn-O1A2, B2× 2	2.075(1)	2.041(3)	2.025(4)	2.022(4)	2.018(3)
	Zn-O1A1, B1× 2	2.158(1)	2.233(2)	2.272(3)	2.299(4)	2.333(3)
	Zn-O2C1, D1× 2	2.075(1)	2.079(3)	2.089(3)	2.090(4)	2.084(3)
	<Zn-O>	2.103	2.117	2.129	2.137	2.145
	V_{Zn}(Å^3)	12.26(5)	12.51(5)	12.62(5)	12.76(5)	12.83(7)
	OAV[b]	18.5	30.7	36.5	42.2	51.5
	M1 along b axis[a]	1.427	1.415	1.401	1.406	1.402
T	Si-O1	1.604(1)	1.619(3)	1.625(4)	1.620(4)	1.617(3)
	Si-O2	1.585(1)	1.603(3)	1.601(3)	1.605(4)	1.604(3)
	Si-O3A1	1.668(1)	1.649(3)	1.633(3)	1.634(4)	1.625(3)
	Si-O3A2	1.687(1)	1.659(3)	1.645(3)	1.640(4)	1.627(3)
	<Si-O>	1.636	1.632	1.626	1.625	1.618
	V_T(Å^3)	2.24(1)	2.22(2)	2.19(2)	2.19(2)	2.16(2)
	TAV[b]	27.9	16.2	13.1	12.0	11.6
	O3A1-Si-O3A2	104.2(1)	107.2(1)	109.2(1)	109.8 (1)	111.2(1)
	Si-O3-Si	135.7(1)	138.0(2)	139.6(2)	139.6(2)	141.6(2)
	O3-O3-O3	165.2(7)	162.8(2)	161.2(3)	161.0(3)	161.3(1)
	O3A1-O3A2	2.647(1)	2.662(2)	2.672(2)	2.679(2)	2.683(4)
	T along b axis[a]	2.263	2.322	2.362	2.375	2.397

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753 Notes : [a]M2 contribution: $(0.5-y/bO1)b$; M1 contribution: $(y/bO2-y/bO1)b$; T contribution: $(0.5-y/bO2)b$.
754 [b]OAV and TAV are angle variance for tetrahedra and octahedra (Robinson et al. 1971).
755 * Data from Ohashi et al. (1996). [§]Data from Morimoto et al. (1975).

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758 Table 4

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$(Ca_{0.5}Zn_{0.5})ZnSi_2O_6$