

SYNTHESIS AND CHARACTERIZATION OF $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ PYROXENES

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ABSTRACT

This thesis concerns cobalt pyroxenes and it is mostly based on the join $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$. This series has an interest both in mineralogy and ceramic science. Regarding ceramic sciences Ca,Co-pyroxenes may be used as a ceramic pink pigment, with good chemical stability and colour properties. In mineralogy it is interesting to stress the analogy with the rock forming quadrilateral pyroxenes formed by diopside-enstatite ($\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$) and hedenbergite-ferrosilite ($\text{CaFeSi}_2\text{O}_6$ - $\text{Fe}_2\text{Si}_2\text{O}_6$) series. Moreover, Ca,Co-pyroxenes provide a crystal chemical model to study the pyroxenes solid solutions where a large ionic radius cation in the M2 site (Ca) is substituted by a smaller cation, such as Mg, Fe and Co.

INTRODUCTION

Cobalt pyroxene in ceramic sciences

Usually, cobalt in pigments is related to the blue hue but the palette is very large: blue, green, yellow, violet, brown and black (Eppler, 2000; Melo *et al.*, 2003; Mimani & Ghosh, 2000). The different hues are obtained by the different coordination number of this element in the structure. If cobalt is in tetrahedral coordination the colour results a deep blue (*e.g.*, blue cobalt pigment, based on CoAl_2O_4 spinel); otherwise, if the coordination number is higher, six or eight, the hue swings to pink (*e.g.*, Co-olivine Co_2SiO_4 , Ca,Co-pyroxenes ($\text{Ca,CoSi}_2\text{O}_6$, or Co-garnet $\text{Co}_3\text{Al}_2\text{Si}_3\text{O}_{12}$).

There are, however, several environmental issues in the use of cobalt, as this element is highly impacting on man, environment and economics being cobalt toxic, polluting and expensive (Kim, 1992). At present, research is in progress to minimize its use and to find phases highly stable to leaching (Ozel *et al.*, 2010). Among the cobalt based pigments, Co-bearing pyroxenes are proposed as interesting candidates.

The pyroxene structure is interesting in ceramic field both for the good stability to the alteration and for the lower cobalt content per formula units respect to the commonly used Co-olivine Co_2SiO_4 (Fores *et al.*, 2000). In this thesis the binary join $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ with pyroxene stoichiometry is studied. At room pressure in this join several pigment phases like Ca,Co-pyroxene, Co-olivine and Co-ackermanite are found, and the resulting pigment colour is investigated by means of colorimetric analysis, in view of application as a ceramic pigment. Synthesis at room pressure and characterization of a cobalt-based pyroxene with the formula $\text{CaCoSi}_2\text{O}_6$ is done in order to define a potential use in ceramics, in view of a possible further investigation on the interaction between pigment, glaze and enamel.

Cobalt pyroxene in mineralogy

At room pressure only the Co-poor part of the join can be synthesized (Ghose *et al.*, 1987). The Co-richer solid solutions require high pressure synthesis (Akimoto *et al.*, 1965) and consequently high production cost. However, the characterization of the end-member $\text{CaCoSi}_2\text{O}_6$ as a pink pigment cannot be separated from the basic knowledge of the entire system $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ from structural and phase equilibria point of views.

In this contest Ca,Co-pyroxenes are synthesized at high pressure ($P = 3$ GPa) in order to have single pyroxene phase and to compare them with quadrilateral pyroxenes. In fact, Ca,Co-pyroxenes have a strong similarity with Ca-Fe and Ca-Mg pyroxenes: the substitution of Co in a $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ join is similar to that of Mg and Fe in $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ - $\text{Fe}_2\text{Si}_2\text{O}_6$ pyroxenes, being the cation radius of Co (0.745 Å) intermediate between that of Mg and Fe. In order to clarify the mechanism of cation substitution in the

join, phase transitions, changes in symmetry and in the structure are investigated and compared to other quadrilateral pyroxenes.

EXPERIMENTAL

Room pressure synthesis

The syntheses were carried out at room pressure, with the aim to determine the best conditions in terms of temperature, time and composition for the synthesis of a pink pigment with a pyroxene structure. We considered the best conditions those where Ca,Co-pyroxene was present as a single phase.

Starting from the Ca-rich end-member (CaCoSi₂O₆), in which in the M1 site there is one atom of Co and in M2 site one atom of Ca, we increased cobalt content by 0.1 atoms per formula units up to the Co-rich end member Co₂Si₂O₆. The process we followed for this synthesis at room temperature was a traditional ceramic route known as “solid state synthesis”, where stoichiometric ratios of oxides and CaCO₃ carbonate were mixed and heated. The starting material were powder of Co₃O₄, CaCO₃, and amorphous SiO₂, which was prepared according to the stoichiometry Ca_{1-x}Co_{1+x}Si₂O₆ (where x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1). A slight silica excess was added in all the samples. After weighting the oxides, they were mixed and crushed in an agate mortar with acetone. Several crushing cycles were done to obtain a homogeneous material. The sample was then reduced in pellets, and heated within an alumina crucible in an electric furnace in air. The heating system increased the temperature with a step of about 200 °C/h up to the desired temperature, and then the samples were annealed for the selected time. At this temperature, reduction of Co³⁺ to Co²⁺ and decarbonation occurred readily. The quenching was done by turning off the power by leaving the samples to cool. Most of the samples appeared like synthesized pellets of different colour, from blue to pink, well separated from the alumina crucible. Table 1 reports the labels of the samples, their nominal composition and the synthesis conditions, as well as the resulting assembling and the colorimetric parameters. After the synthesis, all run products were examined by X-ray powder diffraction, SEM-EDS microprobe, Raman spectroscopy, UV-VIS and colorimetric analysis.

Table 1 - Sample labels, synthesis condition, phases obtained, colour coordinates, and final colour for all the sample synthesized; px: Ca,Co-pyroxene, ol: Co-olivine, tr: tridymite, ak: Co-akermanite.

Sample	Co0	Co0	Co0	Co0	Co0	Co0	Co1	Co1	Co2	Co2	Co3	Co3	Co4	Co4	
temperature (°C)	1000	1000	1000	1100	1100	1150	1000	1000	1000	1000	1000	1000	1000	1000	
time (h)	12	48	120	3	96	24	12	48	12	48	12	48	12	48	
Nominal Ca content	1	1	1	1	1	1	0.9	0.9	0.8	0.8	0.7	0.7	0.6	0.6	
Phase	ak+px+ ol+tr	ak+px+ ol+tr	N.d	N.d	N.d	Px+tr	ak+px+ ol+tr	N.d	ak+px+ ol+tr	N.d	ak+px+ ol+tr	N.d	ak+px+ ol+tr	N.d	
L*	43.33	56.07	58.79	59.76	63.18	66.53	46.75	62.91	48.28	64.96	49.94	66.59	50.98	63.17	
a*	9.17	13.9	18.74	27.16	25.54	25.35	9.07	14.16	8.77	16.67	9.87	18	10.48	18.59	
b*	-36.5	-25.4	-15.6	-8.1	-10.2	-8.85	-32.5	-18.7	-28.3	-15.4	-25.2	-13.4	-20.9	-15.5	
Colour															
Sample	Co5	Co5	Co5	Co5	Co5	Co6	Co6	Co7	Co7	Co8	Co8	Co9	Co9	Co10	Co10
temperature (°C)	1000	1000	1100	1100	1100	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
time (h)	12	48	3	24	96	12	48	12	48	12	48	12	48	12	48
Nominal Ca content	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.3	0.2	0.2	0.1	0.1	0	0
Phase	Px+ol +tr	Px+ol +tr	N.d	N.d	Px+ol +tr	Px+ol +tr	N.d	Px+ol +tr	N.d	Px+ol +tr	N.d	Px+ol +tr	N.d	Ol+tr	Ol+tr
L*	49.91	-	60.46	57.68	68.76	52.97	61.02	54.25	59.1	55.1	58.52	54.66	56.51	56.5	56.01
a*	13.89	-	19.64	23.91	18.7	18.42	18.69	20.58	19.2	21.12	19.41	21.74	20.07	20.5	20.59
b*	-19.9	-	-15.8	-14.8	-8.87	-21.7	-16.7	-22.8	-18.3	-23.1	-19.2	-23.5	-20.6	-21.5	-21.4
Colour															

High pressure synthesis

The starting material for the high pressure experiment was the mixture of phases obtained after the first series of runs at a temperature of 1000 °C and for 12 hours. The high pressure experiments were performed with a piston cylinder apparatus. The starting material, finely ground, was put in a 5 mm inner diameter, 10 mm long, platinum capsule and welded shut. The capsules were placed into a 0.5 inch pyrex-talc piston-cylinder assembly containing an internal graphite furnace (Bromiley *et al.*, 2004).

The experiments were run at $P = 3$ GPa and with a temperature range from 1100 to 1350 °C depending on the samples. The higher temperature of annealing for samples Co6 and Co8 was chosen in order to avoid exsolution. Pressure and temperature were maintained constant for approximately six hours, then the heating system was switched off and the samples were quenched. The temperature was measured with a Pt-Pt10%-Rh thermocouple. The sample with nominal composition $\text{Ca}_2\text{Si}_2\text{O}_6$ was synthesized both with piston cylinder ($P = 3$ GPa, $T = 1200$ °C) obtaining an assemblage of orthopyroxene and quartz, and then it was compressed in a multianvil apparatus at $T = 900$ °C and $P = 7$ GPa, obtaining a single clinopyroxene phase.

An assemblage of Ca,Co-pyroxene crystals sized up to ten microns were obtained (Fig. 1); no glass was found in any sample after the synthesis. XRD powder diffraction and SEM-EDS characterization confirmed that Ca,Co-pyroxene was the only phase, with stoichiometric composition. The experimental conditions of the syntheses are reported in Table 2.

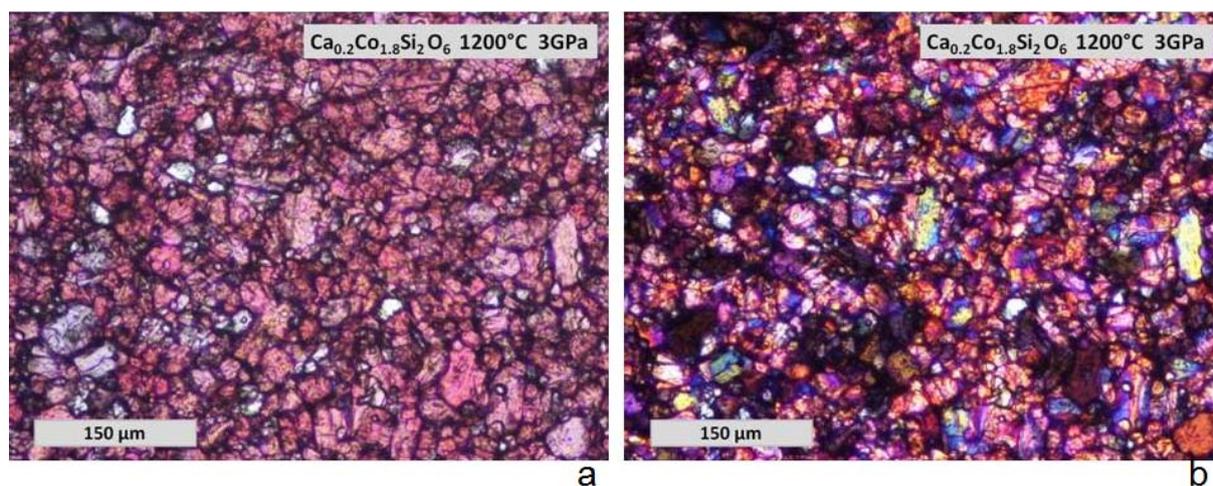


Fig. 1 - Images of the synthesized samples recorded by optical microscope: a) Co8, 1350 °C, 3 GPa (10x); b) Co8, 1350 °C, 3 GPa (10x, NX).

Table 2 - Synthesis condition, chemical analysis (from SEM-EDS) and cell parameters (from PXRD) of the samples. For Co5 and Co6 at 1100 °C and 1200 °C weight % of the two phases are reported; (*) water added in the capsule; (Pig+): monoclinic pyroxene with Ca content less than 0.25. If Ca is higher it is labelled as cpx.

Sample	Nom. Ca	Synthesis condition			Chemical analysis			Phase	Cell parameters				
		P (GPa)	T (°C)	t (h)	Ca	Co	Si		a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)
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	9.789(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	1200	5	0.519(28)	1.488(33)	2.009(6)	cpx	9.753(1)	8.962(1)	5.239(1)	106.78(1)	438.41(9)
Co5	0.5	3	1100	5	0.687(30)	1.319(32)	1.997(7)	cpx+	9.798(1)	8.984(1)	5.258(1)	106.33(1)	445.21(1)
					0.206(51)	1.837(48)	2.007(11)	opx	18.409(1)	8.983(2)	5.238(1)		866.34(1)
Co5	0.5	3	1350	6	0.517(14)	1.498(5)	2.018(23)	cpx	9.751(1)	8.964(1)	5.238(1)	106.83(1)	438.28(8)
Co6	0.4	3	1200*	6	0.626(35)	1.376(36)	1.999(5)	cpx+	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	18.338(3)	8.927(2)	5.207(1)		852.48(9)
Co6	0.4	3	1350		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)

DISCUSSION

Room pressure synthesis

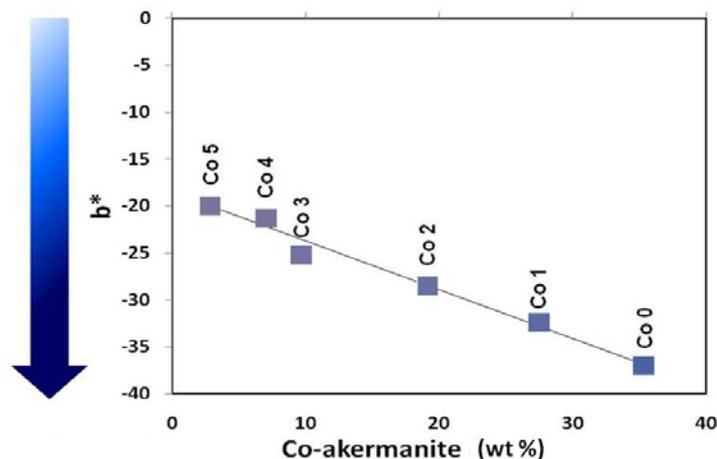
CaCo-pyroxenes can be synthesized at room pressure only in the range $\text{CaCoSi}_2\text{O}_6$ - $\text{Ca}_{0.9}\text{Co}_{1.1}\text{Si}_2\text{O}_6$ and a homogeneous clinopyroxene, suitable as a pure pigment, was obtained at room pressure by annealing at a temperature 1150 °C for 24 hours or 1100 °C for 96 hours. The resulting samples were well crystallized and qualitative and quantitative analyses revealed the presence of $\text{CaCoSi}_2\text{O}_6$ as a single phase. The colorimetric analysis confirmed a deep pink hue. Compared to the olivine based pigment the pyroxene showed a more distinct pink colour, with the need of lower Co-content (*i.e.*, 10 wt.% of Co in the formula $\text{CaCoSi}_2\text{O}_6$ pyroxene with respect to 8 wt.% in Co_2SiO_4 Co-olivine).

During synthesis made at temperature of 1000 °C for 12 hours in the Ca-rich end member $\text{CaCoSi}_2\text{O}_6$ the pyroxene coexisted with Co-olivine and Co-akermanite and the reaction did not reached equilibrium. The point was critical for the presence of a Co-akermanite phase, where cobalt entered in tetrahedral coordination, resulting in a deep blue hue. In this situation the pigment cannot resulted as pink, since the colour blue prevailed even if it was present in small quantities (*e.g.*, in the samples Co4 only 5% mol of Co IV were sufficient to give a blue colour even if the remaining 95% Co was present in octahedral coordination; Fig. 2). As the annealing time or temperature increased, the Co-akermanite disappeared, so that only pyroxene resulted present. Longer duration synthesis from intermediate $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ starting materials gave at equilibrium mixtures of pyroxene, Co-olivine, tridymite, and metastable Co-akermanite.

Co-akermanite was not found for Co-richer composition. The assemblage was texturally and compositionally in equilibrium; therefore we were able to sketch a phase diagram of the join $\text{CaCoSi}_2\text{O}_6$ - $\text{Co}_2\text{Si}_2\text{O}_6$ at room pressure. Three phase regions were found. One was at the Ca richer side of the join, where a single phase pyroxene is stable, with a solid solution between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.9}\text{Co}_{1.1}\text{Si}_2\text{O}_6$. This first region

was limited by a Co-olivine-clinopyroxene-tridymite assemblage; very close, but not at the end of the join, as some Ca is present in olivine solid solution, clinopyroxene disappeared and only olivine and SiO₂ were present. These intermediate mixtures are likely to be less interesting for ceramics as Co-akermanite and olivine pigments are available and well studied (Navrotsky & Coons, 1976; Masse & Muan, 1965).

Fig. 2 - The b* parameters (colour parameters) vs. Co-akermanite content (wt.% fraction) for the samples from Co0 to Co5 (1000 °C for 12 hours).



High pressure synthesis

The syntheses at high pressure gave important results on the crystal chemistry and phase stability of the Ca-Co pyroxenes series. The results obtained in this work, together with literature data, can better define the mechanism of cation substitution and the phase relations in quadrilateral pyroxenes. In particular, the analysis of the system CaCoSi₂O₆-Co₂Si₂O₆ can help to clarify the mechanism of the substitution of large cations like Ca for Co in the M2 site, shedding more light on the substitution of Ca with a smaller cation in pyroxenes.

In fact, along the series, as the Co atoms substitute Ca in the M2 site we observed:

- 1) a phase transition in clinopyroxenes, from C2/c to P2₁/c;
- 2) exsolution of Ca-rich and poor pyroxenes.

This is commonly to other pyroxenes series, when Ca is substituted by Mg or Fe.

Analogies and differences between the series CaCoSi₂O₆-Co₂Si₂O₆ and CaFeSi₂O₆-Fe₂Si₂O₆ and CaMgSi₂O₆-Mg₂Si₂O₆ were then investigated in order to clarify the general mechanism of substitution.

Structural investigations using single crystal data of Ca-Co, and comparing with Ca-Mg and Ca-Fe pyroxenes showed that simple ionic substitution occurred with several structural changes (Mantovani *et al.*, in press). At first, the solid solution occurred by the formation of two subsites in the M2 cavity, M2 and M2'. The observed Raman peak enlargement for samples C2/c with intermediate composition is related to this splitting which induces local disorder: to note, peak enlargement is proportional to displacement parameter in Ca-Co pyroxenes and Ca,Mg-pyroxenes (Tribaudino *et al.*, 2012).

After the phase transition a strong decrease in volume occurred as an effect of chain kinking which reduces the size of M2 polyhedron in addition to the changes in the ionic radius. Again, Raman spectra showed a significant deviation in the linear behaviour both in Di-En and Ca,Co-pyroxenes.

The cell parameters showed the same trend in the three series. We noticed that as the Co, Mg or Fe content increase, the *a* parameters decreased, *b* and *c* changed little, and β increased. The volume, reasonably, decreased since Co, Mg, Fe cations are smaller than Ca. The changes of the cell parameters with compositions were not linear, in any series, as different trends were observed for a Ca-rich and Ca-poor samples. This was an evidence of the phase transition, as shown in the description of cell parameters of Co-pyroxenes. The turnover occurred at different compositions: at about 0.5 Ca a.p.f.u. in Di-En join, at about 0.4 Ca a.p.f.u. for CaCo-CoCo pyroxenes, and 0.3 Ca a.p.f.u. for Hd-Fs. The turnover at the transition was more apparent in the volume

changes; in fact, along the series changes in volume can be modelled by an ionic model, that is a model in which changes in volume are assumed to occur only by the substitution of cations in the M2 site. Being the substituting cations of different ionic radius and volume, the cell volume decreases only by the decrease in size of the substituting cation.

In this model the volume is represented as a difference between the volume of the Ca-rich end member (*i.e.*, Di, Hd or $\text{CaCoSi}_2\text{O}_6$) and the decrease due to the substitution of a smaller cation for Ca:

$$V_x = V_{EM} - Z \cdot 4\pi/3 (R_{Ca} - R_{Fe, Co, Mg}) \cdot (1 - X_{Ca})$$

where the V_x volume for a given Ca content in the series, V_{EM} the volume of the end member diopside, hedenbergite or $\text{CaCoSi}_2\text{O}_6$, Z the number of M2 sites in the unit cell (4 in $C2/c$ and $P2_1/c$), and R_{Ca} and $R_{Fe, Co, Mg}$ the ionic radii of divalent Ca and Fe, Co Mg. The calculated volume is represented by the blue line in Fig. 3.

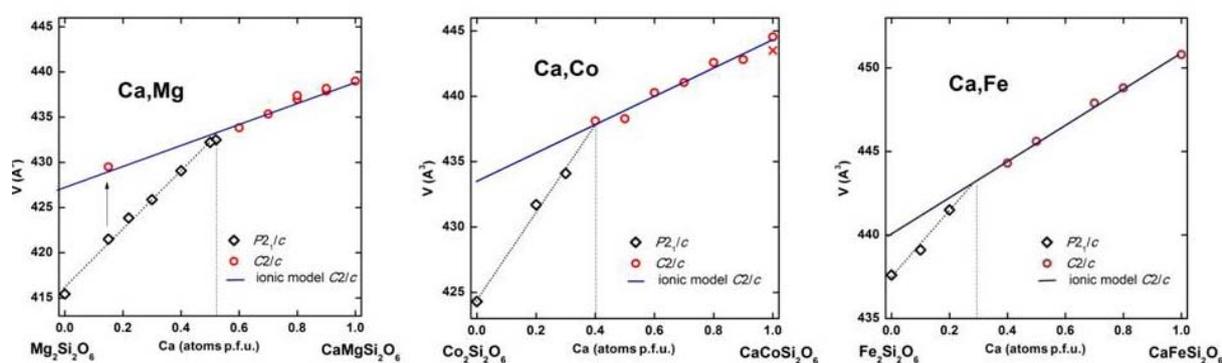


Fig. 3 - Comparison in the cell volume of the three series: blue line represent change in volume modelled by an ionic model, red circles the experimental data for $C2/c$ and black diamond for $P2_1/c$ pyroxenes.

We can notice that in Ca-rich samples, experimental data within the $C2/c$ region (red circles) lie on the line of the ionic model, suggesting that changes in volume can be simply explained by the substitution of a larger cation by a smaller one. In Ca-poor region changes in volume are higher than the predicted ones; the decrease in volume can be related also to an effect of the phase transition. An important result is that within the $C2/c$ structure changes in volume are ideal and the deviation to ionic behaviour is due simply to the phase transition, contrarily to the previous observations by Newton *et al.* (1979).

We can assume that the turnover represents the composition at which the transition occurs. This point in which the volume-composition trend for Ca-poor $P2_1/c$ pyroxenes came across those for Ca-rich samples (indicating both the $C2/c$ symmetry and the ionic model) is the critical composition of the phase transition. This point occurs at a composition of Ca atoms p.f.u. = 0.52 for Di-En (Tribaudino, 2000; Tribaudino *et al.*, 2005), of Ca = 0.4 a.p.f.u. for CaCo and Ca = 0.3 a.p.f.u. for Hd,Fs (Ohashi *et al.*, 1975). The different critical compositions are related to the different ionic radius of Mg (0.72 Å), Fe^{2+} (0.78 Å) and Co (0.745 Å; Fig. 4).

Changes in volume to pinpoint the transition were also used in the series kanoite-diopside ($\text{MnMgSi}_2\text{O}_6$ - $\text{CaMgSi}_2\text{O}_6$) (Arlt & Armbruster, 1997). In this series a sharp decrease in volume was observed at the Ca content of 0.2 a.p.f.u., and like in our samples it was interpreted as an evidence of the phase transition. Since Mn has a ionic radius of 0.83 Å this corresponds to an average M2 ionic volume at the transition of 0.86 Å, again similar to that of our pyroxenes.

An ionic model can explain also the different extension of the miscibility gap in the different series. A well known rule, from an adaptation to silicates of the Hume-Rothery rule used in metals, states that complete isomorphic solid solution occurs for isovalent cations if the difference of ionic radius is less than 15%. In the

examined series the difference was more than 20%, and complete solid solution was not expected to occur. A miscibility gap, of different extent, was revealed by comparison of the phase diagram of the three series at $P = 3$ GPa.

The gap was asymmetric, being solubility much lower in the Ca-poor region. This occurred because the end-members pyroxenes had not the same structure, and the orthorhombic structure of Ca-poor pyroxenes allowed very little Ca entrance. In the orthopyroxenes region of the phase diagram solid solution was then very limited, and quite similar in all the series, whereas in clinopyroxene the solubility was different among the different series.

Fig. 4 shows the miscibility gaps of the three series Di-En, Hd-Fs and Ca-Co at the same pressure plotted together with the ionic radius of the substituting cations and the percentage difference.

What is most apparent is that the pyroxene solubility decreases on the Ca rich side with the substituting cation at the M2 site, from Fe to Co and Mg. Also the temperature of the upper limit of the miscibility gap is related to the cation in M2. For example at about Ca content of 0.5 a.p.f.u. we found single clinopyroxene phase at a temperature of 1500 °C for Di-En, 1200 °C for Ca,Co-pyroxenes and 900 °C for Hd-Fs. Such differences occurred by a change in the size of the substituting cation, that is by an increase of the difference of the ionic radius with Ca. From the above results the volume changes, due to the substitution of a smaller cation for Ca in M2, can be explained by an ionic model.

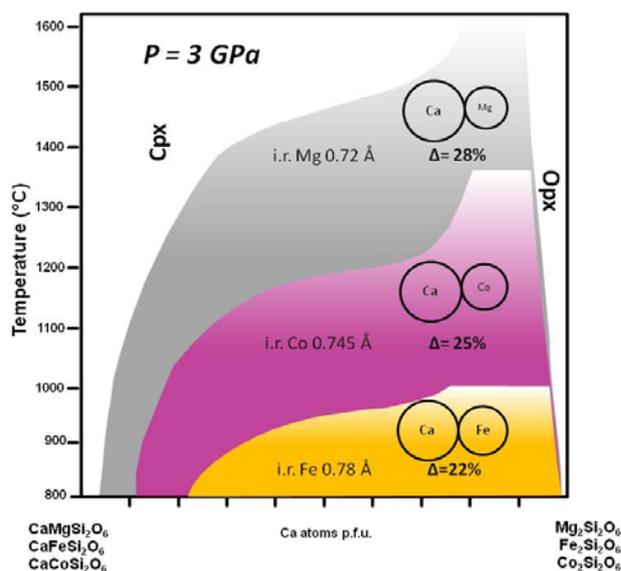


Fig. 4 - Sketch of a phase diagram for the three series examined. Gray colour indicates the miscibility gap of Di-En, pink that of CaCo-pyroxenes series and yellow is referred to Hd-Fs.

REFERENCES

- Akimoto, S., Katsura, T., Syono, Y., Fujisawa, H., Komada, E. (1965): Polymorphic transitions of pyroxenes FeSiO_3 and CoSiO_3 at high pressures and temperatures. *J. Geophys. Res.*, **70**, 5269-5278.
- Arlt, T. & Armbruster, Th. (1997): The temperature-dependent $P2_1/c - C2/c$ phase transition in the clinopyroxene kanoite $\text{MnMg}[\text{Si}_2\text{O}_6]$: a single crystal X-ray and optical study. *Eur. J. Mineral.*, **9**, 953-964.
- Bromiley, G.D., Keppler, H., McCammon, C., Bromiley, F.A., Jacobsen, S.D. (2004): Hydrogen solubility and speciation in natural, gem-quality chromian diopside. *Am. Mineral.*, **89**, 941-949.
- Eppler, R.A. (2000): Colorants for Ceramics. *Kirk-Othmer Encyclopedia of Chemical Technology*. John Wiley & Sons, Inc.
- Fores, A., Llusar, M., Badenes, J.A., Calbo, J., Tena, M.A., Monros, G. (2000): Cobalt minimisation in willemite (CoZnSiO) ceramic pigments. *Green Chem.*, **2**, 93-100.
- Ghose, S., Wan, C., Okamura, F.P. (1987): Crystal structures of $\text{CaNiSi}_2\text{O}_6$ and $\text{CaCoSi}_2\text{O}_6$ and some crystal-chemical relations in $C2/c$ clinopyroxenes. *Am. Mineral.*, **72**, 375-381.
- Kim, J.H., Gibb, H.J., Howe, P.D. (2006): Cobalt and inorganic cobalt compounds. *Concise International Chemical Assessment Document 69*, World Health Organization, ed. 88 p.
- Mantovani, L., Tribaudino, M., Mezzadri, F., Calestani, G., Bromiley, G. (2013): The structure of $(\text{Ca},\text{Co})\text{CoSi}_2\text{O}_6$ pyroxenes and the Ca-M^{2+} substitution in $(\text{Ca},\text{M}^{2+})\text{M}^{2+}\text{Si}_2\text{O}_6$ pyroxenes ($\text{M}^{2+} = \text{Co}, \text{Fe}, \text{Mg}$). *Am. Mineral.*, in press.
- Masse, D.P. & Muan, A. (1965): Phase relations in the system CoO-SiO_2 . *Trans. Metall. Soc. AIME*, **233**, 1448-1449.
- Melo, D.M.A., Cunha, J.D., Fernandes, J.D.G., Bernardi, M.I., Melo, M.A.F., Martinelli, A.E. (2003): Evaluation of CoAl_2O_4 as ceramic pigments. *Mater. Res. Bull.*, **38**, 1559-1564.
- Mimani, T. & Ghosh, S. (2000): Combustion synthesis of cobalt pigments: Blue and pink. *Curr. Sci.*, **78**, 892-896.
- Navrotsky, A. & Coons, W.E. (1976): Thermochemistry of some pyroxenes and related compounds. *Geochim. Cosmochim. Acta*, **40**, 1281-1288.

- Newton, R.C., Charlu, T.V., Anderson, P.A.M., Kleppa, O.J. (1979): Thermochemistry of synthetic clinopyroxenes on the join $\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$. *Geochim. Cosmochim. Acta*, **43**, 55-60.
- Ohashi, Y., Burnham, C.W., Finger, L.W. (1975): The effect of Ca-Fe substitution on the clinopyroxene crystal structure. *Am. Mineral.*, **60**, 423-434.
- Ozel, E., Yurdakul, H., Turan, S., Ardit, M., Cruciani, G., Dondi, M. (2010): Co-doped willemite ceramic pigments: Technological behaviour, crystal structure and optical properties. *J. Eur. Ceram. Soc.*, **30**, 3319-3329.
- Tribaudino, M. (2000): A transmission electron microscope investigation of the $C2/c \rightarrow P2_1/c$ phase transition in clinopyroxenes along the diopside-enstatite ($\text{CaMgSi}_2\text{O}_6$ - $\text{Mg}_2\text{Si}_2\text{O}_6$) join. *Am. Mineral.*, **85**, 707-715.
- Tribaudino, M., Nestola, F., Meneghini, C. (2005): Rietveld refinement of clinopyroxenes with intermediate Ca-content along the join diopside-enstatite. *Can. Mineral.*, **43**, 1411-1421.
- Tribaudino, M., Mantovani, L., Bersani, D., Lottici, P.P. (2012): Raman spectroscopy of $(\text{Ca,Mg})\text{MgSi}_2\text{O}_6$ clinopyroxenes. *Am. Mineral.*, **97**, 1339-1347.