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ABSTRACT

A series of clinopyroxenes along the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ join was synthesized by quenching from melt at 1500°C and subsequent annealing at 1250°C (at 0.0001 GPa). This protocol proved to be the most effective to obtain homogenous, free of impurities and stoichiometric pyroxenes as run products. Electron microprobe analyses in energy-dispersive mode were conducted and single-crystal X-ray diffraction data were collected on the $\text{Ca}(\text{Co}_x\text{Mg}_{1-x})\text{Si}_2\text{O}_6$ pyroxenes, with $x = 0.2, 0.4, 0.5, 0.6$; anisotropic structure refinements were performed. The effects of the cation substitution at the $M1$ site are described at the atomic level. The experimental findings of this study allowed us to extend the comparative analysis of the structural features of pyroxenes with divalent cations at the $M1$ and $M2$ sites.

KEYWORDS: pyroxene, cobalt, site substitution, crystal chemistry

Introduction

Pyroxenes are a class of inosilicates with crystal formula $M2M1T_2O_6$, where $M2$ is a distorted six-/eight-fold-coordinated polyhedron, $M1$ is a more

regular octahedron and T is a slightly distorted tetrahedron (Burnham et al. 1967; Fig.1). Extended solid solutions are possible at the octahedral and tetrahedral sites. Therefore, pyroxenes-like materials may be synthesized, whose properties are not yet explored and with compositional ranges that go beyond those observed in natural ones. This extends the interest in pyroxenes from petrology (as rock-forming minerals) to material science. For example, $\text{NaFeSi}_2\text{O}_6$ was reported as a multiferroic phase (Jodlauk *et al.*, 2007; Redhammer *et al.*, 2008, 2009, 2013), or diopside as a scaffold for prosthetic applications (Ghomi *et al.*, 2012; Karamiana *et al.*, 2014) and Co-pyroxene as a pigment in ceramic materials (Mantovani *et al.*, 2015).

Co-pyroxene is a potential pink-violet pigment; the pink colour is due to the six-fold coordinated Co^{2+} that populates the $M1$ and $M2$ sites (White *et al.*, 1971). The end-member $\text{CaCoSi}_2\text{O}_6$ was recently tested as a pigment for ceramic applications (Mantovani *et al.*, 2015), but with some open issues. First, the temperature range for the synthesis is quite narrow, between 1000 and 1200°C; at lower temperature oxidation to Co^{3+} and formation of stable $\text{Ca}_2\text{CoSi}_2\text{O}_7$ (Co-akermanite) occurs. In Co-akermanite, Co is present in tetrahedral coordination and acts as a blue (instead of pink) pigment; even a low fraction of akermanite in the run product, due to its high colouring efficiency, hides the pink hue of Co^{2+} in octahedral coordination. Moreover, akermanite occurs as a metastable phase also between 1000 and 1200°C, and disappears only after prolonged heating in a silica-oversaturated environment. The $\text{CaCoSi}_2\text{O}_6$ pigment acts as a dye, dissolving in a glass under the aggressive environment in ceramic manufacturing. In fact, Co usually occurs in tetrahedral coordination in a Si-glass and the resulting

colour is blue. Nevertheless, the amount of Co for the synthesis of $\text{CaCoSi}_2\text{O}_6$ is lower than in other Co-based pigments, as CoAl_2O_4 or Co_2SiO_4 . However, the fraction of cobalt in $\text{CaCoSi}_2\text{O}_6$ is still high, considering environmental and economic concerns. Our investigation is focused on solid solutions between diopside (ideally $\text{CaMgSi}_2\text{O}_6$) and $\text{CaCoSi}_2\text{O}_6$. Diopside has a stability field extended up to higher temperature (melting at 1391°C at 0.0001 GPa) and metastable akermanite does not occur in Mg-pyroxenes. Therefore, we may expect a wider stability field for Ca-Mg-Co-pyroxenes, although no data on the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ phase diagram are available. In addition, only a few crystallochemical data are available for pyroxenes of the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ series. In the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ pyroxenes, the *M2* and *T* sites are buffered by the complete occupancy of Ca and Si, respectively, and Co can populate the *M1* only site along with Mg. Hence, structural changes induced by the cation substitution at the *M1* site would be investigated, showing the effect on the structure (at the atomic level) and on the unit-cell volume. We may expect that the substitution of cations with different ionic radii, at a given site, gives rise to a variation of the unit-cell volume. This effect for the *M1* site in pyroxenes has not so far been investigated. Structure refinements on $\text{CaM1Si}_2\text{O}_6$ pyroxenes, based on high-quality single-crystal X-ray diffraction data, are available only for the end-members with *M1* = Mg, Co, Ni, Fe; solid solutions between $\text{CaMgSi}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ and between $\text{CaCoSi}_2\text{O}_6$ and $\text{CaNiSi}_2\text{O}_6$ were described by X-ray Rietveld refinements only (Raudsepp *et al.*, 1990; Pandolfo *et al.*, 2015; Durand *et al.*, 1996). Structure refinements based on single-crystal X-ray data for

Ca(Co,Mg)Si₂O₆ pyroxenes are available from Tabira *et al.* (1993); however, in this case, the composition is non-stoichiometric, as a significant fraction of Co²⁺ at the *M2* site was observed.

The aim of the present study is to improve the synthesis protocol of pyroxene (single) crystals along the CaMgSi₂O₆-CaCoSi₂O₆ series and to describe their crystal-chemistry by electron microprobe analysis in energy-dispersive mode and by single-crystal X-ray diffraction. The results allow us to describe the effect of the cation substitution at *M1* on the structure. It will be shown that the cation substitutions at the *M1* and *M2* sites produce a different effect on the structure, which depends on the inequivalent response of the *M1*- and *M2*-polyhedra to the ionic radius of the cation.

Experimental methods

Synthesis

The samples of this study were synthesized from oxide mixtures of stoichiometric Ca(Co_{*x*}Mg_{1-*x*})Si₂O₆ with *x* = 0.2, 0.4, 0.5, 0.6 (hereafter referred to as Di-Co20, Di-Co40, Di-Co50 and Di-Co60, respectively). The oxide powders were ground in an agate mortar, pressed into pellets, placed into platinum crucibles and heated in a muffle furnace at 1500°C for two hours, and then quenched to obtain amorphous products. Afterwards, the synthesis products were annealed at 1250°C, until the crystallization was completed. Single crystals (up to 500 μm) were obtained. All thermal runs produced pink crystals with slightly different shades. The synthesis was also attempted by solid-state reaction, but even after prolonged treatment (*e.g.*, 30 days at 1150°C), micro-crystals of pyroxene (5-10 μm long), akermanite

and cristobalite were obtained. Moreover, flux growth synthesis was also attempted: the oxide powders were mixed with $\text{Na}_2\text{B}_4\text{O}_7$ acting as flux compound; large crystals up to 1 mm were obtained, but spectroscopic and SEM-EDS analyses showed that the samples contained significant impurities of Co^{3+} and Na. The flux-grown crystals were, therefore, discarded for the present investigation.

Electron microprobe analysis (SEM-EDS)

A few grains of the synthesis products were embedded in epoxy and polished for SEM-EDS analysis using a Jeol 6400 SEM, equipped with an Oxford-INCA EDS, operated at 20 kV. Electron back-scattered images were also collected. The chemical composition data were obtained from the average of 10-15 point analyses; melt-grown samples did not show a deviation from the nominal composition.

Single-crystal X-ray structural refinement

Crystals optically free of defect (under polarized light microscopy) were selected for the X-ray diffraction experiments. Intensity data were collected on a Bruker AXS Smart diffractometer, equipped with an APEX II CCD and operating with $\text{MoK}\alpha$ radiation. Data of the full reflection sphere up to $2\theta = 64^\circ$ were collected, corrected for absorption effect using a multi-scan method (*SADABS*; Sheldrick, 1996). Corrections for Lorentz-polarization effects were also applied. The reflection conditions showed no violation of the extinction rules expected for the $C2/c$ symmetry, as expected for this series.

The *SHELX-97* program (Sheldrick, 1997), implemented in the *WinGX* suite (Farrugia, 1999), was used for the anisotropic structure refinements. The refinements of the synthetic pyroxenes converged with agreement factors between 2.3 and 3.4%. The expected site occupancies, retrieved from stoichiometry and confirmed by SEM-EDS results, required the *M2* site occupied by Ca, *M1* by Co and Mg in different proportions, and the tetrahedral site by Si. The refined site occupancies did not deviate significantly from the expected stoichiometry. Further details pertaining to the data collection protocols and structure refinements are listed in Table 1; fractional atomic coordinates and equivalent displacement parameters are given in Table 2; a list of selected bond lengths is given in Table 3.

The site-labelling scheme proposed by Burnham *et al.* (1967) is used in this paper. In *C2/c* pyroxenes, there are four symmetrically equivalent tetrahedral chains, with two tetrahedra in each unit cell. Each tetrahedral chain is named by a different letter (A, B, C and D). Each tetrahedron of the chain is referred with a different number (1 or 2). The oxygen atoms in each tetrahedron are labelled as O1, O2 and O3, followed by the letter of the chain they belong to, and by 1 or 2 depending on the tetrahedron to which they are bonded. The O3 is a bridging oxygen atom shared between the SiO₄ tetrahedra, the O1 and O2 are the non-bridging oxygen atoms. Using the Burnham's labelling scheme, and according to the site symmetry, Ca has four pairs of symmetrically equivalent *M2*-O distances with O1A1,B1, O2C2,D2, O3C1,D1, and O3C2,D2; Mg and Co are bonded to six oxygen atoms and form three pairs of symmetrically equivalent *M1*-O distances with O1A1,B1, O1A2,B2 and O2C1,D1 (Fig. 1).

Results

M1 polyhedron

In CaCoSi₂O₆-CaMgSi₂O₆ pyroxene series, the only substitution occurs at the *M1* site, where Co can replace Mg. The Co for Mg substitution promotes a slight increase in the average *M1*-O bond distance (up to 0.021 Å, Fig. 2b), in response to the different ionic radii of the two cations (*i.e.*, ^{VI}Co²⁺ 0.745 Å and ^{VI}Mg 0.72 Å, Shannon and Prewitt, 1970). The three independent *M1*-O bonds (Fig. 1) increase differently in response to the Co content (Fig. 2a). Within the entire compositional range (*i.e.*, Co = 0 -1 a.p.f.u.), the *M1*-O1A2B2 distance increases by 0.034 Å, whereas the longer *M1*-O1A1B1 and the shorter *M1*-O2 bond lengths increase only by 0.014 and 0.011 Å, respectively. A similar pattern was observed with the replacement of Fe for Mg (Fig. 2) at the *M1* site of pyroxenes along the CaMgSi₂O₆-CaFeSi₂O₆ series (Raudsepp *et al.*, 1990). As a consequence, the octahedral distortion, measured by the variance of the O-*M1*-O angles of the *M1* polyhedron (Fig. 2c), decreases with Co content of the series, in response to a more regular polyhedron geometry.

M2 polyhedron

The substitution of Co for Mg at the *M1* site affects also the geometry of the *M2* polyhedron. The *M2* polyhedron is asymmetric, the longer distances being that to the bridging oxygen atom of the tetrahedral chain O3 (Fig. 1). On the opposite side of the polyhedron, the *M2* cation is bonded to the non-bridging oxygen atoms O2 and O1. Among the independent *M2*-O3

distances, the $M2-O3C1,D1$ increases by 0.04 Å and the $M2-O3C2,D2$ remains almost constant in response to the Co-content increase from 0 to 1 a.p.f.u. (Fig. 3). On the other hand, both the $M2-O2$ and $M2-O1$ bond lengths decrease with the increase of Co. On the whole, the $M2-O$ bond distances and the $M2$ polyhedral volume increase in response to Co-for-Mg substitution at the $M1$ site, despite the Ca occupancy at the $M2$ site remains unchanged.

The re-arrangement of the $M2-O$ distances is the effect of a slight shift of the $M2$ cation, by about 0.01 Å towards one side of the $M2$ polyhedron. This is clearly shown by the atomic fraction coordinates of the $M2$ site, and in particular by y/b which decreases from 0.3011 in diopside (Bruno *et al.*, 1982) to 0.2990 in $\text{CaCoSi}_2\text{O}_6$ (Ghose *et al.*, 1987). The same shift occurs in the coordinate of Ca in pyroxenes where Fe replaces Mg at the $M1$ site (Nestola *et al.*, 2007).

T polyhedron

The configuration of the T -tetrahedron, in which the T site is fully occupied by Si, is not affected by the cation substitution at the $M1$ site. The polyhedral volume and the independent and average bond distances do not change along the $\text{CaMgSi}_2\text{O}_6$ - $\text{CaCoSi}_2\text{O}_6$ and $\text{CaMgSi}_2\text{O}_6$ - $\text{CaFeSi}_2\text{O}_6$ series (Fig. 4a). The tetrahedral angle involving the two bridging oxygen atoms ($O3\text{-Si-O3}$) is always close to 104.3° (the ideal value is 109.4°). The chemical substitution does not affect the geometry of the tetrahedral chain: the $O3\text{-O3-O3}$ kinking and the Si-O-Si intra-chain tetrahedral angle do not change significantly. The tetrahedral-angle variance (TAV), which measures

the polyhedron distortion, decreases from 27.4 to 25.3 between diopside and Co-pyroxene (Fig. 4b): the only effect on the tetrahedron geometry is a slightly more regular configuration in Co-rich pyroxenes.

Unit-cell parameters

Fig. 5 (a-f) shows the evolution of the unit-cell parameters along Di-Co pyroxenes series. A comparison with the trend observed in Ca(Mg,Fe)Si₂O₆ pyroxenes (with Fe replacing Mg) (Nestola *et al.*, 2007; Raudsepp *et al.*, 1990) is reported. With the increase of Co at the M1 site, the length of the unit-cell edges along [100] and [010] increase, the edge parallel to [001] does not change significantly and the monoclinic β angle decreases. The axial expansion pattern in response to the Co-Mg substitution is $a > b > c$. The little deformation of the (stiff) tetrahedron gives rise to a negligible variation along the c axis; as commonly observed in response to compositional, thermal and compressive strains in pyroxenes (Cameron *et al.*, 1973; Nestola *et al.*, 2007; Tribaudino and Mantovani, 2014).

The unit-cell edge along the c axis may change for a rotation of the SiO₄-unit in the tetrahedral chains (Cameron *et al.*, 1973), measured by the O3-O3-O3 tetrahedral kinking angle, or for an increase in the O3C1-O3C2 distance of the tetrahedron, which is elongated almost parallel to [001]. However, in Di-Co pyroxenes, the cell edge along c does not change, because the decrease of the kinking angle (which would lead to a decrease in the edge length along [001]) is counter-balanced by the increase of the distance O3C1-O3C2.

A calculation of magnitude and orientation of the Eulerian unit-strain ellipsoid between diopside and Co-pyroxene gives further insight into the unit-cell deformation. This was done comparing the unit cell of diopside with that of $\text{CaCoSi}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$, and using the *Winstrain* software (<http://www.rossangel.com>). The unit-strain ellipsoid, with the components reported in Table 4, has the same orientation previously observed in the hedenbergite-diopside series (Nestola *et al.*, 2007), *i.e.* the major deformation (along ϵ_1) occurs on (010), describing an angle of about 36° to [100] (Table 4), and it is governed by the expansions of the $M2\text{-O}3$ bond distances observed here.

Discussion and conclusions

One of the most important experimental findings of this study is that the unit-cell volume of the $M^2\text{Ca}^{M1}(\text{Co,Mg})^T\text{Si}_2\text{O}_6$ pyroxenes vary linearly along the series (Fig. 5f). In general, cell volume and $M1$ polyhedral volume of ($C2/c$) $\text{CaM}1^{2+}\text{Si}_2\text{O}_6$ pyroxenes increase with the (average) ionic radius of the $M1$ cation (Fig. 6 and 7a). Also the $M2$ polyhedral volume increases with the expansion of the $M1$ polyhedral volume; this a ‘steric effect’, which adds to the contribution of ionic radii and Pauling’s bond strengths (Ghose *et al.*, 1987).

In order to cope with the different $M1$ ionic radii and with the $M2$ steric effect, we normalized the unit-cell volumes and the $M1$ and $M2$ polyhedral volumes of Ca,Fe and Ca,Co pyroxenes to those of diopside. In Fig. 7b, the $M2$ and $M1$ polyhedral volumes in $(\text{Ca,Mg})\text{MgSi}_2\text{O}_6$, $(\text{Ca,Fe})\text{FeSi}_2\text{O}_6$ and $(\text{Ca,Co})\text{CoSi}_2\text{O}_6$ pyroxenes are plotted *vs.* the ionic radius of the $M2$ cation.

The diagram shows that the volume of the *M2* polyhedron is related to the *M2* cation radius, whereas the volume of the *M1* polyhedron does not change in response of the *M2* cation radius.

The contributions of the *M2* and *M1* polyhedra to the unit-cell volumes are shown in Figs 8a and 8b. As the unit-cell contains four *M1* and four *M2* polyhedra, the *M2* and *M1* volumes were multiplied by 4, in order to give the overall contribution of the polyhedra to the changes in cell volume.

In samples where the substitution occurs only at the *M1* site, the *M1* polyhedral volume accounts for $\leq 30\%$ of the volume expansion (Fig. 8a), whereas the *M2* eight-fold polyhedron accounts for about 10%, due to the steric effect. Also, the sum of the *M1* and *M2* polyhedral expansions do not account for the entire cell volume. Therefore, we must also consider an expansion in the extra-polyhedral voids.

On the contrary, in pyroxene series with the cation substitution at the *M2* site, the *M2* polyhedral volume accounts, almost completely, for the unit-cell expansion, albeit with some difference between Ca-Fe, Ca-Co and Ca-Mg pyroxenes (Fig. 8b).

The substitution of a given cation with one with longer ionic radius has a very different effect on the unit-cell volume, whether it occurs at the *M2* or at the *M1* site. We can assess the different effect of the *M2* and *M1* cation substitution comparing the *C2/c* structures of the CaMgSi₂O₆-CaCoSi₂O₆ and the CaCoSi₂O₆-CoCoSi₂O₆ series. In the CaMgSi₂O₆-CaCoSi₂O₆ series, the structure is always *C2/c*; in CaCoSi₂O₆-CoCoSi₂O₆ series the structure is *C2/c* between CaCoSi₂O₆ and Ca_{0.4}Co_{0.6}CoSi₂O₆, but it transform to *P2₁/c* at higher Co-content (Mantovani *et al.*, 2014).

The average $M1$ ionic radius and the unit-cell volume between $\text{CaMgSi}_2\text{O}_6$ and $\text{CaCoSi}_2\text{O}_6$ differ respectively by 0.025 \AA and 5 \AA^3 , whereas the $M2$ ionic radius and the cell volume between $\text{CaCoSi}_2\text{O}_6$ and $\text{Ca}_{0.4}\text{Co}_{0.6}\text{CoSi}_2\text{O}_6$, differ by 0.132 \AA and 6.4 \AA^3 (Mantovani *et al.*, 2014). This experimental finding shows how the same substituent can have a completely different effect if the substitution occurs at the $M1$ rather than at $M2$ site.

The different response of the crystal structure to the $M1$ and $M2$ substitutions gives also a clue to interpret the different effect on the unit-cell volume. The larger $M2$ polyhedron allows the cation site to displace along the 2-fold axis; thus, a smaller cation finds its local coordination in a subsite, *i.e.* the $M2'$ site (different from that of Ca), as previously observed by *e.g.* Rossi *et al.* (1987) or Gori *et al.* (2015). The substitution gives rise to a cation shift towards the O1 and O2 oxygen atoms, and thus away from the O3 oxygen atom. In addition, a slight deformation of the polyhedron shape also occurs.

The cation substitution at the $M2$ site has, overall, only a small effect on its polyhedral volume. On the contrary, the $M1$ polyhedron is stiffer, as cations are closely bonded: a substitution with longer ionic-radius cation affects strongly the $M1$ -O bond distances and the polyhedral volume, and the expansion somehow affects the whole structure.

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Figure captions

FIG. 1. The crystal structure of the $C2/c$ clinopyroxenes viewed down $[100]$. The SiO_4 tetrahedra and the $(\text{Mg,Co})\text{O}_6$ octahedra are shown as closed polyhedra. The atoms are labeled after Burnham *et al.* (1967). The crystal structure is visualized by using the *VESTA* software package (Momma and Izumi, 2008).

FIG. 2. (a) $M1$ -O bond-length variation with composition (Mg content) at the $M1$ site in Ca-Fe, Ca-Mg pyroxenes and in the $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ series; (b) Average $M1$ -O bond lengths vs. composition (Mg content) at the $M1$ site; (c) OAV angle variation with composition (Mg content) at the $M1$ site. The $\text{Ca}(\text{Mg,Co})$ series is represented by purple squares, the Ca-Fe and Ca-Mg pyroxenes are represented by red and blue diamond, respectively. [Data of $\text{CaCoSi}_2\text{O}_6$ from Ghose *et al.* (1987); $\text{CaMgSi}_2\text{O}_6$ from Bruno *et al.* (1982); $\text{CaFeSi}_2\text{O}_6$ from Nestola *et al.* (2007) and $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ pyroxenes from this study].

FIG. 3. $M2$ -O bond lengths vs. composition (Mg content) at the $M1$ site. [References as in Fig. 2].

FIG. 4. (a) Si-O bond lengths vs. composition (Mg content) at the $M1$ site; (b) TAV angle variation with composition. [References as in Fig. 2].

FIG. 5. (a-f) Unit-cell parameters vs. Mg content at the $M1$ site in $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ (solid line) and $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ (dashed line) pyroxenes. [Data of $\text{CaCoSi}_2\text{O}_6$, obtained by Rietveld refinement, are taken from Mantovani *et al.* (2014); for the other compositions see references of Fig. 2].

FIG. 6. Cell volume vs. average $M1$ ionic radius for $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$, $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$, $\text{Ca}(\text{Zn,Mn})\text{Si}_2\text{O}_6$ and $\text{Ca}(\text{Co,Ni})\text{Si}_2\text{O}_6$ pyroxenes. [Data of $\text{CaCoSi}_2\text{O}_6$ from Ghose *et al.* (1987); $\text{CaMgSi}_2\text{O}_6$ from Bruno *et al.* (1982); $\text{CaFeSi}_2\text{O}_6$ from Nestola *et al.* (2007); $\text{Ca}(\text{Mg,Fe})\text{Si}_2\text{O}_6$ from Raudsepp *et al.* 1990; $\text{Ca}(\text{Co,Ni})\text{Si}_2\text{O}_6$ from Durand *et al.* 1996; $\text{CaCoSi}_2\text{O}_6$ and $\text{CaNiSi}_2\text{O}_6$ from Ghose *et al.* (1987) and Nestola *et al.* (2005) respectively; $\text{Ca}(\text{Zn,Mn})\text{Si}_2\text{O}_6$ from Nestola *et al.* (2010) and $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ from this study].

FIG. 7. $M1$ and $M2$ polyhedral-volumes ($M2$ in eight-fold coordination) as a function of (a) average ionic radius of the cation at $M1$, with the $M2$ site fully occupied by Ca in $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ pyroxenes; (b) average ionic radius of the cation at $M2$ (in eight-fold coordination) in Ca-Co, Ca-Fe and Ca-Mg pyroxenes, with the $M1$ site filled respectively by Co, Fe and Mg, and with Ca-Co, Ca-Fe, Ca-Mg substitution at the $M2$ site. The volumes of the end-members were normalized to the value of diopside: *i.e.* the unit-cell, $M1$ and $M2$ volumes were corrected by subtracting the difference between those in diopside and hedenbergite for $(\text{Ca,Fe})\text{FeSi}_2\text{O}_6$, and in diopside and $\text{CaCoSi}_2\text{O}_6$ for $(\text{Ca,Co})\text{CoSi}_2\text{O}_6$ pyroxenes. [Data of $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ from this study; $(\text{Ca,Co})\text{CoSi}_2\text{O}_6$ from Mantovani *et al.* (2013) and Ghose *et al.* (1987); $(\text{Ca,Mg})\text{MgSi}_2\text{O}_6$ from Tribaudino *et al.* (2005) and Bruno *et al.* (1982); $(\text{Ca,Fe})\text{FeSi}_2\text{O}_6$ from Ohashi *et al.* (1975) and Nestola *et al.* (2007)]. The volume of polyhedra was calculated by using the *VESTA* software package (Momma and Izumi, 2008).

FIG. 8. (a) Polyhedral-volume difference vs. cell-volume difference in $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ and $\text{CaFeSi}_2\text{O}_6$ pyroxenes with cation substitution at the $M1$ site. (b) Polyhedral-volume difference vs. cell-volume difference with cation substitution at the $M2$ site in $(\text{Ca,Co})\text{CoSi}_2\text{O}_6$, $(\text{Ca,Mg})\text{MgSi}_2\text{O}_6$, and $(\text{Ca,Fe})\text{FeSi}_2\text{O}_6$ pyroxenes. [Data of $\text{Ca}(\text{Mg,Co})\text{Si}_2\text{O}_6$ from this study; $\text{CaFeSi}_2\text{O}_6$ from Nestola *et al.* (2007); $(\text{Ca,Co})\text{CoSi}_2\text{O}_6$ from Mantovani *et al.* (2013) and Ghose *et al.* (1987); $(\text{Ca,Mg})\text{MgSi}_2\text{O}_6$ from Tribaudino *et al.* (2005) and Bruno *et al.* (1982); $(\text{Ca,Fe})\text{FeSi}_2\text{O}_6$ from Ohashi *et al.* (1975)].