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Structures and Electron Distributions of α-Co_2SiO_4 and α-Ni_2SiO_4 (Olivine Structure)

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Abstract

The single-crystal X-ray study of α-Co_2SiO_4 and α-Ni_2SiO_4 (olivine structure) has revealed the structural characteristics, the net atomic charges, and the distributions of the aspherical electron density around the Co and Ni atoms. The Si atoms, occupying tetrahedral sites, are less ionic than octahedral transition-metal ions such as Co^{2+} and Ni^{2+}. A previous report that transition-metal ions are less ionic than the Mg^{2+} ion in the olivine structure is supported by this study. Aspherical positive and negative peaks around the Co and Ni atoms are observed in the difference Fourier synthesis through distorted octahedra. A structural comparison shows that both of two distinct sites for α-Ni_2SiO_4 are much more regular compared with those of α-Co_2SiO_4 and α-Mg_2SiO_4 (forsterite). Crystallographic quantities such as cell dimensions and interatomic distances of α-Mg_2SiO_4 cannot be defined as an interpolation of Co and Ni compounds because of the absence of 3*d* electrons and the difference in atomic charges. The cell parameters are: $a = 4{\cdot}7797\,(8)$, $b = 10{\cdot}2976\,(6)$, $c = 5{\cdot}9986\,(3)$ Å (α-Co_2SiO_4); $a = 4{\cdot}7277\,(5)$, $b = 10{\cdot}1173\,(5)$, $c = 5{\cdot}9125\,(4)$ Å (α-Ni_2SiO_4). The mean $M(1)$—O, $M(2)$—O, and Si—O distances are 2·118 (1), 2·139 (1) and 1·639 (1) Å for α-Co_2SiO_4, and 2·080 (1), 2·099 (1) and 1·640 (1) Å for α-Ni_2SiO_4. The final R values of refinements using 2010 and 1819 reflections were 0·028 and 0·029 for the Co and Ni compounds, respectively.

Introduction

To further our understanding of the characteristics of atomic bonds in silicates, it is important to know the net atomic charges and the electron distributions of the atoms. The asphericity of the electron distributions around the Ni, Co, and Fe atoms in nearly regular octahedra of γ-Fe_2SiO_4, γ-Co_2SiO_4, and γ-Ni_2SiO_4 (spinel structure) was observed by means of the difference Fourier technique (Marumo, Isobe, Saito, Yagi & Akimoto, 1974; Marumo, Isobe & Akimoto, 1977). This asphericity was ascribed to the 3*d* electrons of the transition metals because of its relationship to crystal-field theory. Recently, the approach of observing the distribution of 3*d* electrons has been extended to the deformed octahedra of crystals having olivine structures [Mn_2SiO_4 and Fe_2SiO_4 (Fujino, Sasaki, Takéuchi & Sadanaga, 1981)] and orthopyroxene structures [$Fe_2Si_2O_6$ and $Co_2Si_2O_6$ (Sasaki, Takéuchi, Fujino & Akimoto, 1982)]. On the other hand, a procedure to estimate net atomic charges in silicate crystals was proposed by Sasaki, Fujino, Takéuchi & Sadanaga (1980) after their comparison of the following two approaches: (1) the extended L-shell refinement based on the differences of atomic scattering factors; (2) the integration of electron density of an *effective distribution radius*. By using the above procedure, Fujino *et al.* (1981) estimated the charges of the constituent atoms in some olivines such as α-Mg_2SiO_4 (forsterite), α-Fe_2SiO_4 (fayalite), and α-Mn_2SiO_4 (tephroite), and found that the transition metals in the olivine structure are less ionic than the Mg^{2+} ions, and that the larger $M(2)$ site in the structure is more ionic than $M(1)$.

In the regular octahedral crystal field, the Co atom has the configuration $(t_{2g})^5\ (e_g)^2$, and that of Ni is $(t_{2g})^6\ (e_g)^2$. Compared to the divalent Fe and Mn atoms having the $(t_{2g})^4\ (e_g)^2$ and $(t_{2g})^3\ (e_g)^2$ electron configurations, the localization effect of the electrons can be expected to be greater in the Co and Ni olivines.

The crystal structures of α-Co_2SiO_4 and α-Ni_2SiO_4 have already been reported (Brown, 1970; Morimoto, Tokonami, Watanabe & Koto, 1974; Lager &

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Meagher, 1978). However, the electron density distributions and atomic charges of these compounds have not yet been reported.

Based on their X-ray study of $Ni_{1.03}Mg_{0.97}SiO_4$, Rajamani, Brown & Prewitt (1975) found that the Ni atom strongly favors the smaller $M(1)$ site of Ni–Mg olivine. On the other hand, the Ni atom is only slightly enriched in the smaller $M(1)$ site of orthopyroxene. According to Ghose, Okamura, Wan & Ohashi (1974), the Co atom shows a strong preference for the larger $M(2)$ site in orthopyroxene in contrast to its strong preference for the smaller $M(1)$ site in olivine. In order to explain the above site preferences, careful analysis of such crystal-chemical factors as cation size, charge, and the crystal-field effect is necessary.

Experimental

Single crystals of α-Co_2SiO_4 were synthesized by slow cooling of a mixture of SiO_2 and CoO powders from 1773 K. Crystals of α-Ni_2SiO_4 were grown using the flux method by Dr M. Ojima, ISSP, University of Tokyo. Observations using a polarized microscope along with Weissenberg photographs showed that the crystals were free from inclusions and cracks. Single crystals were ground into spheres about 0·2 mm in diameter and then the layer of surface damage was chemically etched away. Intensity data up to $2\theta = 134°$ were collected in the ω–2θ scan mode by an automated Philips PW 1100 four-circle diffractometer using Mo $K\alpha$ radiation monochromatized by a graphite plate. The experimental conditions and crystallographic data are summarized in Table 1. The cell dimensions were obtained on the four-circle diffractometer using the method of least squares. Of the 2113 independent reflections collected for α-Co_2SiO_4, 2010 greater than $3\sigma_F$ were used in the refinement. Likewise, 1819 of the 1936 independent reflections collected for α-Ni_2SiO_4 were used. Intensities were corrected for Lorentz, polarization and absorption factors using the program *PTPHI* prepared by Philips. The atomic scattering factors were taken from the following sources: *International Tables for X-ray Crystallography* (1974) (Co^{2+}, Ni^{2+}, O^{1-}), *International Tables* (1968) with modification (Co^{1+}, Ni^{1+}, Si^{3+}), Fukamachi (1971) (Si^{2+}), and Tokonami (1965) (O^{2-}); all anomalous-dispersion factors were taken from *International Tables* (1974).

Table 1. *Crystallographic data and experimental conditions for* α-Co_2SiO_4 *and* α-Ni_2SiO_4

	α-Co_2SiO_4	α-Ni_2SiO_4
a (Å)	4·7797 (8)	4·7277 (5)
b (Å)	10·2976 (6)	10·1173 (5)
c (Å)	5·9986 (3)	5·9125 (4)
V (Å^3)	295·23 (5)	282·80 (4)
Space group	*Pbnm*	*Pbnm*
Chemical unit	4	4
D_x (g cm^{-3})	4·723	4·919
μ (Mo $K\alpha$) (cm^{-1})	118·6	134·7
Diameter of crystals (mm)	0·21	0·20
Scan speed (deg min^{-1})	4	4
Scan width [deg (2θ)]	$1·7 + 0·3 \tan\theta$	$1·5 + 0·3 \tan\theta$
Number of scans	3	3
Maximum 2θ for Mo $K\alpha$ (°)	134	134
Number of reflections		
measured	2113	1936
used	2010	1819

Table 2. *Final atomic coordinates and equivalent isotropic temperature factors for* α-Co_2SiO_4 *and* α-Ni_2SiO_4

	x	y	z	B_{eq}* (Å^2)
Co_2SiO_4				
Co(1)	0·0	0·0	0·0	0·46
Co(2)	0·99123 (5)	0·27639 (2)	0·25	0·45
Si	0·42824 (10)	0·09483 (5)	0·25	0·36
O(1)	0·76733 (22)	0·09232 (12)	0·25	0·46
O(2)	0·21584 (24)	0·44864 (11)	0·25	0·49
O(3)	0·28153 (17)	0·16398 (8)	0·03347 (14)	0·53
Ni_2SiO_4				
Ni(1)	0·0	0·0	0·0	0·37
Ni(2)	0·99242 (6)	0·27374 (2)	0·25	0·37
Si	0·42710 (12)	0·09429 (6)	0·25	0·29
O(1)	0·76940 (28)	0·09329 (15)	0·25	0·39
O(2)	0·21716 (29)	0·44513 (14)	0·25	0·39
O(3)	0·27438 (21)	0·16311 (10)	0·03010 (17)	0·42

$^*B_{eq} = (\frac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j)/10.$

Table 3. *Final anisotropic temperature factors* ($\times 10^4$) *for* α-Co_2SiO_4 *and* α-Ni_2SiO_4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co_2SiO_4						
Co(1)	429 (4)	133 (1)	290 (3)	−4 (2)	−43 (3)	−34 (1)
Co(2)	542 (5)	97 (1)	317 (3)	1 (2)	0	0
Si	330 (10)	91 (2)	275 (7)	3 (4)	0	0
O(1)	343 (22)	131 (6)	353 (16)	16 (9)	0	0
O(2)	553 (24)	94 (5)	381 (16)	−17 (10)	0	0
O(3)	543 (17)	144 (4)	324 (11)	9 (7)	−26 (12)	50 (6)
Ni_2SiO_4						
Ni(1)	370 (5)	103 (1)	250 (3)	−5 (2)	−38 (4)	−21 (1)
Ni(2)	443 (6)	77 (1)	277 (3)	7 (3)	0	0
Si	302 (13)	71 (3)	222 (8)	−12 (5)	0	0
O(1)	285 (27)	114 (7)	325 (20)	4 (11)	0	0
O(2)	439 (29)	80 (6)	328 (20)	7 (12)	0	0
O(3)	476 (21)	115 (5)	269 (13)	6 (8)	−30 (14)	33 (7)

In addition to the atomic coordinates and thermal parameters, isotropic extinction parameters (Zachariasen, 1967; Coppens & Hamilton, 1970; Becker & Coppens, 1974) and occupancies of valence electrons were simultaneously refined in the final stages; the least-squares program *EARTH* (Sasaki *et al.*, 1980) which is a modified version of *LINUS* (Coppens & Hamilton, 1970) was used. The least-squares refinement converged to $R = 0·0277$ ($R_w = 0·0280$, where $w = 1$) for α-Co_2SiO_4, and $R = 0·0289$ ($R_w = 0·0310$)

for α-Ni_2SiO_4. The final atomic coordinates and anisotropic temperature factors are listed in Tables 2 and 3, respectively.* The interatomic distances were calculated using the program *ORFFE* (Busing, Martin & Levy, 1964) and are given in Fig. 1.

The procedures for the determination of the net atomic charges are the same as those described by Sasaki *et al.* (1980) and Fujino *et al.* (1981). The effective charges denoted as *L* 1 were obtained from the least-squares calculations where a residual factor was minimized in terms of the scattering factors for valence electrons. On the other hand, the charges denoted as EDR were estimated by integrating electron density within the sphere of an *effective distribution radius* (Fujino *et al.*, 1981) from the center of the atom, and by correcting the termination errors of the Fourier series.

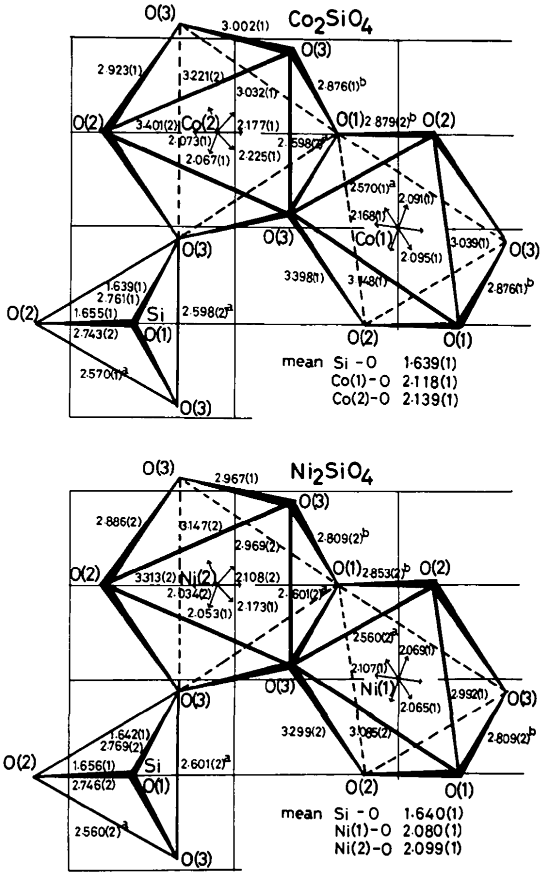

Fig. 1. Projections of crystal structures on (100) for α-Co_2SiO_4 (top) and α-Ni_2SiO_4 (bottom). Interatomic distances (Å) are shown; the values denoted by superscripts *a* and *b* correspond to tetrahedron–octahedron and octahedron–octahedron edge distances, respectively.

Results and discussion

Structural aspects of Mg *and transition-metal olivines*

From consideration of ionic-radii arguments (Shannon & Prewitt, 1969) and cell dimensions, the crystal structures of α-Co_2SiO_4 and α-Ni_2SiO_4 are expected to be close to that of forsterite (α-Mg_2SiO_4). If the ionic size has a significant effect on the crystal structure, the structure of forsterite should be defined as the interpolation of the present two olivine structures. However, plots of the cell dimensions and interatomic distances *versus* the ionic-radius ratio r_M/r_{Si} show that α-Mg_2SiO_4 deviates significantly from the other transition-metal olivines (Figs. 2 and 3). The absence of *d*-orbital electrons in Mg may explain the deviations. Moreover, the ionicity seems to be correlated to the deviations because the trend in electrostatic energy is similar to that in bond distances as seen by comparison of the solid and broken lines in Fig. 3 (also see Tamada, 1980).

The mean interatomic distances of Si—O, *M*(1)—O, and *M*(2)—O obtained in this study are 1·639, 2·118, and 2·139 Å for α-Co_2SiO_4 and 1·640, 2·080, and 2·099 Å for α-Ni_2SiO_4. A comparison with forsterite reveals that the mean *M*(1)—O distances of α-Co_2SiO_4 and α-Ni_2SiO_4 are 1·6% larger and 0·7% smaller than the mean Mg(1)—O distance, respectively, and the mean *M*(2)—O distances are 0·5% larger and 1·4% smaller than the mean Mg(2)—O distance, where Mg(1)—O = 2·094 and Mg(2)—O = 2·129 Å (Fujino *et al.*, 1981). The distortion factors of Co, Ni and Mg olivines were calculated from $(1/n)\ \sum_{i=1}^{n} [(r_i - r)/r]^2 \times$

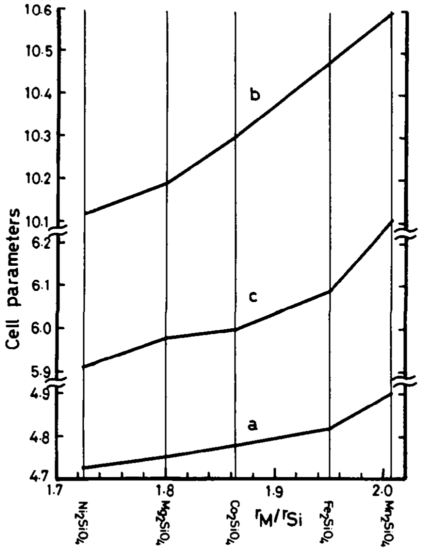

Fig. 2. Cell dimensions *versus* the ionic-radius ratio r_M/r_{Si} for Mg, Mn, Fe, Co, and Ni olivines.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38750 (23pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

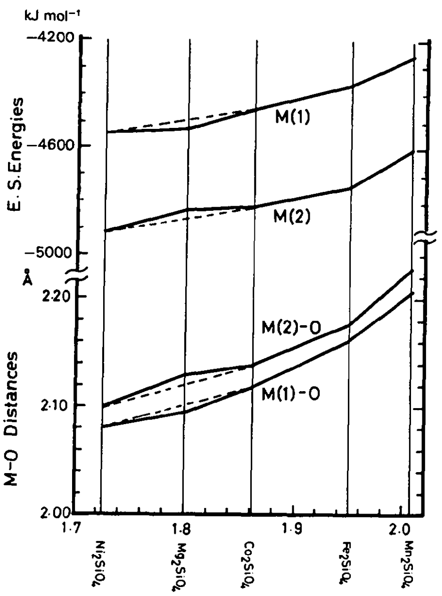

Fig. 3. Mean interatomic distances (Å) and electrostatic energies of cations (kJ mol^{-1}) for various olivines *versus* ionic-radius ratio r_M/r_{Si}.

10^4, where r_i is the ith M—O distance of the octahedron, r the mean M—O distance and $n = 6$. The values are 2·8, 0·8 and 1·6 for $M(1)$ sites and 11·3, 7·4 and 11·2 for $M(2)$ sites, respectively. It is notable that the octahedra of α-Ni_2SiO_4 are much more regular compared with those of other olivines. The interatomic distances and cell parameters of α-Co_2SiO_4 obtained from the present study are slightly smaller than those found by Morimoto *et al.* (1974). Those of α-Ni_2SiO_4 agree well with the results of Lager & Meagher (1978).

Net atomic charges

The net atomic charges (EDR) of the Si atoms are between +2·2 (1) and +2·4 e in α-Co_2SiO_4 and α-Ni_2SiO_4 (Table 4). The charges for O atoms range from −1·2 (1) to −1·5 e. The charges so far examined on the Si and O atoms can be compared to those optimized by lattice-energy calculation with an interatomic potential function [+2·276 e for Si; −1·569 e for O (Matsui & Matsumoto, 1982)]. The atomic charges (EDR) of the Co and Ni atoms are between +1·5 and 1·8 e. The ratio of the estimated charge to the formal charge suggests that the tetrahedral Si atom has more covalent character than either the Co or Ni atoms. On the other hand, compared with the octahedral Mg atoms which have an atomic charge of +1·7 to 1·8 e in the same structure (Fujino *et al.*, 1981), we have a systematic trend where the ionic charge on the Mg atom is greater than or equal to that on the transition metals such as Co and Ni. This trend may be acceptable in view of the electrostatic potential energies (Tamada, 1977, 1980). Fujino *et al.* (1981) reported that the atomic charge of the $M(2)$ site is larger than that of the $M(1)$ site for the Mg, Mn, and Fe olivines. In Table 4, atomic charges on each of these sites are almost identical but the atomic charges ($L1$) of Co olivine are in accordance with the above report. As a whole, the $M(2)$ site probably has more ionic character than the $M(1)$ site for a series of these olivines.

Residual electron density distribution

In the silicate-spinel structure Marumo *et al.* (1974, 1977) reported eight positive peaks of residual electron density around the Co and Ni atoms in nearly regular octahedra. Because of the lack of theoretical information about highly distorted octahedra, it is of interest to see the electron distributions of Co and Ni atoms in olivine structures having distorted octahedra with symmetry i [$M(1)$] and m [$M(2)$]. Octahedral Co^{2+} and Ni^{2+} ions having $3d^7$ and $3d^8$ electron configurations are known to have the high-spin state in the $M(1)$ and $M(2)$ sites of the olivine structure.

The difference Fourier syntheses were carried out using the final $|F_{obs}| - |F_{calc}|$ data after refinement of $L1$. The residual electron density distributions around Co and Ni atoms are shown in Fig. 4, in which each section parallel to (100) is piled up within the range of an octahedron; contours from −0·6 to 0·6 e Å^{-3} have been omitted; the interval is 0·2 e Å^{-3}. The patterns of residual peaks shown in Fig. 4 are more complicated compared with those for α-Mn_2SiO_4 and α-Fe_2SiO_4 where four positive peaks around the Fe atom, and two positive and two negative peaks around the Mn atom were observed in distorted octahedra. However, the following characteristics for Co and Ni olivines may be noted: (1) in Co olivine, the positive peaks around the cation are arranged almost parallel to the (010) plane passing through the cation center, with the negative peaks situated above and below the plane; (2) in Ni olivine, the positive and negative peak arrangements are more complicated than for Co olivine and high negative peaks (> |−1·2 e Å^{-3}|) can be observed for both $M(1)$ and $M(2)$ sites; (3) the maximum and minimum heights of residual peaks are 1·6 and −1·0 e Å^{-3} (Co

Table 4. *Net atomic charges* (e) *of* α-Co_2SiO_4 *and* α-Ni_2SiO_4

	$M(1)$	$M(2)$	Si	O(1)	O(2)	O(3)
Co_2SiO_4						
EDR	1·6 (1)	1·5 (1)	2·2 (1)	−1·2 (1)	−1·2 (1)	−1·4 (1)
$L1$	1·6 (1)	2·1 (1)	2·4 (2)	−1·4 (1)	−1·4 (1)	−1·6 (1)
Ni_2SiO_4						
EDR	1·8 (1)	1·7 (1)	2·4 (1)	−1·5 (1)	−1·5 (1)	−1·5 (1)
$L1$	1·7 (2)	1·8 (2)	2·3 (2)	−1·4 (1)	−1·4 (1)	−1·4 (1)

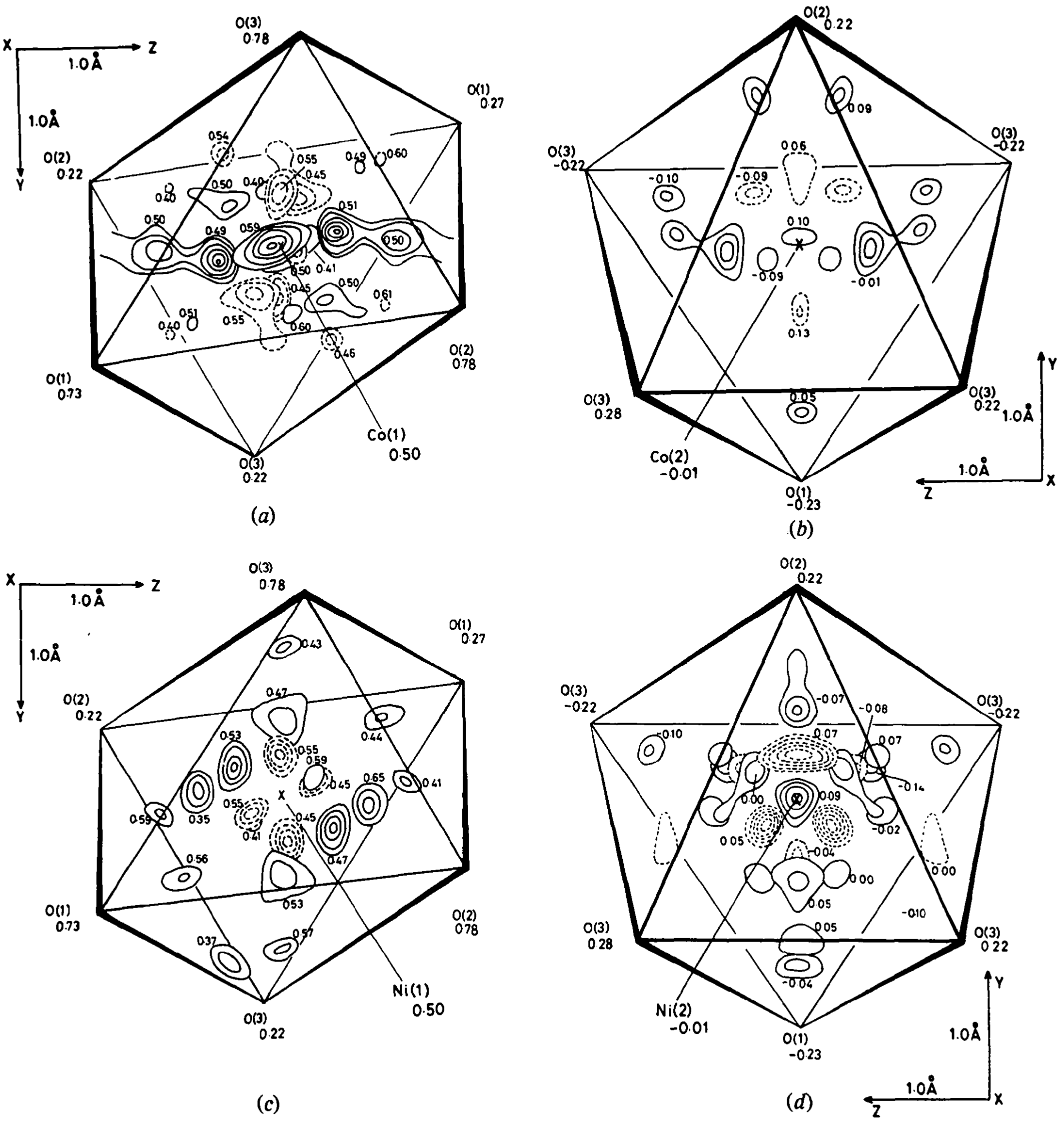

Fig. 4. The projections of residual electron density distributions around (*a*) the $M(1)$ site of Co_2SiO_4, (*b*) $M(2)$ of Co_2SiO_4, (*c*) $M(1)$ of Ni_2SiO_4, and (*d*) $M(2)$ of Ni_2SiO_4, where each section parallel to (100) of the difference Fourier maps is piled up within the range of an octahedron. Contours greater than $|\pm 0{\cdot}16|$ e Å^{-3} are shown. Contour intervals are 0·2 e Å^{-3}. Positive and negative values are indicated by solid and broken lines, respectively. Numbers beside each peak indicate the x fractional coordinate of the center of the peak.

olivine), and 1·2 and −1·4 e Å^{-3} (Ni olivine), respectively. Although the distribution described above is correlated with the features expected for the regular octahedra, the interpretation of these aspherical electron distributions is so difficult that we must limit our report to systematic presentations of the difference Fourier maps for a series of olivines.

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Adjustment of Restraints in the Refinement of Methemerythrin* and Azidomethemerythrin at 2·0 Å Resolution

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Abstract

Restrained least-squares refinement of the met and azidomet forms of hemerythrin has been carried out at 2·0 Å resolution. Average values for the Fe—ligand bond distances from the four subunits in the asymmetric unit were used as restraints in the following refinement cycle. The process was repeated until the restraints and Fe—X bond distances no longer changed significantly. Considerable variation is observed in each type of Fe—X bond, the Fe—N and Fe—O_{carboxy} bonds being longer than 2·0 Å, the Fe—$O_{\mu\text{-oxo}}$ bonds being shorter. Systematic errors caused by absorption, anomalous scattering, and the limited resolution of the diffraction data do not account for the variation and lead to the tentative conclusion that the observed bond lengths are characteristic of the binuclear Fe complexes found in these proteins.

Introduction

In the restrained least-squares refinement (Waser, 1963; Konnert, 1976; Hendrickson & Konnert, 1980) of novel metalloprotein structures, the choice of restraints to apply to the metal–ligand distances is not trivial. These distances are of great interest and should be free of bias introduced by the use of inappropriate values. If no model compounds are known, one is unsure of the appropriate distances for use as restraints. Even if model compounds can provide initial target values, the question remains whether these would be appropriate for a metal complex bound to a protein matrix. In particular, in metalloproteins, one must allow for possible differences in angular and distance parameters induced by the protein.

In the case of methemerythrins from *Themiste dyscritum* (Stenkamp, Sieker, Jensen & Sanders-Loehr, 1981; Stenkamp, Sieker & Jensen, 1983), we are unaware of appropriate model compounds for the binuclear, non-heme Fe complex in this oxygen transport protein. While some EXAFS distances are available for the metal complex (Elam, Stern, McCallum & Sanders-Loehr, 1982; Hendrickson, Co, Smith, Hodgson & Klippenstein, 1982), they are not consistent enough to provide definitive restraint information. In the earlier restrained least-squares refinement of the met form of the protein, we simply restrained all Fe—O and Fe—N distances to 2·0 Å. The resulting bond lengths (Stenkamp, Sieker & Jensen, 1983) ranged from 1·84 to 2·16 Å. Comparison of the bonds suggested possible differences in length within bonds of

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[*] This form of the protein has been referred to as met-, metaquo-, methydroxo- and methemerythrin. The background to the name changes is covered elsewhere (Stenkamp, Sieker & Jensen, 1983). We revert to the simpler name since no exogenous Fe ligand has yet been identified in this form of the protein.

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