



LABORATORI NAZIONALI DI FRASCATI
SIS – Pubblicazioni

LNF-96/035 (P)
29 Luglio 1996

Revised Version
Settembre 1996

The Local Structure of Ca-Na Pyroxenes. I.XANES study at the Na K-edge

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Abstract

X-ray absorption Na K-edge spectra have been recorded on synthetic endmember jadeite and on a series of natural Ca-Na pyroxenes compositionally straddling the Jd-Di. The disordered C2/c members of the series are systematically different from the ordered P2/n members. These differences can be interpreted and explained by comparing the experimental spectra with theoretical spectra. These have been calculated by the multiple-scattering formalism from the atomic positional parameters determined by single-crystal X-ray diffraction structure refinement on the same samples. In the full multiple scattering region of the spectrum (1075 to 1095 eV) C-pyroxenes exhibit three features which reflect the 6-2 configuration of the O back-scattering atoms around the Na absorber located at the center of the cluster (site M2 of the jadeite structure). P-pyroxenes show more complicated spectra in which at least four (possibly five) features can be recognized; they reflect the two types of configuration (6-2 and 4-2-2) of oxygens around Na in the two independent M2 and M21 eight-fold coordinated sites of the omphacite structure. A weak, sometimes poorly resolved peak at 1079 eV is diagnostic and discriminates C- from P-pyroxenes. The Garnet Ridge C2/c impure jadeite exhibits a spectrum which is intermediate between those of jadeite and omphacite. The Hedin-Lundqvist potential proves best for these insulating materials and allows multiple-scattering calculations agreeing well with experiments. The assesment of the local electronic properties of compositionally and structurally complex minerals such as clinopyroxenes is thus enhanced.

KEY WORDS: jadeite; omphacite; X-ray absorption spectroscopy; synchrotron; sodium

Submitted to Phys. Chem. Min.

Introduction

Ca–Na pyroxenes (Morimoto et al. 1988) have been studied extensively during the past three decades because of the peculiar behaviour of their solid solutions: endmembers crystallize in the disordered $C2/c$ space group (diopside: Warren and Bragg 1928; jadeite: Prewitt and Burnham 1966; aegirine and kosmochlor: Clark et al. 1969; hedenbergite: Cameron et al. 1973), whereas intermediate members can either be disordered as the endmembers are (omphacite p.p. and aegirin–augite: Clark and Papike 1968), or they are ordered and then have lower symmetry (omphacite p.p.: Clark and Papike 1966, 1968; Matsumoto and Banno 1970; Matsumoto et al. 1975).

Studies of Ca–Na pyroxenes can be combined on four main lines of investigation: (i) establishing the correct crystal structure and space group symmetry; (ii) determining the compositional extent of the ordered structure versus the disordered one, also in relation to the presence of solvi and as a function of temperature (T), pressure (P) and time (t); (iii) assessing the role of vacancies; (iv) interpreting the phenomenological (microtextural) and thermodynamical aspects of the order–disorder and exsolution relationships.

All these topics have been dealt with using a variety of methods: X–ray, electron and neutron diffractions on both single crystals as well as powder mounts, Mössbauer spectroscopy, transmission electron microscopy, thermochemistry, synthesis and equilibrium studies, kinetics, experimental and theoretical thermodynamics, statistical mechanics modelling, etc.. However, agreement is far from being reached, in as much as the choice of the method affects the result, each method having its own merits and shortcomings. E.g., order–disorder relationships determined by single–crystal X–ray diffraction structure refinement (SC–XRef), by far the most widespread method, may be biased because they usually disregard the possible presence of vacancies, or omit from calculation of the M2 site occupancy such ions as Fe^{2+} or Mn^{2+} , which often compete with Na and Ca to enter M2 beside entering their preferred M1 site.

X–ray absorption spectroscopy (XAS), an element–specific technique, particularly sensitive to local structure, can provide new insight into order–disorder relationships and local environments across the entire diopside– (omphacite)–jadeite compositional join. Information about short– range–order (SRO) gathered by this technique complements well that about long–range–order (LRO) best obtained by X–ray diffraction. Yet XAS has been rarely used, essentially because these pyroxenes contain light elements (Ca, Na, Mg, Al, Si, O); the absorption edges of most if not all these atoms lie outside the range of energies where standard XAS apparatus equipped with crystal monochromators provides high–quality spectra, and O even demand for grating systems.

We have now carried out well–resolved determinations of the Na, Mg and Al K–edges in a series of Ca–Na pyroxenes (Mottana et al. 1996). They provide novel data, but they can be interpreted properly only by comparison to and with the support of theoretical calculations performed *ab initio* on the basis of the one–electron multiple scattering theory (MS), starting from crystal structure data determined by SC–XRef. We report here the results obtained for the Na K–edge, and discuss them in comparison with our previous studies on the Ca K–edge (Davoli et al. 1987; Paris et al. 1995).

The aim of this paper is to give information on the order–disorder relationships occurring in the eight–fold coordinated cation site of the Ca–Na pyroxene structure. Results on the Mg

and Al K-edges, relevant mostly to the order-disorder relationships in the six-fold coordinated cation site, have also been announced (Mottana et al. 1996), but they will be dealt with in detail in a following paper. Later on, we will turn to other topics the significance of which became clear during our evaluation of the XAS experiments.

Since this contribution is the first of a small series, we deem it useful to begin with a review of the state of art.

State of the art

Space group symmetry and crystal structure

Clark and Papike (1966) first discovered the primitive space group symmetry in the intermediate members of the Di-Jd solid solution series by verifying the presence of hkl reflections with $h+k=2n+1$ and of h0l reflections with $l=2n+1$ in precession photographs taken on the Tiburon omphacite of composition $\text{Di}_{42}\text{Jd}_{38}\text{Hd}_{10}\text{Aeg}_{10}$. They interpreted these reflections (forbidden in the C2/c space group established for clinopyroxenes by Warren and Bragg 1928) as indicating the P2 space group. Consequently they solved the omphacite structure as containing 4 M1, 4 M2 and 4 T independent sites per unit cell.

In their continuing studies on clinopyroxenes (Clark and Papike 1968; Clark et al. 1969) they also showed that the ordered structure is compositionally limited in a region roughly symmetrical astride composition $\text{Di}_{50}\text{Jd}_{50}$ ("ideal" omphacite) and extending from $\text{Di}_{65}\text{Jd}_{35}$ to $\text{Di}_{35}\text{Jd}_{65}$ along the Di(+Hd+Ts)-Jd join of the Di(+Hd+CaTs)-Jd-Aeg triangle (Fig. 1); the ordered region decreases in width with increasing Aeg content to nought at the boundary line with the aegirin-augite field, i.e. at $\text{Al}/(\text{Al}+\text{Fe}^{3+}) = 0.5$. Furthermore, they confirmed Warner's (1964) previous finding that the clinopyroxene with composition $\text{Di}_{56}\text{Jd}_{21}\text{Hd}_{12}\text{Aeg}_{11}$ in the Eiksundsdal eclogite is C2/c although compositionally falling in the omphacite field. It therefore became established that there are two types of Ca-Na clinopyroxenes which fall in the omphacite compositional field: the C- and P-type omphacites.

Fig. 1 – Triangular plot of for Ca-Na clinopyroxenes (Morimoto et al., 1988) showing the compositions of the samples studied and the field of ordered P-omphacite as originally proposed by Clark and Papike (1968). Samples: 1 = Di, 2 = Ala-1, 3 = Px-1, 4 = 68- MV-45, 5 = M.1, 6 = GR-P1-25, 7 = KY#3, 8 = MZ, 9 = Jd (see Table I).

Table I – Chemical compositions (wt%) and formulae (at. p.f.u. on the basis of 4 metal atoms, charge-balanced by the method of Mottana 1986) of the examined Ca–Na pyroxenes.

Oxides (wt %)	<i>Di</i>	<i>Ala-1</i>	<i>Px-1</i>	<i>68</i>	<i>MV 45</i>	<i>M.1</i>	<i>GR</i>	<i>P1 25</i>	<i>KY#3</i>	<i>MZ</i>	<i>Jd</i>
SiO ₂	55.49	54.74	53.94	54.50	56.55	57.47	58.00	58.97	59.45		
Al ₂ O ₃	0.00	0.51	0.66	11.50	13.05	17.14	20.40	23.77	25.22		
Cr ₂ O ₃	0.00	0.01	0.21	0.03	0.00	0.00	0.01	0.00	0.00		
TiO ₂	0.00	0.00	0.26	0.04	0.00	0.31	0.00	0.00	0.00		
Fe ₂ O ₃	0.00	1.94	1.18	0.91	0.00	1.09	0.46	0.36	0.00		
FeO	0.00	1.16	1.87	4.32	2.70	2.94	2.59	0.08	0.00		
MnO	0.00	0.02	0.07	0.01	0.00	0.06	0.10	0.02	0.00		
MgO	18.61	17.02	16.93	8.70	7.95	3.92	2.21	0.97	0.00		
CaO	25.90	25.13	24.59	12.55	13.05	5.40	3.49	1.43	0.00		
Na ₂ O	0.00	0.38	0.24	6.30	7.28	11.23	12.51	14.42	15.33		
K ₂ O	0.00	0.01	0.00	0.03	0.00	0.01	0.10	0.01	0.00		
sum	100.00	100.92	99.95	98.89	100.58	99.57	99.87	100.02	100.00		
Structural formulae (on the basis of 4 metal atoms)											
Si	2.000	1.976	1.969	1.963	1.981	2.005	1.999	1.994	2.000		
Al(IV)	0.000	0.022	0.028	0.037	0.019	—	0.001	0.006	0.000		
Al(VI)	0.000	—	—	0.451	0.519	0.705	0.828	0.942	1.000		
Ti	0.000	0.000	0.007	0.001	0.000	0.008	0.000	0.000	0.000		
Fe ³⁺	0.000	0.053	0.034	0.024	—	0.029	0.012	0.009	0.000		
Cr	0.000	0.001	0.006	0.000	0.000	0.000	0.000	0.000	0.000		
Fe ²⁺	0.000	0.035	0.057	0.130	0.080	0.086	0.075	0.002	0.000		
Mn	0.000	0.001	0.002	0.000	0.000	0.002	0.003	0.001	0.000		
Mg	1.000	0.916	0.921	0.467	0.415	0.204	0.113	0.049	0.000		
Ca	1.000	0.972	0.961	0.484	0.490	0.202	0.129	0.051	0.000		
Na	0.000	0.027	0.017	0.440	0.496	0.760	0.835	0.946	1.000		
K	0.000	0.000	0.000	0.000	0.001	0.000	0.004	0.000	0.000		
Components (mol %)											
Q	100.0	97.3	98.3	55.1	49.8	24.4	15.9	5.2	0.0		
Ae	0.0	2.7	1.7	2.3	0.0	3.0	1.2	0.9	0.0		
Jd	0.0	0.0	0.0	42.5	50.2	72.8	82.9	93.9	100.0		

Di – endmember diopside, synthesized hydrothermally at 3 kbar, 700°C, 21 h (cf. Bondi et al., 1981)

Ala-1 – gem quality colourless "alalite" diopside in rodingite, Val d'Ala, Italy (MMUR 18362/732)

Px-1 – green diopside in skarn, Canada [incl. SrO 0.035, BaO 0.006, H₂O 0.03]

68-MV-45 – dark green omphacite in eclogite, Rif. Alpetto, Monviso, Italy (cf. Mottana, 1971)

M.1 – light green omphacite in vein, Lago Mucrone, Biella, Italy (Edgar et al., 1969)

GR-P1-25 – light green omphacite in eclogite, Garnet Ridge, AZ, U.S.A. (Watson & Morton, 1968)

KY#3 – white jadeite from jade worker's tomb, Kaminaljuyú, Guatemala (USNM 106443)

MZ – light green jadeite, rough, Manzanal, Motagua valley, Guatemala (USNM 112538-3)

Jd – endmember jadeite, synthesized at 30 kbar, 1200°C, 3 h (cf. Wood et al., 1980)

Several natural examples of both types were described during the following years (C2/c: Mottana et al. 1968; Heritsch 1973; McCallister et al. 1974; etc. – P2: Ogniben 1968; Heritsch

1973; Black 1974; etc.). Of particular interest was the discovery at Bouhendep of a "ferro-omphacite" of composition $\text{Jd}_{45}\text{Hd}_{43}\text{Aeg}_8\text{Di}_4$; this is the ferrous analogue of omphacite, with Mg mostly substituted by Fe^{2+} , and is ordered on a primitive space group symmetry described as P2 (Black 1970).

However, shortly after publication, the correctness of Clark and Papike's (1968) P2 space group choice was questioned. Matsumoto and Banno (1970) claimed discovery of the P2/n space group in an omphacite of composition $\text{Di}_{44}\text{Jd}_{34}\text{Aeg}_{14}\text{Hd}_8$ from the Iratsu eclogite; and, by a systematic re-study using long-exposure Weissenberg photographs, Matsumoto et al. (1975) conclusively showed that in most omphacites h0l reflections are absent only when h+l is odd, thus leaving as the only possible space groups P2/n and Pn. Furthermore, a careful evaluation of 1090 non-equivalent reflections collected with a four-circle diffractometer made it possible for them to solve the Iratsu omphacite structure. They also carried out a re-determination of the Tiburon omphacite structure directly by X-ray diffraction as well as by reconsidering its electron diffraction pattern (Phakey and Ghose 1973) and Mössbauer spectrum (Bancroft et al. 1969), and found it to be P2/n too. At the same time and independently, the same conclusion was reached by Curtis et al. (1975), who studied the Red Wine "ferro-omphacite" of composition $\text{Jd}_{41}\text{Hd}_{35}\text{Aeg}_{14}\text{Di}_6$, which is peculiar also for its high content of an as yet poorly defined titanian component.

The final word on the omphacite space group controversy is Rossi et al.'s (1983), as a conclusion of a long series of cooperative studies which entailed dozens of structure refinements on crystals from eclogite in Italy (Bondi et al. 1978; Mottana et al. 1979; Rossi et al. 1981), Norway (Smith et al. 1980), Switzerland and Lesotho (Rossi et al. 1981). They ruled that the observed weak h0l extra reflections with $h+l=2n+1$ were due to multiple reflection phenomena since they disappear with small variations of the azimuthal ϕ angle (Rossi et al. 1981 p. 22; 1983 p. 249); thus, they concluded that the only permitted space group for primitive (ordered) omphacite is P2/n. The P2/n omphacite structure has 2 M2, 2 M1 and 2 T individual cation sites.

The P2/n space group has now become unchallenged among X-ray diffraction crystallographers (e.g., Yokoyama et al. 1976; Walitzi and Walter 1980; Cameron and Papike 1981; Sasaki et al. 1981; etc.). Nevertheless, P2/n is certainly not the only space group possible in omphacitic pyroxenes. Electron diffraction studies show that during topotactic replacement of augite by omphacite other space groups such as P2/c and P2 can also occur, which were interpreted to be metastable products of a sliding replacement reaction the final outcome of which, at equilibrium, would be the P2/n space group (Carpenter and Okay 1978; Carpenter 1979); however, alternatively, they may reflect local ordering conditions at a very small scale, i.e. short-range-order (SRO).

Order-disorder relationships

While the controversy on the true space group symmetry was on, another type of research was underway, prompted by a speculation by Champness (1973) on the possible order-disorder relationships which would occur in omphacites crystallized as the C-type at high temperature and transformed to P on cooling.

Fleet et al. (1978) first assessed such T-dependent continuous order-disorder relationship

by measuring in 0-level **b**-axis precession photographs of omphacites heated at increasing temperature (at constant $P = 18$ Kbar) the intensity variation of the $10\bar{1}$ Friedel pairs normalized against the $20\bar{2}$ K_α Friedel pair. The same type of approach permitted Carpenter (1981a) to follow the kinetics of disordering as a function of P (at 18 and 30 Kbar), T (from 750 to 1260 C) and t (from 1.5 min to 16 days), and to establish that the equilibrium order/disorder temperature is 865 ± 10 C for a Tauern omphacite having the composition $Jd_{48}Di_{45}Hd_6Aeg_1$. Carpenter's result confirmed, at experimental conditions close to those of omphacite natural formation, a much simpler study made at room P by Walitzi and Walter (1980): for a Stirian omphacite having Jd_{39} they had found a transformation T of 875 ± 20 C.

A different, but complementary approach was followed by Rossi et al. (1983): they measured SRO in a series of crystals occurring in the Nybö eclogite pod as a function of composition by monitoring the ratio I_{050}/I_{060} directly with the four-circle diffractometer. Disorder was found to increase as the crystal composition deviated from $Di_{50}Jd_{50}$ (the "ideal" omphacite composition) first under a regime of LRO then, for compositions farther away, of SRO. The degrees of order varied following bell-shaped curves, the most ordered P -omphacite found by Rossi et al. (1983) being sample PVB-670 of Bearth (1965) and Edgar et al. (1969) [re-labelled LM1 by Rossi et al. 1983] with composition $Jd_{49}Di_{40}Hd_6Aeg_2CEn_3$, which occurs as a vein at Lago Mucrone near Biella. Furthermore, the curves of degrees of order turned out to be different in the omphacites from three eclogite sets of different origin, each set being characterized by a different P - T - t history.

Mottana (1983) tried rationalizing these and other results by a different method of determining the degree of order (isotags in an **a-b** plot), but came to no more far-reaching conclusion. However, Rossi et al.'s (1983) and Mottana's (1983) studies showed unequivocally that the compositions at which transition from P - to C -omphacite occurs can be both Di -richer and Jd -richer than those stated by Clark and Papike (1968): in different geological environments, the P -omphacite region may extend from Jd_{31-38} to Jd_{65-72} . The symmetric model phase diagram based on coupled substitutions in two non-equivalent sites calculated by Davidson and Burton (1987) fits these results adequately, although a more comprehensive treatment of SRO in omphacitic pyroxenes would require an approximation based on clusters larger than pairs (Burton and Davidson, 1988).

Most recently, the character of the order-disorder transition in omphacites has been studied again by systematic crystal-structure refinements of grains heated and at room pressure. The two omphacites used are from Münchberg ($Jd_{52}Di_{41}Hd_7$) and Nybö ($Di_{48}Jd_{39}Aeg_9Hd_4$). The SC-Ref results were quantitatively interpreted by the Landau theory (Carpenter et al. 1990a,b): both the equilibrium and the kinetic results indicate that the character of the C to P transition is close to being tricritical (Fig. 2).

As a matter of fact, the local aspects of order-disorder relationships in clinopyroxenes had been studied first by Mössbauer spectroscopy (Bancroft et al. 1969; Williams et al. 1970; Matsui et al. 1972), but they could not be explained satisfactorily till Aldridge et al. (1978) carried out a systematic study on the same samples quenched by Fleet et al. (1978) from various P - T conditions and starting from correct $C2/c$ and $P2/n$ structural models. The three Fe^{2+} doublets and one Fe^{3+} doublet needed to fit the spectra could be explained easily by considering all Fe^{2+} and Fe^{3+} located in the M1 (and M11) site (i.e., assuming negligible Fe^{2+}

in M2 viz. M21), and by taking into account (Ca, Na) next-nearest-neighbour (NNN) interaction effects on ferrous iron; surprisingly, the effects of (Ca, Na) ordering were found not to change appreciably on going from the C2/c to the P2/n space group. Thus, in both types of omphacites the M2 configurations occurring as NNN to Fe²⁺ located in M1 were interpreted to be 1Ca+2Na, 2Ca+1Na, and 3Ca. No 3Na configuration was observed, and it was thought that it could not occur probably because the charge on Fe²⁺ in M1 would be too low.

Fig. 2 – Composition (X) vs. temperature (T) diagram showing the tricritical behaviour of the solid solutions in the Di–Jd join and the present-day understanding on the extent of the solvi (modified after Davidson and Burton, 1987).

Aldridge et al.'s (1978) final interpretation is that Na tends to occupy the M2 positions surrounding a M1 site occupied by Al, while Ca does the same for those occupied by Fe²⁺. Clearly, these configurations modify the random population of the M2 sites typical of a C2/c pyroxene, and because of charge balance requirements they induce SRO into both the six-fold (Mg, Fe²⁺ <-> Al, Fe³⁺) and eight-fold coordinated (Ca <-> Na) cation sites.

To come to a conclusion; it is now understood that most if not all misunderstandings about order-disorder relationships in omphacites which were matter of debate in the past derived from the different cation ordering models assumed to be present in the "ideal" (here meant as "extremely ordered") P-omphacite. Clark and Papike's (1968) structural model for ordered P2 omphacite, with 2Mg and 2Al segregated in 4 distinct M1 sites, and 2Ca and 2Na also in 4 M2 sites, led Bancroft et al. (1969) and Williams (1971) to wrong fittings of their Mössbauer spectra and to a wrong interpretation of local ordering. Changing space group symmetry from P2 to P2/n (Matsumoto et al. 1975) implied changing the structural model: not only there is a new symmetry constraint due to the glide, but the number of cation sites in the unit cell must be halved, and only 2 M1 and 2 M2 sites need to be considered to justify the observed Mössbauer spectra.

Thus, in the currently favoured model (Rossi et al. 1983): (i) Mg and Al are considered to be partitioned over two slightly distorted octahedral sites (M1 for Mg and M11 for Al), both of point symmetry 2, which are edge-connected so as to form a chain parallel to the tetrahedral T chain; (ii) Na and Ca are thought to be locally ordered over two eight-fold coordinated sites (M2 and M21) again of point symmetry 2; these sites are separated one from the other because

of the interposition of the oxygen atoms which link the M11 octahedra of the octahedral chain with the T2 tetrahedra of the tetrahedral chain. However, contrary to Mg and Al, which occupy independently their sites (but not completely, because of the possible simultaneous presence in them of Fe^{2+} and Fe^{3+} , respectively, as minor substituting cations), the Ca and Na atoms are believed to be intrinsically disordered over their two sites.

The amount of such a local disorder over M2 and M21 is another matter of debate. Matsumoto et al. (1975) suggested the ratios $\text{Na}/\text{Ca}=2/1$ and $\text{Na}/\text{Ca}=1/2$, respectively, their model being a modification of the occupancies $2/3 \text{ Na} + 1/3 \text{ Ca}$ in M2 and $1/3 \text{ Na} + 2/3 \text{ Ca}$ in M21 determined by Clark and Papike (1968), which they had entered into their model. On the other hand, Rossi et al. (1983), while confirming that M1 and M11 are completely filled up with Mg and Al respectively ("full octahedral order"), found that M2 and M21 are only partially filled ("partial eight-fold site local disorder"). Consequently, they claim that M2 and M21 tend to a "maximum" possible state of order such as $3/4 \text{ Na} + 1/4 \text{ Ca}$ for M2, and $1/4 \text{ Na} + 3/4 \text{ Ca}$ for M21. Thus, they confute on the basis of considerations on local charge balance requirements the "ideal" omphacite of both Fleet et al. (1978) and Mottana (1983), which had been stated to have the occupancies $0.00 \text{ Ca} + 1.00 \text{ Na}$ for M2 and $1.00 \text{ Ca} + 0.00 \text{ Na}$ for M21 so as to attain the 0.50 Ca and 0.50 Na values for X (= M2+M21) required by the chemical formula.

By contrast, Fleet et al. (1978 p. 1105) had considered (and cast aside) charge balance as not being the sole criterion regulating the ordering process, and rather had drawn attention on the ionic radii difference; they had accepted as likely the complete ordering of Mg and Al over M1 and M11 because of the large ionic radii difference (0.72 and 0.53 \AA , respectively), but had argued that the tendency of Ca and Na to order over M2 and M21 is strongly diminished as a result of the very small difference of their ionic radii (1.00 and 1.02 \AA , respectively). Fleet et al. (1978) add another significant piece of evidence against conclusions drawn from XRD evidence only; they claim that, since the X-ray scattering factors of Mg^{2+} and Al^{3+} are very similar and the P2/n structure is not greatly distorted relative to the equivalent C2/c structure, the "visibility" of an ordered Mg-rich omphacite is largely associated with the partial order of the M2-type cations (Fleet et al. 1978 p. 1104).

Rossi et al. (1981 p. 43) explicitly state that they could refine the site distribution of Na and Ca between the two M2 sites simply through their scattering curves, whereas any attempt of them to find a single and straightforward method to determine the populations of the M1 and M11 sites had been unsuccessful. Only by an indirect, empirical and iterative method combining mean bond distances, charges, number of determined electrons, and with constraints based on the known chemical analysis as well as other basic assumptions, they could find a satisfactory solution (Rossi et al. 1981 p. 41). In other words: disorder between Ca and Na in the M2, M21 sites was determined directly by them, whereas the alleged very high degree of order between Mg and Al in the M1, M11 sites had only been inferred.

Since most later refinements mainly followed Rossi's procedure (e.g., Carpenter et al. 1990a,b), the present situation is that we know for sure that in the P-omphacite crystal structure Ca and Na are partially ordered, but we only assume that there is a full ordering of Mg and Al.

Role of vacancies

To further add to uncertainty, it should be remembered that crystal-structure refinements based on single-crystal X-ray diffraction procedures actually average the contributions of all cations present in the sample, and therefore do not identify the crystal-chemical role which each individual cation species has in the complex process of ordering of omphacites. Moreover, the crystal-structure calculation constraint that sites must be filled so as to satisfy charge balance requirements (full-occupancy model) is not always tenable.

Positively, McCormick (1986) demonstrated it to be wrong for a number of omphacites where the deficit in the EMP analysis and ensuing deviation from the stoichiometric formula is not due to analytical problems (or to the fact that Fe is entirely computed as Fe²⁺, another very common cause of error), but derives instead from the presence of structural vacancies. Deviations are greatest in the highly aluminous pyroxenes from eclogites in kimberlites, and have been found to be related to the presence of the Ca-Eskola component, Ca_{0.5}[]_{0.5}AlSi₂O₆ (Smyth et al. 1980; McCormick 1986). Omitting this possibility leads to refinements that, although apparently satisfactory in their R-factors, do not actually explain the non-stoichiometry of the formula determined from the EMP analysis (McCormick 1986). The SC-XRef of a kimberlitic clinopyroxene taking into account the Ca-Eskola component showed that, although most vacancies (at least 90%) occur in M2, some are present even in M1. Thus, two vacancy end-members may be needed to fully describe a pyroxene; moreover additional problem is that electron channelling indicated that some Fe and Mg (Fe > Mg) reside in M2, at least in these high-T omphacite pyroxenes of eclogite nodules in kimberlite (McCormick 1986).

Microtextures and exsolution

Whatever the correct structural model may be (see above), it is unanimously assumed that Ca,Na and Mg,Al order-disorder is the driving force for omphacite to reach in time the P2/n symmetry, believed to be the equilibrium one at lower temperatures. The volumetric extent of the ordered structure would increase with time through the crystal because of the growth of antiphase domains (APD). At low temperature, where the ordered state is most stable, APD's tend to grow large so as to reduce the free energy of the system to a minimum (Carpenter 1981b, 1983; Lardeaux et al. 1986; van Roermund and Lardeaux 1991).

Carpenter (1981b), in an epochal paper for eclogite research, was able to show that omphacites from different localities having undergone different P-T-t trajectories have antiphase domains different in size as a function mainly of the attained T. This opened the way to Mottana's (1983) inference that the degree of order is related to the maximum T attained during eclogite facies metamorphism as well as to the time elapsed from the acme of it, with the thermal regime of the subducted crust during uplift usually being less influential, except that at a certain moment (or closure temperature) it quenches the attained APD size.

At equilibrium, the P2/n ordered omphacite field is thought to be centered on the ideal omphacite composition Ca_{0.5}Na_{0.5}Mg_{0.5}Al_{0.5}Si₂O₆, and is enclosed (both compositionally and as a function of temperature) within a field of C2/c disordered clinopyroxene through a curved phase boundary that closes at a fairly high critical temperature. The phase boundary changes at low temperature into two solvi (Fig. 2): on one end, a P-omphacite solid solution enriched in Di component coexists with a C-type Di-rich omphacite solid solution (left), and at the opposite

end a P-omphacite solid solution enriched in Jd- component coexists with a C-type, Jd-rich clinopyroxene (Carpenter 1978; Carpenter and Smith 1981). Thus single-crystal X-ray diffraction by itself could not solve the omphacite problem, and needs to be supplemented by TEM.

XAS Spectroscopy

To the aim of studying short-range order (SRO), X-ray absorption spectroscopy (XAS), a non-destructive, element-specific technique, is likely to be the most promising method (Hawthorne 1993). However, studies on omphacites by XAS are still very limited in number.

Davoli et al. (1983, 1987) related the variation of the Ca K-edge XANES of a number of omphacites along the Di-Jd join, to the variation in the geometrical configuration of the coordination polyhedron around Ca. Diopside and Di-rich omphacites with C2/c space group symmetry were shown to have Ca residing in only one type of M2 polyhedron with a 4-2-2 configuration: the Ca absorber is at the centre of a distorted cube of oxygens having 4 short bonds (ca. 2.35 Å), 2 intermediate ones (ca. 2.56 Å), and 2 long bonds (> ca. 2.70 Å); all bonds are nearly symmetrically distributed in pairs around the central atom. On the other hand, Jd-rich omphacites, which also have C2/c symmetry, were shown to have Ca at the centre of a polyhedron having the same 6-2 configuration as M2 (= Na) in jadeite: 6 Ca-O bonds are nearly equal and 2.36– 2.41 Å long, so that the pertaining oxygens form a tight half-sphere around the absorber, whereas the remaining 2 bonds are longer than 2.70 Å and stand up like a spike at only one side of the coordination polyhedron. In omphacites of intermediate composition having Ca:Na ca. 1:1, consequently with the P2/n space group, Davoli et al.'s (1987) Ca K-edge XANES spectra showed evidence for the presence of two configurations ("double edge"), i.e., the concomitant presence of two independent eight-fold coordinated sites, as already made clear by X-ray diffraction refinements. Ca appears to be disordered over both sites; therefore, it appears that Ca can adapt itself to the structural environment; dictated by the major element Na.

These relationships were originally deduced from a simple but correct fingerprint evaluation of experimental spectra (Davoli et al. 1987). However, they found recently full confirmation from theoretical MS calculations (Paris et al. 1995). These were performed ab initio starting from the atomic positional parameters obtained by crystal structure refinement, and showed in addition that the type of such second-shell neighbours as Al and Mg may sensibly affect a Ca K-edge XANES spectrum.

Samples

Two synthetic end members, Di and Jd, and seven natural Ca-Na pyroxenes ranging in composition from $\text{Di}_{92}\text{Hd}_4\text{Aeg}_3\text{Jd}_1$ to $\text{Jd}_{94}\text{Di}_5\text{Aeg}_1$ (Table I and Fig. 1) were studied. Three of them are the same samples already reported for the Ca K-edge (Davoli et al. 1987).

All but three of the natural pyroxenes had their structures refined to $R = 0.017\text{--}0.034$ by the late Giuseppe Rossi (pers. comm. 1987). Diopside Px-1 was, at his indication, taken as identical to the Gouverneur diopside (Rossi et al. 1982), and our natural jadeites as essentially the same as the Quincinetto jadeite (Rossi et al. 1981); the positional parameters of these were used for our calculations. As for our synthetic pyroxenes, we assumed, on the basis of the

close similarity of the unit-cells, that our diopside has the same atomic positional parameters as the synthetic diopside refined by Cameron et al. (1973). By contrast, our synthetic jadeite is taken as structurally identical to the Santa Rita natural jadeite refined by Prewitt and Burnham (1966) as, to our knowledge, no SC-XRef was ever made on a synthetic jadeite because of lack of suitable crystals.

Experimental technique

Samples were first carefully purified, the grains appropriate for EMP and SC-XRef selected and analyzed, and an aliquot of the rest ground to coarse powder, mixed with Si and di-methyl-phtalate, ground again to fine powder, and run in a powder diffractometer, either a Philips 1700 or an automated Seifert PAD II (cf. Mottana et al. 1992) to determine the unit-cell parameters (Table II) by the least-squares programs of Garvey (1986) and Burnham (1991). Another aliquot of the coarse powders were set aside for XAS spectroscopy. Table III reports the atomic positional data determined by SC-XRef by Giuseppe Rossi, and used as input data for our MS calculations.

X-ray absorption spectroscopy

All experimental XAS spectra were collected at UVSOR, the synchrotron radiation source of Institute of Molecular Science (I.M.S.) at Okazaki, Japan, at the soft X-ray beamline BL7A, equipped with a crystal monochromator, where K-edge XANES spectra for light element as Na can be taken with resolution 0.25 eV (Murata et al. 1992). The UVSOR is a 750 MeV dedicated electron storage ring (Watanabe 1991) which usually operates at 200 mA current with a lifetime of about 4 h. Beamline BL7A derives synchrotron radiation intense enough to be used for XAS by a superconducting wiggler under an acceptance angle of 1 mrad in the horizontal plane and of 0.15 mrad in the vertical plane, yielding photons in the energy range 800–4000 eV. The beamline is equipped with a monochromator of the double-crystal type of beryl cut along the (10 $\bar{1}$ 0) plane. Energy calibration is made before and after each run by reference to the known angle of a very sharp dip occurring at the K-edge of Al. The K-edge of Na was scanned at steps of 0.1 eV.

The sample is spread as a very fine film on a piece of graphite tape which is adhesive on both sides. The other side of the tape is stuck onto the first photocathode of an electron multiplier. The entire monochromator plus sample system is held in a vacuum chamber at 1×10^{-7} torr.

Table II – Unit-cell parameters and volumes of the examined Ca-Na pyroxenes.

<i>Unit-cell parameters</i>	<i>Di</i>	<i>Ala-1</i>	<i>Px-1</i>	<i>68 MV 45</i>	<i>M.1</i>	<i>GR P1 25</i>	<i>KY#3</i>	<i>MZ</i>	<i>Jd</i>
a (Å)	9.748(3)	9.750(1)	9.760(2)	9.612(1)	9.566(1)	9.510(1)	9.471(6)	9.439(1)	9.416(2)
b (Å)	8.927(2)	8.921(1)	8.925(1)	8.794(1)	8.769(1)	8.666(1)	8.608(6)	8.585(4)	8.564(2)
c (Å)	5.250(1)	5.251(1)	5.258(1)	5.248(1)	5.252(1)	5.246(1)	5.235(1)	5.226(2)	5.226(3)
β (°)	105.83(1)	105.81(1)	105.85(1)	106.79(1)	106.93(1)	107.31(1)	107.97(5)	107.46(2)	107.58(2)
V (Å ³)	439.5(2)	439.5(2)	440.6(1)	425.5(1)	421.5(1)	412.7(1)	404.9(3)	404.0(2)	401.7(2)
sp. gr.	n.d.	C2/c	C2/c	P2/n	P2/n	C2/c	C2/c	C2/c	n.d.

Table III – Atomic positional parameters of the Ca-Na pyroxenes of Table I determined anew by Giuseppe Rossi.

Di	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T	0.2862	0.0933	0.2293
M1	0	0.9082	0.2500
M2	0	0.3015	0.2500
O1	0.1156	0.0873	0.1422
O2	0.3611	0.2500	0.3180
O3	0.3505	0.0176	0.9953
Ala-1	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T	0.2862	0.0934	0.2294
M1	0	0.9084	0.2500
M2	0	0.3015	0.2500
O1	0.1154	0.0870	0.1424
O2	0.3610	0.2499	0.3180
O3	0.3506	0.0174	0.9952
68-MV-45	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T1	0.5389	0.3460	0.2285
T2	0.5374	0.1610	0.7310
M1	0.2500	0.1578	0.2500
M11	0.2500	0.3470	0.7500
M2	0.2500	0.5512	0.2500
M21	0.2500	0.9505	0.7500
O11	0.3635	0.3372	0.1234
O12	0.3612	0.1756	0.6461
O21	0.6134	0.5085	0.3084
O22	0.6064	0.9976	0.8051
O31	0.6052	0.2655	0.0032
O32	0.5989	0.2393	0.4974
M.1	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T1	0.5394	0.3481	0.2266
T2	0.5372	0.1631	0.7309
M1	0.2500	0.1598	0.2500
M11	0.2500	0.3480	0.7500
M2	0.2500	0.5526	0.2500
M21	0.2500	0.9504	0.7500
O11	0.3634	0.3382	0.1232
O12	0.3621	0.1767	0.6475
O21	0.6138	0.5090	0.3091
O22	0.6063	0.9974	0.8054
O31	0.6057	0.2663	0.0037
O32	0.5981	0.2398	0.4984
GR-P1-25	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T	0.2897	0.0928	0.2292
M1	0	0.9048	0.7500
M2	0	0.3000	0.2500
O1	0.1100	0.0787	0.1314
O2	0.3610	0.2599	0.2980
O3	0.3526	0.0084	0.0052
Jd	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
T	0.2906	0.0934	0.2277
M1	0	0.9040	0.7500
M2	0	0.3009	0.2500
O1	0.1090	0.0763	0.1275
O2	0.3608	0.2630	0.2929
O3	0.3533	0.0070	0.0058

Theoretical calculations

Theoretical calculation of the XANES spectra was carried out at I.N.F.N.–L.N.F., Frascati, Italy, by means of the CONTINUUM computer code developed by C.R. Natoli and his co-workers. This calculation is based on the one-electron multiple-scattering (MS) theory (Lee and Pendry 1975), implemented independently both computationally and theoretically (by considering multiple-scattering paths for the outgoing photoelectrons) by Natoli (cf. Natoli et al. 1990; Wu et al. 1996a,b), and by Durham (Durham et al. 1982; Durham 1988).

Results

Experimental Na K-edge XANES spectra of synthetic jadeite Jd and of two natural jadeites from Guatemala (Kaminaljuyú KY#3 and Manzanal MZ) are given in Fig. 3. Figure 4 reports the spectra of two omphacites from Italy (Biella M.1 and Monviso 68–MV–45), while in Fig. 5 an impure jadeite from Garnet Ridge, Arizona, U.S.A. (GR–P1–25) is shown. The energy and intensity data for the full set are given in Table IV. Neither spectra nor data are presented for diopsides, although they too were measured, because their Na contents (ca. 1 wt%) are too low to allow successful recording.

Fig. 3 – Experimental (dotted) and MS calculated (continuous and dashed lines) XANES spectra at the Na K-edge of Ca–Na clinopyroxenes close in composition to the Jd apex of the triangle of Fig. 1. Individual spectra have been normalized at the high energy side (>1120 eV) after correcting the background. The continuous line spectrum was calculated with the H–L potential and the dashed line spectrum by the X_{α} method. See text for explanations.

Fig. 4 – Experimental and MS calculated XANES spectra at the Na K-edge of Ca-Na pyroxenes of omphacite composition (Fig. 1). Same conditions as Fig. 3; see text for explanations.

Fig. 5 – Experimental and MS calculated XANES spectrum at the K-edge of Na of impure jadeite (Fig. 1). Same conditions as Fig. 3; see text for explanations.

TABLE IV – X-ray absorption energies (eV) of the observed experimental XANES features of Ca-Na clinopyroxenes

<i>Sample</i>	<i>A</i>	<i>A'</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>	<i>G</i>
68-MV-45	1077.1		1081.6	1088.3				1112
M.1	1076.6	1079	1081.8	1088.2			1104	1113
GR-P1-25	1076.7	1079	1081.7	1088.0	*	*	1106	1113
KY#3	1076.8	*	1081.8	1088.0	1093	1097	1106	1113.6
MZ	1076.8		1081.6	1087.7	*	*	1106	1113
Jd	1076.8		1081.9	1088.0	1093	1097	1108	1113

NOTES.

Energy estimated errors are 0.2 eV from A to C and 1 eV onwards.

* peak present but S/N ratio too low to warrant precise measurement.

A first-glance inspection of the spectra permits recognizing that the recorded features divide in two energy regions, as theoretically anticipated by the MS theory (e.g. Benfatto and Natoli 1986):

- (i) a full multiple scattering (FMS) region consisting of a small number of features arising from the contribution of many if not infinite MS paths and extending up to ca. +15 eV above the edge inflection at 1075.5 eV; FMS is directly followed by
- (ii) an intermediate multiple scattering (IMS) region at higher energy up to 1125 eV, where few features occur which arise from a small number of MS paths of lower order.

Because our interpretation regards only the XANES features, the spectra do not extend to the high above-edge energies characteristic of the single scattering (SS) region, where smooth oscillations occur as the result of the photoelectron being backscattered only once against the neighbouring atoms (EXAFS regime), according to the well-established theoretical and experimental framework first developed by Sayers et al. (1971).

Some samples display a very weak pre-edge at ca. 1074 eV, in the form of a hump on the raising slope to the first edge feature A, and this is seen in the natural jadeite from Manzanal MZ. From simple inspection it also turns out that our samples can easily be divided in two groups on the basis of their XANES spectra. The first group comprises synthetic jadeite Jd and the two natural jadeites from Guatemala (Fig. 3); the second one the two natural omphacites from Italy (Fig. 4). The Garnet Ridge impure jadeite (Fig. 5) has characteristics which set it in an intermediate position between the two groups. This group division is best clarified by the relative peak positions (Table IV), which were established by determining the first derivatives.

The three jadeites (Fig. 3) have rather simple spectra comprising three features in the FMS region, at 1076.8 (A), ca. 1081.8 (B), and 1088 (C) eV, respectively; these features are very well reflected in the derivatives (Fig. 6a,b). There is a hint of a feature (A') located inbetween A and B, in the form of a shoulder on the raising slope of edgetop B, which shows up rather well only in the first derivative plot (Fig. 6a). In the IMS region, the jadeite spectra have a significant bump (G) at ca. 1113 eV, which is preceded by very weak, almost imperceptible undulations (D, E and F); however, none of these IMS features shows up when plotting the derivatives (Fig. 6a,b).

Fig. 6 – First (a) and second (b) derivatives of all the experimental XANES spectra at the Na K-edge.

The two ordered omphacites (Fig. 4) have their three main FMS features (A, B, C) in common with jadeites, but they clearly display an additional feature, rather blurred, between the first and second peak. This feature is best seen in the Biella M.1 spectrum, where it stands up as a definite small peak at 1079 eV (A'). Additionally, in omphacites the edgetop B is considerably stronger than it is in jadeites or, alternatively, feature A not only is less distinct, but also much weaker.

The difference between the two groups of spectra may be appreciated best from their first derivative spectra (Fig. 6a): omphacites show a flat, rather noisy plateau at ca. 1079 eV, i.e., just where the jadeites have a pronounced minimum. In the IMS region the omphacite spectra display the same wide bump (G) at ca. 1113 eV already present in the jadeite spectra, and also an appreciable wide bump (F) at ca. 1106 eV, again best to be seen in the Biella spectrum (precisely at 1104 eV). However, once again, nothing shows up in the derivative spectra (Fig. 6a,b).

The Garnet Ridge impure jadeite (Fig. 5) has characteristics in common with both groups; peak A' is distinctly present (Table IV) albeit small, and the B to A intensity ratio is essentially the same as in omphacites; however, the IMS region is as flat as those of jadeites are. Note, nevertheless, that the Garnet Ridge first derivative spectrum has a better structured A feature than any other spectrum (Fig. 6a), while being flat in the same energy region of the second derivative spectrum (Fig. 6b).

Discussion

The general appearance of the experimental Na K-edge spectra is similar to that of the previously recorded Ca K-edge spectra of the same clinopyroxenes (Davoli et al. 1983, 1987); there too the spectrum for the endmember composition (diopside, in that case) appeared to be rather simple, to become progressively more complicated and blurred with increasing substitution of the absorber atom (Ca) by the competing Na atom.

In order to interpret their Ca K-edge experimental spectra, Davoli et al. (1987) made use of the XANES fingerprinting technique. Although fully justified at that time, this practice provoked criticism, lately (Quartieri et al. 1995), on the ground of the present-day possibility of computing XAS spectra from atomic positional data. In fact, Chaboy and Quartieri (1995) and Quartieri et al. (1995), using the same CONTINUUM computer code (Natoli and Benfatto 1986), could compute Ca K-edge spectra for garnets and deduce good agreement with their experimental spectra. However, their criticism on Davoli et al.'s (1987) results proved untenable as soon as Paris et al. (1995) computed the Ca K-edge XANES spectra for clinopyroxenes from the atomic positional parameters by making use of the same code. Paris et al. (1995) demonstrated that the calculated spectra agree quite well with Davoli et al.'s (1987) experimental spectra; thus, they could also endorse Davoli et al.'s (1987) conclusion that Ca in diopside occupies one only type of site, while in omphacite it is distributed over two non-equivalent sites, one having the same geometry as the Ca site in diopside, and the second one that of Na in jadeite (see above).

We shall discuss our experimental findings at the Na K-edge by following the same line of thought as Paris et al. (1995), however improved on account of recent achievements made by our group on olivines and garnets (Wu et al. 1996a,b).

Thus: (i) we have computed the Na K-edge XANES spectra of all our clinopyroxenes starting from their atomic positional parameters as obtained by single crystal XRD refinement (see above); then: (ii) the computed XAS spectra, considered to reflect LRO, are compared with our experimental spectra; finally: (iii) we will try to explain the observed spectral differences under the assumption that, if present and within limits, they are due to SRO phenomena escaping XRD detection, but duly detected by XAS. We deem that in this way we shall get better insight in the omphacite local structure.

Our theoretical spectra were computed stepwise with clusters of increasing size up to convergence (cf. Wu et al. 1996a). Calculation started from a simple cluster consisting only in the absorber plus its first coordination shell (1 Na + 8 O), then it continued by adding farther shells up to the number of atoms (including the absorber) above which addition of other atoms no longer produces significant changes in the output. This procedure already proved to give valid results for olivines (Wu et al. 1996a), in that it not only simulates the spectra satisfactorily, but is also significant from the symmetry viewpoint. In other words: after a certain number of added atoms, the cluster attains the same space group symmetry as the mineral as a whole. By contrast, the very first calculated cluster has the point symmetry of the absorber atom site (2, see above).

The convergent C2/c cluster contains 56 atoms for jadeite, while over 80 atoms are needed for omphacites with P2/n symmetry as well as for the Garnet Ridge impure jadeite. Note, however, that while the given omphacite final calculated spectra are the sum of two independent cluster spectra, one each for the clusters around M2 and M21 which have different positional parameters, the Garnet Ridge spectrum is the result of a computation performed for a single very large cluster.

The theoretical spectra plotted here do show another improvement in our calculation technique with respect to our previous work on olivines (Wu et al. 1996a): they were computed using both the real part of the Hedin and Lundqvist's (1971) energy dependent complex potential (H-L), and Slater's (1979) X_{α} self-consistent potential. We tried in this way to estimate best the scattering conditions of our samples.

Jadeite

For jadeites, the theoretical spectrum (Fig. 3 top), calculated with the H-L potential (Hedin and Lundqvist 1971) compares rather well with the experimental spectra. By contrast, the spectrum calculated with the X_{α} potential shows a number of discrepancies, in the FMS region and in the IMS region as well. In particular, there is a shift between the two spectra which increases with increasing energy, and in the IMS region of the X_{α} plot there is a number of rather strong features not obvious in the experimental spectrum.

The H-L energy scale best fits the experimental data, particularly in the FMS region, but in the IMS all features are smooth as in the experimental spectrum. The reason is that the H-L potential contains a complex imaginary contributing part which gives a more reliable overall result for insulating materials such as our clinopyroxenes. Therefore, we endorse the conclusion reached for garnets at the Ca K-edge by Chaboy and Quartieri (1995).

The major difference between the experimental and calculated spectra of jadeites is in the well-known broadening of all features to be seen in the former ones (Fig. 3). Line broadening conceals the fact that the first and fairly strong edge feature A at 1076.8 eV contains the

contributions of two weak features (at -2 and 0 eV in the calculated spectrum); similarly, edgetop B at 1081.9 eV envelopes at least three theoretical features (at $+2.5$, $+4$, and $+6$ eV).

A careful comparative examination of the three jadeite experimental spectra shows that some of those hidden contributions occasionally show up. E.g., feature A of the Kaminaljuyú KY#3 jadeite spectrum has a detectable shoulder on its high-energy side that we believe to reflect the second calculated feature. Furthermore, every jadeite experimental spectrum displays an asymmetry on the high-energy side of edgetop B which may as well reflect the third calculated contribution to it. These are all features reflecting the state of SRO present in natural samples, and are unlikely to be seen in the synthetic sample, which is chemically stoichiometric and structurally disordered because of the high-temperature of synthesis (1200 °C: Na volatilization) and of the rapid quenching. We have no way of sorting this out, at present.

Thus we believe synthetic jadeite Jd to reflect best the "ideal" Na K-edge spectrum for jadeite and its LRO structural conditions, while the small differences perceived between sample Jd and the two Guatemalan jadeites would reflect the SRO of the latter.

As for feature C, which is present but minor in all jadeite samples, the MZ spectrum is the only one which shows it flat on top even despite the smoothing, thus reflecting the fact that feature C arises from two contributions almost overlapping even in the theoretical spectrum. To our understanding, this behaviour of the MZ spectrum turns out from a peculiar distribution of chemical impurities in this clinopyroxene structure that enhances some particular MS paths while depressing others. Although making themselves visible in the Na K-edge spectrum, those impurities need not to be substituting for Na; actually, they may represent any type of atom, the only constraint being that this atom interferes along the path of the photoelectron emitted by Na during excitation.

So much for the FMS region. When turning to the IMS region, interpretation is best made by making use of the X_{α} plot, as the H-L plot is practically flat (Fig. 3). Both synthetic Jd and the natural Kaminaljuyú KY#3 jadeite have undulations at 1100 – 1120 eV which could only be explained as reflecting features enhanced in the calculation with the X_{α} potential. It is difficult to see them in the Manzanal MZ spectrum.

It appears, therefore, that a particularly cautious study needs to be made when evaluating experimental spectra, and a comparison with calculated spectra is always required in order not to overlook fine features which may contain meaningful information. Work is in progress to better quantify residuals so as to explain the differential features via a physical model; however, we stress the point that, before attempting any treatment of residuals, the pre-requisite of the attainment of a reliable calculated spectrum has to be reached, and this in turn requires a successful solution of such problems as the choice of the muffin tin model and of the potentials.

Fig. 3 gives at the bottom the simulated spectrum of diopside with all its Ca atoms substituted by Na, as the representative of an extreme case of local structure having diopside-like geometry but Na as the absorber atom (i.e., with Na in a 4 – 2 – 2 cluster of oxygens and with Mg as the NNN). This purely theoretical spectrum is different from the Na K-edge spectrum calculated for jadeite (top), both in the number of features and, essentially, in their intensities. However, this spectrum is remarkably similar to the Ca K-edge spectrum simulated by Paris et al. (1995 Fig. 5b) for a diopside having Mg substituted by Al (i.e., with Ca in a 4 – 2 – 2 cluster of oxygens and with Al as NNN).

From the comparison of the two Na K-edge spectra simulated for the two configurations (diopside-like and jadeite-like i.e., 4-2-2 and 6-2), two important indications may be deduced: (i) most differences are in the 1075–1085 eV range, i.e., the range which was already indicated as diagnostic between the jadeite and omphacite spectra; (ii) changing the oxygen configuration around the Na absorber changes the intensity ratio between the first two features A and B, the most prominent ones of the spectra. Subordinately, (iii) the features in the IMS region are being displaced to lower energies.

Omphacite

Omphacite experimental and calculated spectra (Fig. 4) confirm the model already discussed for jadeite, despite the lower symmetry and more complex compositions. Again the calculation based on the H-L potential fits the FMS region of the experimental spectra better than the X_{α} one, both in the energy scale and in the computed features; again the X_{α} potential seems to give better hints on the IMS region better than the H-L one, despite exaggerating the features present there.

The plot based on H-L potentials reproduces well the major feature that discriminates C2/c jadeites from P2/n omphacites, i.e., feature A' at 1079 eV (see above); it also accounts for the substantially increased intensity of feature B with respect to feature A. We interpret this as reflecting the contribution of the 4-2-2 oxygen configuration referred above, i.e., the presence of Na in both the diopside-like and jadeite-like sites M2 and M21 of omphacites.

Our simulations are not as successful for omphacites as they were for jadeites. This is distressing for (as stated above) the omphacite spectra were calculated directly on the basis of the determined atomic positional parameters for each sample (Table III), whereas the jadeite spectrum was calculated from those of two natural samples similar but not identical to ours. The explanation probably lies in our as yet imperfect handling of the primitive space group as well as in the lower quality of our experimental spectra where the signal to noise ratio is substantially lowered because of the lesser number of Na atoms present in the samples (Table I). We came to this conclusion after simulating the Garnet Ridge spectrum, which compares much better with the experimental spectrum than those of omphacites do: in fact, the Garnet Ridge impure jadeite is C2/c and contains almost twice as many Na atoms as our omphacites.

The Garnet Ridge GR-P1-25 theoretical spectrum (Fig. 5) is richer in calculated FMS features than any other spectrum, and compares fairly well with the experimental spectrum, although, as with omphacites, problems are still there when intensities are considered; yet, one can easily distinguish four major features envelopped within the edge, plus the same feature C which is present in all our clinopyroxene spectra. Again, the IMS region is best reproduced when using the X_{α} potential, although this creates abnormally enhanced features. It is tempting to relate features A, A' and B in the experimental spectrum to the calculated features, and explain them as due to two pairs of Na atoms differently distributed in M2 and M21. However, it cannot be so, because the Garnet Ridge impure jadeite, being C2/c, contains only one type of 8-fold coordinated site where both Na and Ca are hosted at random.

The occurrence of such many features can only be explained by considering the structural contributions of different types of next-nearest-neighbour (NNN) environments: in other words, Na would interact at distance with either Ca and Na or Mg and Al, located in M2 and

M1, respectively. This interpretation awaits for quantification, in that it requires deconvolution of the spectrum in a much more detailed way than currently possible, or spectra with higher energy resolution and better signal to noise ratio.

Conclusions

The measured Na K-edge spectra of Ca-Na, jadeite–diopside series clinopyroxenes, and their theoretical calculation permits a number of firm conclusions to be made about the local structure of these important rock-forming minerals.

- (1) Jadeite and omphacite can easily be distinguished by the XAS method: the former, being C2/c and therefore more symmetric than the latter (P2/n), has less features in both the FMS and IMS regions; discrimination between the two species is best accomplished in the FMS region, where jadeite has three well-resolved peaks (A, B, and C; see Fig. 3), and omphacite has a blurred first feature, resulting from the overlap of at least two weak features (A, A'), possibly even three, followed by a comparatively more intense second feature B (edgetop) and a well-resolved third peak C (see Fig. 4).
- (2) Small chemical changes (alternatively, SRO effects) in the jadeites can be detected by the presence of additional very weak shoulders on top of the three mentioned major features of the spectra; when the chemical substitution become significant (as in impure jadeite), it is made recognizable by the reduction of the intensity ratio between the two first features A and B, and by the formation of a small additional feature A' located inbetween them (Fig. 5).
- (3) With further increasing substitution of Na by Ca (i.e., in omphacites), the additional intermediate feature A' increases in intensity to become higher than the first feature A, while the intensity of the second feature (edgetop B) also increases. It is impossible, at the present stage of our investigation, to state precisely whether or how much the changes in the Na K-edge of omphacites only reflect changes in bulk composition, or they are also sensitive to changes in the state of order, from LRO to SRO.
- (4) In omphacites, SRO is likely to be responsible for the weak oscillations occurring in the IMS region of the spectra. Although calculations making use of the X_α potential always result in well-featured IMS regions for all clinopyroxenes, the experimental spectra are too weak in this region to be of any use for jadeite, and become useful only for omphacites. These are the very samples where SRO has been shown to occur and to be strong by crystal structure determination via the single crystal X-ray diffraction technique: in omphacites, the IMS region is always structured although poorly resolved despite of the increased inherent noise.
- (5) Extreme care must be exercised when evaluating the XANES spectra of clinopyroxenes: indeed they are easy to discriminate by the fingerprinting technique, but they are very difficult to probe when the supporting calculations are made. The choice of the muffin tin model and of the appropriate potential is crucial in getting meaningful calculated spectra; in turn this is a pre-requisite to attempting any type of quantification of the observed spectral differences.
- (6) As expected, Na K-edge spectra are mirror images of the already published Ca K-edge spectra (Davoli et al. 1983, 1987); this is also confirmed by the calculated spectra, which

are consistent with those calculated at the Ca K-edge (Paris et al. 1995). Both experimental and theoretical Ca and Na K-edge spectra support the model that Ca and Na in P2/n omphacites do not segregate in either the M2 or the M21 atom site, but distribute over both sites in non-equivalent amounts, where they assume the local configuration dictated by the 4-2-2 vs. 6-2 geometrical distribution of their first-nearest-neighbours oxygens.

Therefore, XANES shows itself to be a very practical method to acquire information on local structure, even in these chemically and structurally complex samples, and in spite of the long-known prejudice against the weak energy involved in Na K-edge spectroscopy. Certainly, Na K-edge spectra are still less resolved than other high-energy spectra such as, e.g., those at the Ca K-edge; yet, they can be deciphered proficiently and interpreted semi-quantitatively, provided the corresponding MS calculated spectra are available for comparison.

Acknowledgements

Crystal-structure refinements were carried out by the late Giuseppe Rossi as a part of a project on alpine omphacites carried out jointly with A.M. that initiated in 1976 and continued till his premature death. Synthetic samples were kindly donated by Profs. M. Bondi, L. Morten and D.C. Rubie. Natural samples are either our own, or from Museo di Mineralogia dell'Università di Roma (MMUR) and U.S. National Museum (USNM) of Washington. Financial support was granted by M.U.R.S.T. under Project "Cristallochimica e Petrogenesi". Experimental work was performed with support from UVSOR, I.M.S., through proposal No. 6-D-567. Furthermore, this work has been supported by the Bayerisches Geoinstitut, Universität Bayreuth, under the E.C. "Human Capital and Mobility - Access to Large Scale Facilities" Program (contract No. ERBCHGECT940053 to D.C. Rubie). Z.W. acknowledges a temporary contract by the Department of Geological Sciences of Università di Roma 3 during which most calculations could be carried out. Discussions and critical remarks by C.R. Natoli and F. Seifert are gratefully acknowledged because they improved significantly the manuscript; all remaining errors are entirely our own. The contributions of two anonymous referees were also beneficial.

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