

An in-situ high temperature study of the phase transition in the system *jadeite* – *augite**

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ABSTRACT: Powder of natural ordered *omphacite* of intermediate composition Jd50% - Aug50% has been heat-treated and studied in-situ with X-Ray diffraction. During heating different degrees of ordering occur until complete disorder is reached and the space group changes from P2/n to C2/c. The transition occurs close to the upper level of the stability field, at temperatures over 1025 °C. The breakdown process involves the formation of *albite*, *nepheline* and a Na-poor *pyroxene* phase.

Key-words: *omphacite*, phase transition, high temperature XRD.

ΠΕΡΙΛΗΨΗ: Δείγμα ομφακίτη με ενδιάμεση σύσταση Ιαδείτης 50% - Διοψίδιος 50% μελετήθηκε με τη μέθοδο διάθλασης ακτίνων X σε λεπτή σκόνη in-situ και σε υψηλές θερμοκρασίες. Κατά τη θέρμανση παρατηρούνται διάφοροι βαθμοί τάξης και βαθμιαία κατάσταση πλήρους αταξίας, με σύγχρονη μεταβολή του κρυσταλλικού συστήματος από P2/n σε C2/c. Η αλλαγή φάσης συμβαίνει κοντά στο ανώτερο όριο του πεδίου σταθερότητας, σε θερμοκρασίες ανώτερες των 1025 °C. Η διαδικασία κατάρρευσης περιλαμβάνει το σχηματισμό αλβίτη, νεφελίνη και φτωχού σε Na πυρόξενου.
Λέξεις-κλειδιά: *omphacite*, ομφακίτη, αλλαγή φάσης, XRD υψηλών θερμοκρασιών.

INTRODUCTION

The name *omphacite* derives from the greek word *omphax* (THEOPHRASTUS, 315 B.C.), which means unripe grapes and describes “a green *clinopyroxene* occurring in eclogites and related rocks” (DEER *et al.*, 1992). *Omphacites* are inosilicates, belong to the *pyroxene* group and have monoclinic symmetry. They are mainly solid solutions of *jadeite* NaAlSi₂O₆ and *diopside* CaMgSi₂O₆. Fe²⁺ is incorporated in the *omphacite* structure as *hedenbergite* component CaFe²⁺Si₂O₆ and Fe³⁺ in the form of *acmite* component NaFe³⁺Si₂O₆. The chemical formula can be expressed as M₂M₁Si₂O₆. The M₂ site contains Ca and Na, the ratio of Na/(Na+Ca) can be between 0.2 and 0.8. M₁ represents octahedrally coordinated cations such as Al, Mg, Fe, the ratio of Al/(Al+Fe³⁺) being greater than 0.5. Substitutions among octahedrally coordinated cations may also include elements such as Mn²⁺, Cr³⁺ and Ti⁴⁺.

The *clinopyroxene* structure is based on single silicate tetrahedra, which form chains that run along the *c* axis. Bonded to them are octahedral M₁ chains. The M₁ site is a relatively undistorted octahedron, but the M₂ site is an irregular polyhedron of 8-fold coordination. The solid solution end members and *omphacites* formed at high temperatures have the space group C2/c. The C2/c structure requires cation disorder within the M₁ as well as within the M₂ sites. The zig zag chains of edge sharing M₁ octahedra run parallel to the crystallographic *c*-axes. The zig zag chains of irregular edge sharing M₂ polyhedra, occupied by larger cations (i.e. Ca²⁺

for diopside, Na¹⁺ for jadeite) run also parallel to the *c* axes and share common edges with the M₁ octahedra.

At lower temperatures there is a tendency for the cations to order within the M₁ and M₂ sites. At sufficiently low temperatures, *omphacite* at intermediate compositions (Na_{0.5}Ca_{0.5}) (Al_{0.5}Mg_{0.5})Si₂O₆ is a cation ordered pyroxene with two distinct M₁ and two M₂ sites, denoted as M₁, M₁₁ and M₂, M₂₁ (labeling after MATSUMOTO *et al.*, 1975). The symmetry is reduced to P2/n (Fig. 1). The tetrahedral chain consists of two crystallographically distinct, but slightly different tetrahedra Si₁ and Si₂, which alternate along the *c* axis (MATSUMOTO *et al.*, 1975). The degree of Mg, Al order on M₁ sites is coupled with the Ca, Na ordering on M₂ sites. The best ordered structure appears to be a compromise solution in which alternate M₁ sites are occupied by Mg and Al, while alternate M₂ sites are statistically occupied by ¼Na, ¾Ca, and ¾Na, ¼Ca (FLEET *et al.*, 1978; ROSSI *et al.*, 1983).

Omphacites are very important in petrology because of their occurrence in rocks metamorphosed under high pressure conditions e.g. eclogite. It is also found in alkaline rocks, e.g. nephelinite (PATI *et al.*, 2000). They have a wide thermobaric range of stability. This study presents an in situ high temperature investigation of the phase transition in *omphacite* that will help reveal the changes occurring in *omphacite*-bearing rocks under low pressure - high temperature conditions. Regarding to the *omphacite* decomposition, according to MYSEN & GRIFFIN (1973) the degree of breakdown and the composition of the breakdown products largely depend on

In-situ μελέτη της μεταβολής φάσης στο σύστημα Ιαδείτης - Αυγίτης σε υψηλές θερμοκρασίες

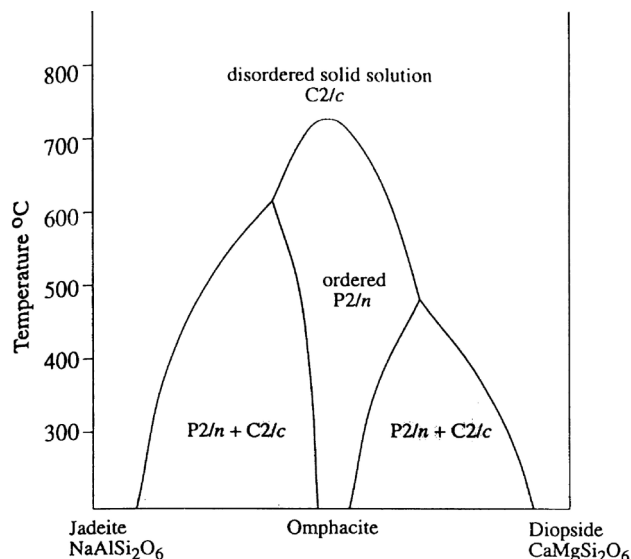


Fig. 1. Schematic phase diagram of omphacite (after CARPENTER, 1980).

the P-T history of the rock. Breakdown occurs during retrograde metamorphism as well as with increasing T, the later case is studied here. KUSHIRO (1969) suggests that an *omphacite* which is uplifted and cooled along a P-T gradient less than about 20 bars/degree could retain its jadeite in solution, while heating would result in instability and consequent exsolution of *jadeite*. Stoichiometry is maintained during *jadeite* exsolution by oxidation of Fe^{2+} to Fe^{3+} (MYSEN & GRIFFIN, 1973).

EXPERIMENTAL

The material used for this study is a well characterized, ordered omphacite from the island of Syros, Greece. Its structure and chemical formula has been described in KATERINOPOULOU *et al.* (2007). The space group was found to be P2/n and the unit cell constants were calculated as: $a=9.5794(7)$ Å, $b=8.7747(5)$ Å, $c=5.2561(3)$ Å and $\beta=106.892(1)^\circ$. Its chemical formula is: $(\text{Ca}_{0.490} \text{Na}_{0.525}) (\text{Al}_{0.434} \text{Ti}_{0.002} \text{Fe}^{3+}_{0.107} \text{Fe}^{2+}_{0.024} \text{Mn}_{0.005} \text{Mg}_{0.424}) (\text{Si}_{1.989} \text{Al}_{0.011})$, end member composition: $\text{Jd}_{42} \text{Ae}_{11} \text{Q}_{47}$.

Pure *omphacite* was carefully handpicked from a fraction of 0.317mm of the crushed rock. It was then powdered under ethanol to avoid preferred orientation and qualitatively checked for purity with X-Ray diffraction.

The step scan X-ray powder diffraction measurements at high temperatures were carried out on a $\Theta - \Theta$ Philips X'Pert diffractometer system, equipped with a PAAR HTK - 16 high temperature chamber and operated with a Cu X-Ray tube. The temperature range was 25 °C - 1150 °C. The powdered samples were applied on the Pt-band and measured with a fixed divergence slit of 0.5°, receiving slit of 0.3 mm width, soller slit 0.04 rad, antiscatter slit 0.5°, generator power at 40 kV and 50 mA.

The powder was first heated in air in a closed system, up to a temperature of 1100 °C, while a diffraction pattern was taken every 50 °C. The sample was then tempered with a cooling rate of -1 °C/min and an XRD pattern was taken after cooling down at 25 °C. To avoid oxidation of iron, another experiment was performed under Argon flow (1 lt/min), after the chamber had been twice evacuated.

The produced XRD patterns were treated with the RIETVELD method, using the software TOPAS 2.0 (CHEARY & COELHO, 1992). The background was fitted with a 4th order Chebychev polynomial and the Fundamental Parameters Approach (FPD) was used for the profile fitting. The indexing of all the XRD patterns was made with the program TOPAS. Each pattern was refined separately assuming the P2/n symmetry (PAVESE *et al.*, 2000). Unit cell constants were first determined with least square methods (software Unitcell, HOLLAND & REDFERN, 1997), for the room temperature measurement. These were then used as starting values subsequently for each pattern at higher temperatures with the software TOPAS.

RESULTS

In Fig. 2 the XRD pattern of Syros *omphacite* at room temperature before heating is shown. Reflections with $h+k=2n+1$ such as 031, 320 and 230 appear only in the ordered P2/n phase. The strongest reflections of this type are shown with arrows, although they strongly overlap. From 25 °C to 850 °C a small but continuous shift of all the reflections to lower 2θ values is observed, caused by lattice expansions. Former studies report phase transition temperatures for *omphacite* of 750 °C (FLEET *et al.*, 1978) and 850 °C (CARPENTER *et al.*, 1990). However, no change in the relative intensities of the peaks is observed here for the Syros *omphacite*. The patterns up to 850 °C remain nearly unchanged. From 875 °C to 950 °C the intensity of some peaks increases with increasing temperature, without any shape change. The intensity of the strongest *omphacite* peak $\bar{2}21$ is suddenly reduced from 875 °C to 900 °C, it increases again at 925 °C and reaches its former intensity value at 950 °C (Fig. 3). With increasing temperature from 925 °C to 1000 °C the intensities of the peaks in the region $2\theta = 35 - 37^\circ$ are starting to change. The relative intensities of the peaks now indicate that the $h+k=2n+1$ peaks i.e. 031, 320, 230 have partly disappeared or decreased in intensity (Fig. 4). At 1050 °C the XRD pattern changes and can now be attributed to *albite*, *nepheline* and Fe-bearing *diopside* (Fig. 5). At 1100 °C more peaks are absent and after cooling down to 25 °C the pattern can be evaluated as Fe-bearing *diopside* plus *albite*. The lost lines have not reappeared and the intensity is generally lower than in the original pattern of the untreated sample.

The peak caused by superimposing of hkl 631 and 352, originally occurs at $2\theta = 77.76^\circ$ and it shows the largest shift to lower 2θ values with increasing temperature. It becomes very broad at about 850 °C (Fig. 6). The lattice parameters are shown in Fig. 7 together with literature data from PAVESE

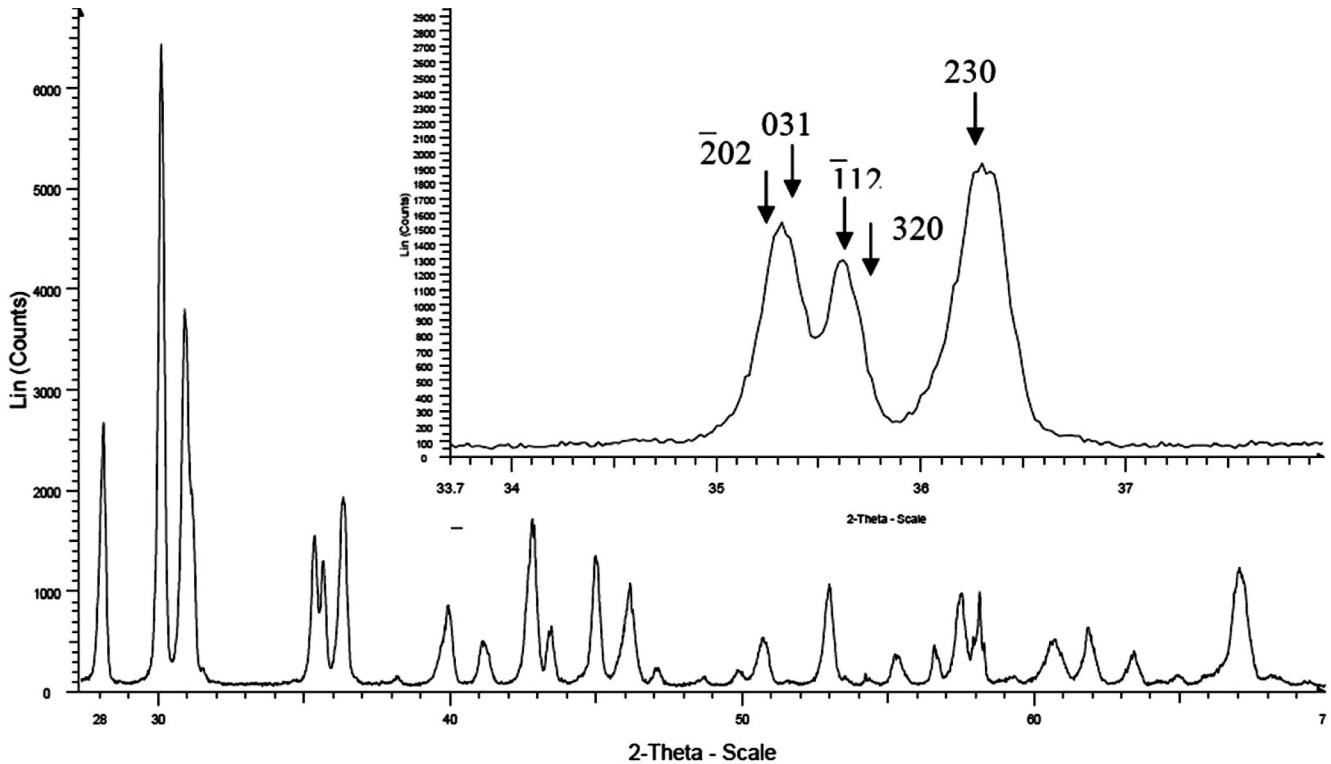


Fig. 2. XRD pattern of ordered *omphacite* at room temperature.

et al. (2000).

The temperature region where the main changes are occurring was further investigated with experiments under Argon, to avoid oxidation. Patterns were taken from 800 °C and every 25 °C up to a temperature of 1150 °C. Then a slow cooling rate was applied until 800 °C, where the temperature was held constant. At this temperature Further XRD patterns were taken after 1, 2 and 26 hours. There was no change observed in these last XRD patterns.

The strongest omphacite peak $\bar{2}21$ is again reduced from 800 °C to 900 °C and increases again at 950 °C. The decomposition can be observed at 1025 °C. The reverse procedure is impossible to monitor, as the peaks of Na-rich phases *albite* and *nepheline* gradually disappear with increasing temperature (Fig. 8). This effect is attributed to Na-evaporation. Cooling under argon was performed between 1100 °C and 800 °C with a step width of 25 °C. The XRD patterns show practically no differences. The final pattern at room temperature (25 °C) after treatment can be evaluated as Fe-bearing diopside.

Heating rapidly (2 °C/min) rather than gradually (1 °C/min) at 1000 °C has an effect on the XRD pattern. Some peaks disappear or change shape when a slower heating rate is applied. The omphacite breakdown is time dependent (kinetic's effect) and the shape of the pattern depends on the heating rate but cooling has practically no effect, as Na phases evaporate rapidly.

DISCUSSION

The in situ high temperature XRD patterns monitor the cation disordering in *omphacite*. The change of the pattern suggests that a phase transition occurs. Systematic absence of reflections of the type $h+k = 2n+1$, such as 031, 320, 230 at $2\theta = 35 - 37^\circ$ (Fig. 1) indicate that the cation distribution changes in the structure, causing a change in the space group from

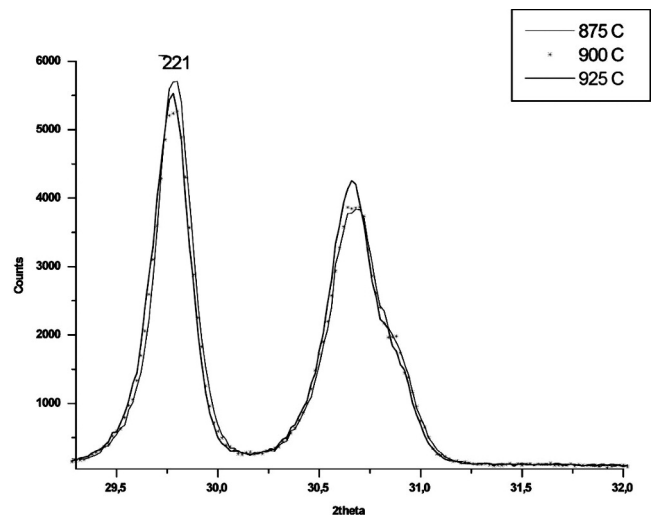


Fig. 3. The change in intensity of the strongest *omphacite* peak $\bar{2}21$ around 900 °C is shown. Patterns at 875 °C in black thin line, at 900 °C in stars and at 925 °C in grey line.

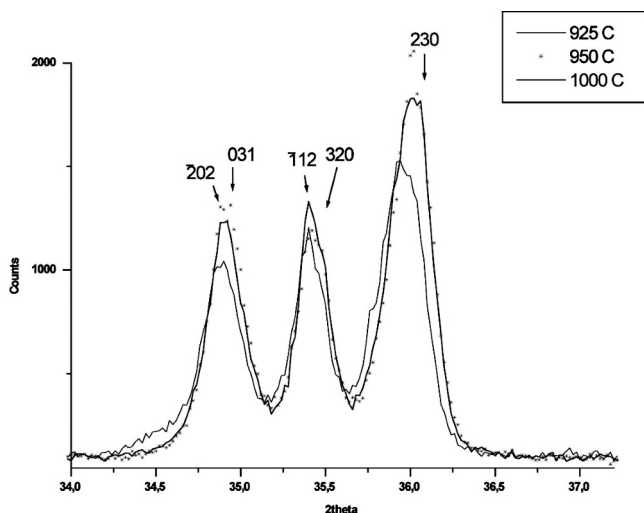


Fig. 4. Change in intensity of the superlattice peaks. Patterns at 925°C (black thin line) 950 °C (stars) 1000 °C (grey line).

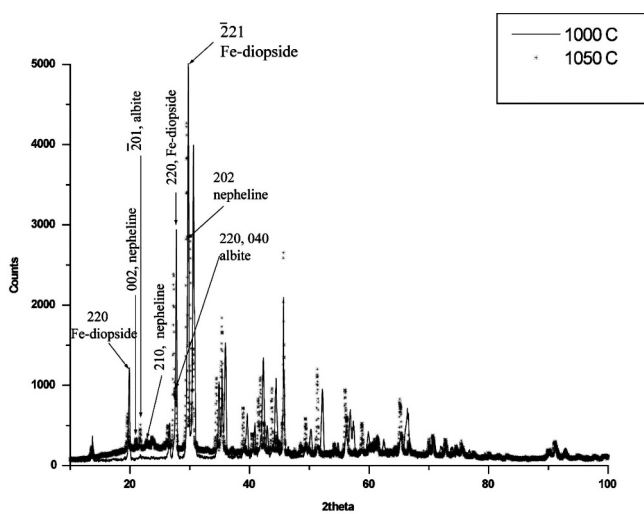


Fig. 5. At 1050 °C the XRD pattern is totally different. Patterns at 1000 °C (line), 1050 °C (stars).

P2/n to C2/c. *Omphacite* with the space group C2/c has generally a lower monoclinic angle than the ordered space group P2/n. From 700 °C the monoclinic angle β decreases with temperature and all lattice parameters, with the exception of c show a discontinuity from linearity (Fig. 7). The anomalous behaviour of the lattice parameter c shows that the parameter is not very sensitive to structural changes caused by order – disorder processes. A second discontinuity appears above 1000 °C, where the breakdown of *omphacite* begins. The Lorenzian profile of the peak indexed 631, 352 (Fig. 6) shows similar behaviour. The behaviour of the patterns indicates that disordering occurs continuously over a range of temperatures, from 700 °C – 1000 °C. Slow diffusion of cations with temperature creates intermediate, metastable states of disordering until the *omphacite* finally breaks down to *diopside*,

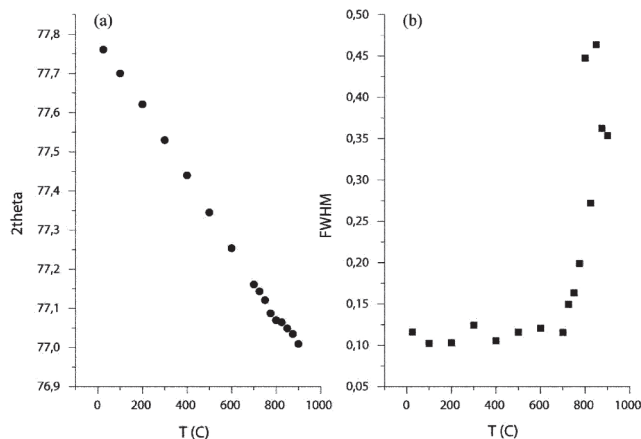
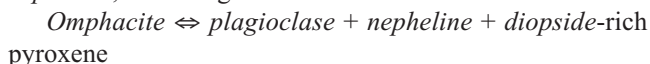


Fig. 6. (a) 2theta shift of the hkl 631 and (b) Lorenzian full width at half maximum (FWHM) of 631 as a function of temperature. Symbols are larger than esd's.

albite and *nepheline*. These experimental results show that the order-disorder transformation is not an abrupt transformation, as suggested by FLEET *et al.* (1978), instead it occurs through a procedure of successive gradual transformations. Similar behaviour of lattice parameters in Lambda transitions is observed in other silicates (GHAZI-BAYAT *et al.*, 1993).

Omphacite breakdown at ambient pressure occurs at 1025 °C as indicated by the results of these experiments. This temperature is somewhat lower than the one occurring from the subsolidus curve proposed by GASPARIK (1984) for iron-free *omphacite*. The breakdown products are *diopside*, *albite* and *nepheline*, according to the reaction:



Omphacite is a solid solution of *jadeite* and *diopside*. Phase equilibria of Di-Jd pyroxenes at high temperatures were experimentally studied by ROBERTSON *et al.* (1957) and BELL & CALB (1969), who showed that the jadeitic component breaks down with increasing temperature to *albite* and *nepheline*. Coexistence of *clinopyroxene* with *nepheline* and *plagioclase* occurs in low P and high T conditions of formation. This seems not to be the case on Syros Island, as this paragenesis is not observed on the studied metagabbros, but this mineral association of coexisting *nepheline*, *albite* and Na-poor *pyroxene* in rocks could be used as indicative of low-P and high-T conditions.

At rising temperatures, the intensity decrease in the strongest *omphacite* peak $\bar{2}21$ around 900 °C is an indication of the space group change (Fig. 3). At higher temperatures the hkl planes become well defined, peaks appear sharper and the intensity of the corresponding reflection increases again. This effect has been consistently observed in two independent experiments (with and without Argon in the chamber). The shape and intensity of XRD peaks is directly related to the crystallinity and the crystal size. During heating the diffusion and rearrangement of the ions caused the peaks to be less well defined. It is safe to assume that defects

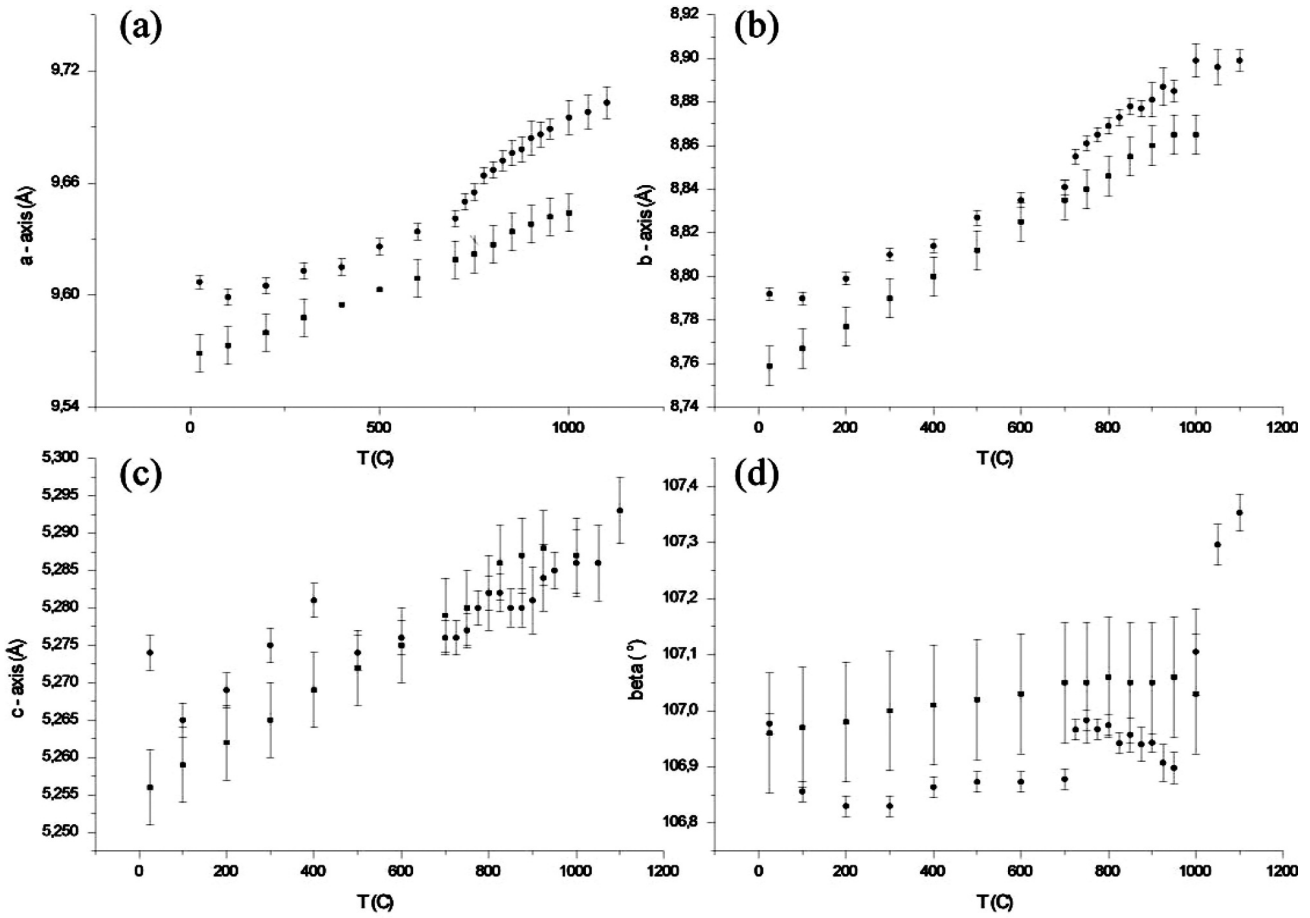


Fig. 7. Lattice parameters as a function of temperature (a) a lattice parameter (b) b lattice parameter (c) c lattice parameter (d) monoclinic angle β . Circles: lattice parameters of this study. Squares: literature data of PAVESE *et al.* (2000).

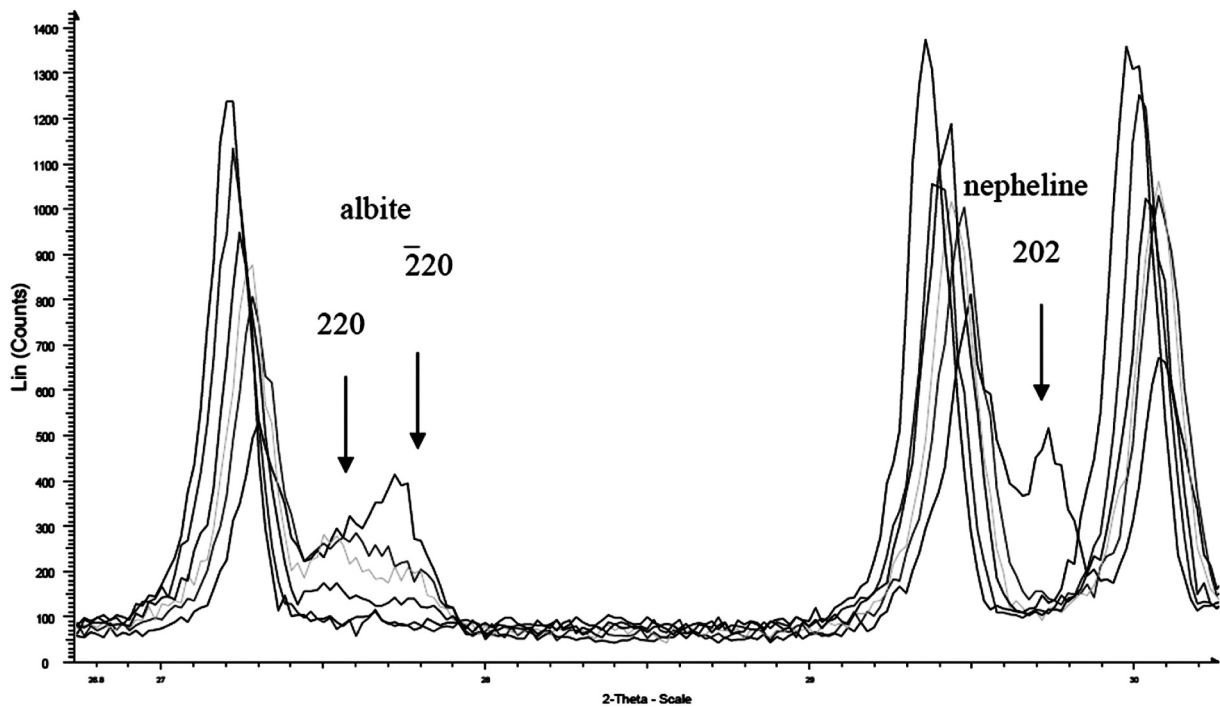


Fig. 8. XRD patterns from 1025 °C (highest intensity) to 1150 °C (lowest intensity). The 202 *nepheline* peak and the 220, $\bar{2}20$ *albite* peaks gradually decrease in intensity until they fully disappear.

have appeared in the lattice of the treated sample during the transition and the final product of heating is a material not as well crystallized as the starting phase, thus giving broader peaks with less intensity. Under the heating conditions applied, disordering preceded breakdown and occurred over a range of temperature in a series of steps, following the Oswald step rule, which predicts the sequence of transition through metastable phases to an equilibrium phase (CARPENTER, 1978). Different degrees of order are achieved during heating. Complete disorder required for the space group C2/c is reached at a stage near the upper limit of the stability field of omphacite at ambient pressures (~1025 °C). At these high temperatures the fastest transformation path that reduces the free energy is the formation of a Na-poor pyroxene phase.

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