

Article

Structural Breakdown of Natural Epidote and Clinozoisite in High-T and Low-P Conditions and Characterization of Its Products

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Abstract: A heat treatment was performed on selected epidote and clinozoisite crystals to establish the nature of any changes in the optical and crystal-chemical properties and to identify a breakdown product using a wide spectrum of analytical methods. Natural samples were heated from 900 to 1200 °C under atmospheric pressure in ambient oxidation conditions for 12 h. Epidote and clinozoisite were stable at 900 °C; those heated at 1000 °C, 1100 °C, and 1200 °C exhibited signs of breakdown, with the development of cracks and fissures. The average chemical composition of epidote is $\text{Ca}_{2.000}\text{Al}_{2.211}\text{Fe}_{0.742}\text{Si}_{2.994}\text{O}_{12}(\text{OH})$, while that of clinozoisite is $\text{Ca}_{2.017}\text{Al}_{2.626}\text{Fe}_{0.319}\text{Si}_{3.002}\text{O}_{12}(\text{OH})$. The breakdown products identified by electron microanalysis, powder X-ray diffraction, Raman spectroscopy, and high-resolution transmission electron microscopy were anorthite, pyroxene compositionally close to esseneite, and wollastonite. The decomposition of the epidote-clinozoisite solid solution is controlled by the following reaction: 4 epidote/clinozoisite $\rightarrow$ 2 pyroxene + 2 wollastonite + 4 anorthite + 2 H₂O. Pyroxene likely contains a significant proportion of tetrahedral Fe³⁺ as documented by the Mössbauer spectroscopy. Moreover, the presence of hematite in the Mössbauer spectrum of the clinozoisite sample heated at 1200 °C can result from the following reaction: 4 epidote $\rightarrow$ pyroxene + 3 wollastonite + 4 anorthite + hematite + 2 H₂O.

Keywords: epidote; clinozoisite; heat treatment; structure breakdown; esseneite



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1. Introduction

Epidote and clinozoisite are monoclinic sorosilicate minerals belonging to the epidote supergroup; their formulae can be written as $^{\text{A1}}\text{Ca}^{\text{A2}}\text{Ca}^{\text{M1}}\text{Al}^{\text{M2}}\text{Al}^{\text{M3}}\text{Fe}^{3+}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$ and $^{\text{A1}}\text{Ca}^{\text{A2}}\text{Ca}^{\text{M1}}\text{Al}^{\text{M2}}\text{Al}^{\text{M3}}\text{Al}(\text{Si}_2\text{O}_7)(\text{SiO}_4)\text{O}(\text{OH})$, respectively [1]. The A(1) and A(2) sites with a coordination number (CN) >6 are mainly occupied by Ca, while M(1), M(2), and M(3) sites with CN = 6 primarily contain Al and Fe³⁺ [2]. The crystal structure of epidote is complex and consists of single silicate tetrahedra SiO₄ and double silicate tetrahedra Si₂O₇, as well as continuous chains of AlO₆ and AlO₄(OH)₂ octahedra running parallel to the *b* axis [3]. Several studies showed that Fe³⁺ preferentially occupies the M3 site [2–4], and that the amount of Fe³⁺ at the M1 and M2 sites is not very extensive [5].

The crystal structure and crystal chemistry of epidote-clinozoisite series at room or low temperature have been investigated extensively using several analytical methods

and theoretical models [2–23]. However, not many studies have been devoted to high-temperature (HT) epidote-clinozoisite behavior during in situ HT experiments, despite the importance of these minerals in the field of metamorphic and/or magmatic petrology [4]. A single-crystal diffraction study in situ HT was only performed on Sr-piemontite [24]. This X-ray diffraction study was not sufficient to monitor the T-induced disordering phenomenon in epidote [24]. A unit-cell thermal expansion of clinozoisite at high temperature [25] and a unit-cell compression of epidote at high pressure [26] were described. A low-T experiment was performed on epidote with a composition of $(\text{Ca}_{1.98}\text{Mn}_{0.02})(\text{Fe}_{0.81}\text{Al}_{2.19})\text{Si}_3\text{O}_{12}(\text{OH})$ with a neutron structure refinement at 15 K [12]. In addition, an examination of OH stretching modes and their pleochroic scheme was performed using single-crystal polarized infrared (FTIR) spectroscopy at room T [2].

Epidote supergroup minerals have a wide range of stability. Epidotes are, however, stable over a wide range of pressure and temperature conditions in continental and oceanic crust [27,28]. They were found in shallow geothermal fields at a few hundred meters of depth, suggesting a pressure of much less than 0.1 GPa and a temperature below 200 °C [29]. Commonly, epidote breaks down in the range of 600 to 700 °C, but incorporation of REE can stabilize it [3]. Allanite may occur in a variety of igneous rocks with high crystallization temperature and has been reported at 1050 °C, 3 to 4.5 GPa [30]. An increasing number of experimental studies have revealed that the epidote-supergroup minerals have huge stability fields which extend to 7 GPa pressure and to more than 1200 °C temperature [27]. The stability of epidote is controlled by pressure, temperature, the Al/Fe³⁺ ratio, oxygen fugacity, and fluid composition [7,23,31].

A few experimental studies on epidote stability have been published. The effects of temperature on the crystal structure of epidote at 293 and 1070 K (~20 °C, ~797 °C) [4], the behavior of epidote at high pressure (10 GPa) and high temperature (1200 K; ~927 °C) [28], and the impact of low temperature on epidote structure [2] were studied. Powder X-ray diffraction data at 1070 K showed epidote stability within the temperature range, and crystallinity was maintained [4]. The thermal stability of epidote up to 1070 K was observed in this study; the absence of dehydration and/or nonconvergent ordering of Al and Fe³⁺ between different octahedral sites and/or convergent ordering on M3 were likely due to the slow kinetics of the aforementioned processes [4]. The instability of epidote was defined at T > 1200 K with breakdown products including anorthite and hedenbergitic pyroxene with no corundum or hematite found; the breakdown reaction was as follows: epidote → anorthite + pyroxene ± Al₂O₃ ± Fe₂O₃ + H₂O [2]. The pressure plays an important role in epidote stability; the breakdown is more rapid with increasing pressure.

This experimental study was focused on the breakdown reactions and products of epidote-clinozoisite series after heating at temperatures on the upper edge of their stability at various pressures under variable experimental conditions. The natural samples were selected, in contrast to previous works mostly done on synthetic samples, to describe the possible effects of chemical inhomogeneity and diffusion on the mineral breakdown. Firstly, the influence of variable Fe/Al ratio on low-P experiment products was determined. After the experiments, several analytical methods were applied to study structural changes and phase transitions including the nanoscale identification of breakdown products by high-resolution transmission electron microscopy (HRTEM).

2. Materials and Methods

Optically and chemically very homogeneous single crystals were selected for experiments. Crystals of natural dark-green epidote were collected from Pfarrerb near the Sobotín metabasite massif in the southern part of Hrubý Jeseník Mountains, Czech Republic (ES). Natural brownish green clinozoisite crystals were from Alchuri, Shigar Valley, Skardu district, Baluchistan, Pakistan (CP).

Samples were divided into several groups required for different heating procedures. One sample from each group was not heat-treated and was used as a standard (marked as 0), while other samples were treated (labeled according to temperature). Both sets of

samples were heated in a muffle furnace in an air atmosphere for 12 h. Samples were subsequently cooled to ambient temperature for 12 h. A list of samples is provided in Table 1.

Table 1. List of the studied samples.

Temperature	Epidote, Czech Republic (Sobotín)	Clinzoisite, Pakistan (Baluchistan)
25 °C	ES-0	CP-0
900 °C	ES-9	CP-9
1000 °C	ES-10	CP-10
1100 °C	ES-11	CP-11
1200 °C	ES-12	CP-12

Chemical analysis was performed with the Cameca SX100 electron microprobe (Cameca company, part of Ametek group, Gennevilliers Cedex, France) operated in wavelength-dispersion mode at the Masaryk University, Brno, Czech Republic, under the following conditions: accelerating voltage 15 kV, beam current 20 nA, and beam diameter 5 μm . The samples were analyzed with the following standards: wollastonite ($\text{SiK}\alpha$, $\text{CaK}\alpha$), TiO_2 ($\text{TiK}\alpha$), Al_2O_3 ($\text{AlK}\alpha$), pure Cr ($\text{CrK}\alpha$), fayalite ($\text{FeK}\alpha$), rhodonite ($\text{MnK}\alpha$), MgO ($\text{Mg K}\alpha$), pure Ni ($\text{NiK}\alpha$), albite ($\text{NaK}\alpha$), orthoclase ($\text{KK}\alpha$), $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$ glass ($\text{RbL}\alpha$), pollucite ($\text{CsL}\alpha$), barite ($\text{BaL}\alpha$), SrTiO_3 ($\text{SrL}\alpha$), BaF_2 ($\text{FK}\alpha$), and NaCl ($\text{ClK}\alpha$). Detection limits of the measured elements varied between 0.01 and 0.05 wt.% with Ba, F, and Cl always below the detection limit. Peak counting times were 10 to 40 s during measurements depending on the expected concentration of the element in the mineral phase. Major elements were measured using shorter times, whereas longer times were applied for elements with a low concentration. The chemical formula of epidote-super group minerals was calculated on the basis of $\sum (\text{A} + \text{M} + \text{T}) = 8$ cations with the procedure following epidote-super group nomenclature [1].

Powder X-ray diffraction analyses were determined using a BRUKER D8 Advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) at the Laboratory of X-ray diffraction SOLIPHA (Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava, Slovakia) under the following conditions: Bragg-Brentano geometry (Theta-2Theta), Cu anticathode ($\text{K}\alpha_1 = 1.5406 \text{ \AA}$), accelerating voltage 40 kV, and beam current 40 mA. Ni $\text{K}\beta$ filters were used for stripping $\text{K}\beta$ radiation, and data were obtained using the BRUKER LynxEye detector. The step size was $0.01^\circ 2\theta$, the counting time was 3 s per step, and measurements ranged from 2° to $65^\circ 2\theta$. Analyzed scans were fitted, and lattice parameters were refined with BRUKER DIFFRACplus TOPAS software using the structural models for appropriate mineral phases—anorthite [32], pyroxene esseneite [33], and wollastonite [34].

The ^{57}Fe Mössbauer spectra were obtained at room temperature (298 K) using a standard constant acceleration spectrometer with a $^{57}\text{Co}/\text{Rh}$ radioactive source. Calibration of the apparatus was performed by a 12.5 μm foil of metallic α -Fe and a commercial (Amersham) calibration pellet of sodium nitroprusside (surface density $\sim 5 \text{ mg Fe}/\text{cm}^2$) for high- ($\pm 10.5 \text{ mm/s}$) and low-velocity ($\pm 4.5 \text{ mm/s}$) regions, respectively. However, all isomer shifts herein are quoted with respect to the room-temperature Mössbauer spectrum of α -Fe. Errors in determination of particular spectral components including relative area, isomer shift (IS), quadrupole splitting (QS) (and/or quadrupole shift), line width (Γ), and hyperfine magnetic field (B_{hf}) were estimated to be $\pm 1\%$, $\pm 0.02 \text{ mm/s}$, $\pm 0.03 \text{ mm/s}$, $\pm 0.03 \text{ mm/s}$, and $\pm 0.3 \text{ T}$, respectively (Institute of Nuclear and Physical Engineering, Faculty of Electrical Engineering and Information Technology, The Slovak University of Technology, Bratislava).

Raman spectra of low-P-treated epidote and clinozoisite were acquired on a LabRAM HR Evolution (Horiba, Jobin Yvon, Palaiseau, France) Raman spectrometer system with a Peltier-cooled CCD detector and Olympus BX-41 microscope (Masaryk University, Department of Geological Sciences, Brno, Czech Republic). The Raman spectra were excited by a 532 nm (diode) laser and collected in the range between 100 cm^{-1} and 4000 cm^{-1} with a

resolution of 2 cm^{-1} . Multiple spot analyses on different areas of epidote produced similar spectra and confirmed the spectral reproducibility. No surface damage was observed after the laser illumination of the measurement. The acquired Raman spectra were processed using the Peakfit (Systat software, Inc., San Jose, CA, USA) software package. Band fitting was done using the Lorentz function with variable width; the fitting was gradually refined until it produced reproducible results with a square regression coefficient greater than 0.995.

High-resolution transmission electron microscopy (HRTEM) characterization was performed on a Jeol JEM ARM 200cF (JEOL Ltd., Akishima, Tokyo, Japan) analytical transmission electron microscope (TEM) operated at 200 kV that was equipped with a JEOL JED 2300 SDD detector for X-ray energy-dispersive spectroscopy (EDS) microanalysis (Center STU for Nanodiagnostic, The Slovak University of Technology, Bratislava, Slovakia). EDS microanalysis was used to study breakdown products and to distinguish between individual phases. Samples for TEM examination were prepared using a standard technique, which involved mechanical grinding of parent material followed by making a suspension of produced powders and ethanol, before undergoing sonication for 10 min. A drop of suspension was then deposited on a carbon-coated TEM Cu-grid. After drying in the air, the samples were examined by TEM.

3. Results

Both ES and CP samples displayed only weak chemical zoning in backscattered electron (BSE) images with small variations in Al and Fe^{3+} content (Figures 1 and 2) and the average chemical composition listed in Table 2. The main difference between samples was in their Fe/Al ratio. Epidote from Sobotín was $\text{M}^{3+}\text{Fe}^{3+}$ -dominant (0.68–0.80 apfu), while clinozoisite samples had Fe^{3+} in the range 0.29–0.33 apfu (Table 2, Figure 3). The content of other cations including Ca, Mg, Ti, V, and Cr was very low or below the detection limit in both types of samples.

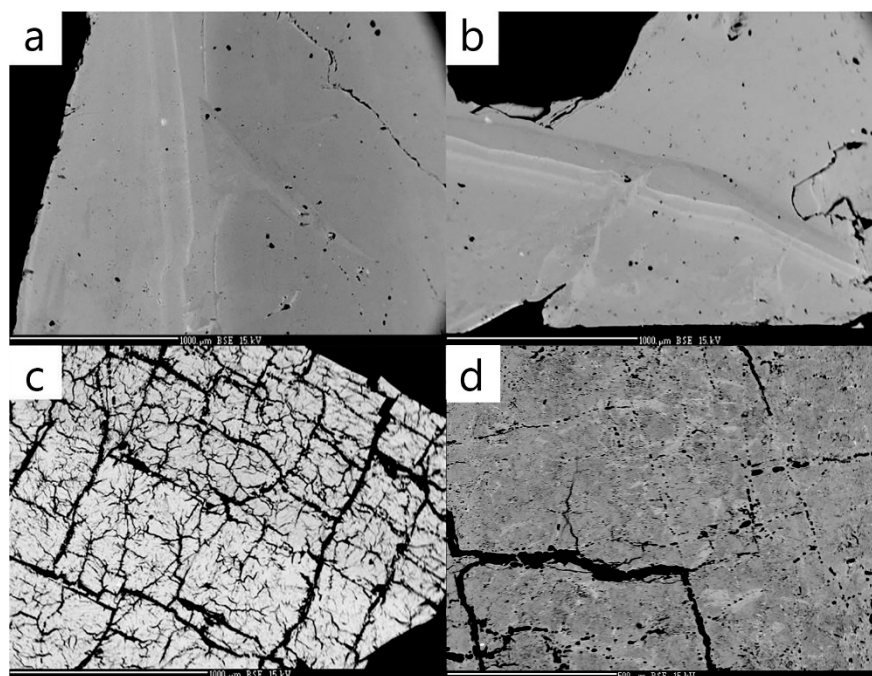


Figure 1. BSE images of heat-treated epidote: (a) ES-0; (b) ES-9; (c) ES-10; (d) ES-11. The untreated natural sample (a) and sample treated at $900\text{ }^{\circ}\text{C}$ (b) displayed only the weak chemical zoning caused by small variations in Al and Fe^{3+} content; samples heated over $1000\text{ }^{\circ}\text{C}$ formed breakdown products firstly as a homogeneous mass (c), while those heated at $1100\text{ }^{\circ}\text{C}$ formed domains with a slightly different composition (d).

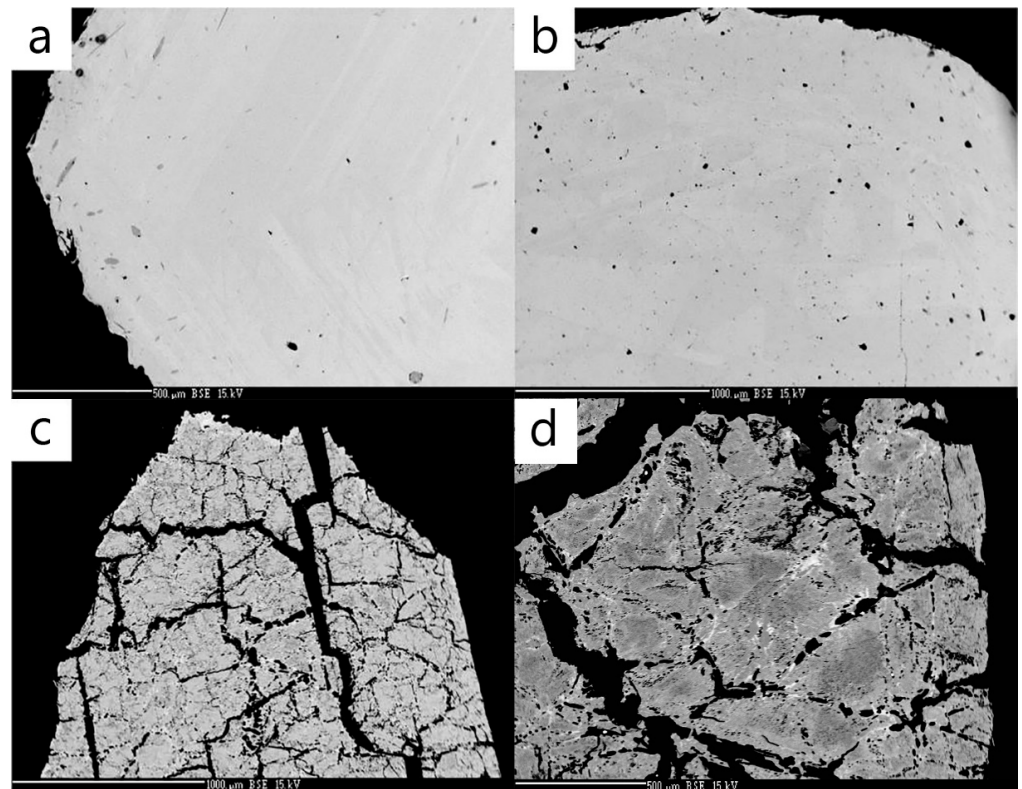


Figure 2. BSE images of heat-treated clinozoisite: (a) CP-0; (b) CP-9; (c) CP-10; (d) CP-11. The untreated natural sample (a) and sample treated at 900 °C (b) displayed only the weak chemical zoning caused by small variations in Al and Fe^{3+} content; as in previous samples, heating over 1000 °C led to the formation of breakdown products firstly as a homogeneous mass (c), whereas, at 1100 °C, domains with slightly different composition were formed (d).

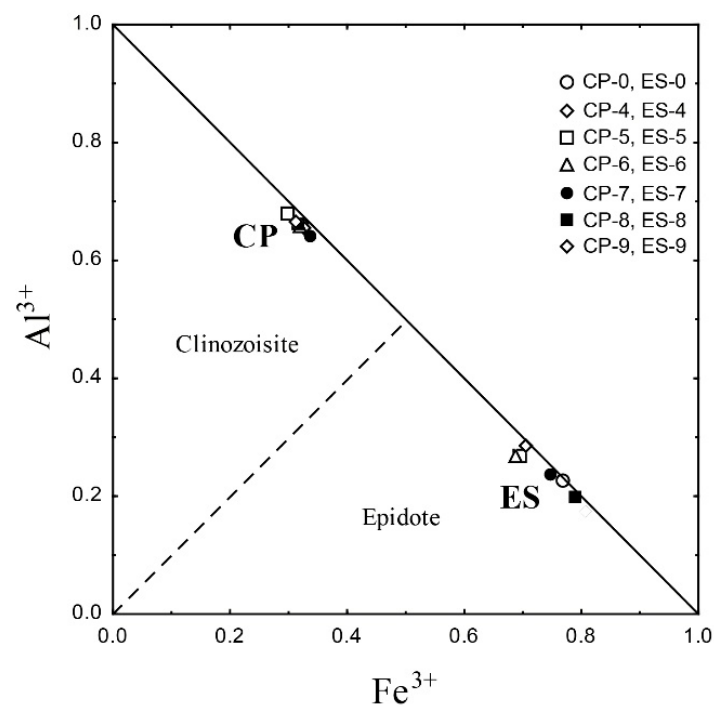


Figure 3. Diagram of Al- Fe^{3+} substitution in studied samples. Epidote was M^3Fe^{3+} -dominant in contrast to Al-dominant clinozoisite samples, as documented by the different positions of ES and CP analyses in the diagram.

Table 2. Electron microprobe analyses (in wt.% of oxides and apfu of cations) of epidote (ES) and clinozoisite (CP).

	ES	ES	ES	ES	CP	CP	CP
P ₂ O ₅	0.00	0.00	0.00	0.04	0.07	0.04	0.02
SiO ₂	37.10	38.23	38.08	37.94	38.75	38.93	38.97
TiO ₂	0.01	0.07	0.06	0.16	0.14	0.16	0.08
Al ₂ O ₃	21.96	25.14	25.54	25.11	29.20	29.37	29.41
V ₂ O ₃	0.00	0.09	0.05	0.04	0.03	0.08	0.09
Cr ₂ O ₃	0.00	0.02	0.00	0.01	0.05	0.08	0.07
Fe ₂ O ₃	15.01	11.42	10.40	10.67	5.43	5.64	5.17
MnO	0.01	0.02	0.05	0.04	0.05	0.01	0.03
MgO	0.02	0.00	0.01	0.02	0.10	0.08	0.07
NiO	0.01	0.00	0.05	0.00	0.00	0.01	0.03
CaO	24.16	23.86	23.99	23.97	24.29	24.36	24.52
Na ₂ O	0.02	0.00	0.01	0.00	0.05	0.00	0.02
K ₂ O	0.00	0.00	0.00	0.01	0.00	0.02	0.02
H ₂ O *	1.88	1.91	1.91	1.90	1.95	1.95	1.95
Total	100.17	100.74	100.14	99.86	100.10	100.71	100.47
Si ⁴⁺	2.961	2.995	2.990	2.994	2.989	2.986	2.990
P ⁵⁺	0.000	0.000	0.000	0.002	0.005	0.002	0.001
Al ³⁺	0.039	0.005	0.010	0.003	0.007	0.012	0.009
T	3.000	3.000	3.000	3.000	3.000	3.000	3.000
Al ³⁺	1.000	1.000	1.000	1.000	1.000	1.000	1.000
M2	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Mg ²⁺	0.002	0.000	0.001	0.003	0.012	0.009	0.008
Ni ²⁺	0.000	0.000	0.003	0.000	0.000	0.000	0.002
Fe ³⁺	0.901	0.673	0.614	0.634	0.315	0.326	0.299
Mn ³⁺	0.001	0.002	0.003	0.002	0.004	0.001	0.002
V ³⁺	0.000	0.005	0.003	0.003	0.002	0.005	0.005
Cr ³⁺	0.000	0.001	0.000	0.001	0.003	0.005	0.004
Al ³⁺	0.095	0.319	0.375	0.358	0.664	0.654	0.681
M3	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Al ³⁺	0.932	0.998	0.978	0.975	0.984	0.989	0.969
Ti ⁴⁺	0.001	0.004	0.003	0.009	0.008	0.009	0.004
M1	0.932	1.003	0.981	0.984	0.992	0.998	0.973
Ca ²⁺	0.996	1.000	0.998	0.999	0.992	1.000	0.997
Na ⁺	0.004	0.000	0.002	0.001	0.008	0.000	0.003
A1	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ca ²⁺	1.070	1.003	1.020	1.028	1.016	1.003	1.019
A2	1.070	1.003	1.020	1.029	1.016	1.005	1.021
OH [−]	1.000	1.000	1.000	1.000	1.000	1.000	1.000

* H₂O calculated for 1 OH per formula unit.

After heating at 900 °C, neither sample showed signs of phase transitions, whereas, in samples heated at more than 1000 °C, a new mineral association with plagioclase (anorthite), pyroxene (with a composition close to esseneite), and wollastonite evolved. The breakdown products formed a homogeneous mass retaining the original composition of epidote and clinozoisite in samples heated up to 1100 °C, but samples heated at 1200 °C contained domains enriched or depleted in Fe³⁺ (Figures 1 and 2; Tables 3 and 4).

Table 3. Electron microprobe analyses (in wt.% of oxides) of the epidote breakdown products (bulk from area with 5 µm diameter).

	ES-10	ES-10	ES-10	ES-11	ES-11	ES-11	ES-11	ES-11	ES-11	ES-12	ES-12	ES-12	ES-12
P ₂ O ₅	0.01	0.04	0.00	0.19	0.01	0.00	0.00	0.00	0.00	0.01	0.06	0.05	0.01
SiO ₂	37.04	38.75	36.45	37.24	37.49	37.49	37.25	38.69	38.70	38.16	38.21	37.96	
TiO ₂	0.00	0.00	0.03	0.16	0.02	0.01	0.04	0.00	0.03	0.00	0.03	0.19	
Al ₂ O ₃	23.35	21.73	23.15	23.42	26.58	24.14	21.81	27.38	21.41	24.29	28.34	27.89	
V ₂ O ₃	0.00	0.05	0.01	0.04	0.00	0.06	0.03	0.07	0.01	0.00	0.02	0.08	
Cr ₂ O ₃	0.01	0.00	0.02	0.00	0.01	0.02	0.03	0.00	0.01	0.01	0.00	0.00	
Fe ₂ O ₃	13.08	14.82	12.24	12.01	10.63	12.45	16.34	9.12	16.35	12.40	9.25	12.99	
MnO	0.05	0.01	0.02	0.58	0.04	0.04	0.02	0.07	0.03	0.02	0.08	0.06	
MgO	0.02	0.00	0.01	0.04	0.03	0.03	0.01	0.03	0.00	0.02	0.00	0.00	
NiO	0.00	0.01	0.00	0.02	0.03	0.01	0.00	0.01	0.00	0.00	0.01	0.00	
CaO	23.96	23.77	23.48	25.77	23.04	24.68	24.13	22.55	24.21	24.02	22.49	23.00	
Na ₂ O	0.01	0.02	0.02	0.05	0.01	0.01	0.00	0.01	0.01	0.04	0.00	0.05	
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.02	0.00	0.00	0.01	
Total	97.53	99.19	95.41	99.51	97.89	98.93	99.67	97.92	100.78	99.03	98.46	102.24	

Table 4. Electron microprobe analyses (in wt.% of oxides) of the clinozoisite breakdown products (bulk from area with 5 µm diameter).

	CP-10	CP-10	CP-10	CP-10	CP-10	CP-10	CP-11	CP-11	CP-11	CP-11	CP-12	CP-12	CP-12
P ₂ O ₅	0.06	0.05	0.00	0.00	0.02	0.01	0.23	0.04	0.00	0.01	0.03	0.05	0.02
SiO ₂	41.82	40.58	37.59	38.78	35.48	39.35	33.23	38.67	41.81	39.35	39.03	39.17	43.16
TiO ₂	0.06	0.07	0.15	0.14	0.17	0.15	0.61	0.17	0.03	0.03	0.06	0.14	0.09
Al ₂ O ₃	28.53	27.78	28.74	28.97	22.65	26.12	15.39	30.90	33.12	29.12	31.06	28.04	29.96
V ₂ O ₃	0.09	0.00	0.03	0.00	0.06	0.12	0.29	0.01	0.00	0.07	0.04	0.15	0.09
Cr ₂ O ₃	0.07	0.06	0.08	0.03	0.06	0.09	0.28	0.01	0.00	0.02	0.05	0.10	0.03
Fe ₂ O ₃	0.00	3.85	4.80	5.76	5.55	3.99	13.93	3.70	0.00	5.04	4.25	5.30	0.00
MnO	0.00	0.04	0.09	0.02	0.13	0.02	0.21	0.05	0.00	0.02	0.06	0.12	0.06
MgO	0.04	0.04	0.10	0.03	0.15	0.03	0.16	0.07	0.00	0.06	0.07	0.06	0.02
NiO	0.00	0.00	0.03	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.02	0.02
CaO	22.87	23.37	22.42	25.43	34.36	29.63	35.35	23.08	20.34	23.41	25.42	24.88	23.50
Na ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.02	0.00	0.01
K ₂ O	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.01	0.00	0.01	0.01
Total	93.53	95.84	94.03	99.17	98.63	99.53	99.66	96.69	95.34	97.13	100.07	98.03	96.96

This suggests that breakdown products were intergrown on the nanoscale. Moreover, in both sets of samples heated from 1000 °C to 1200 °C, a system of crystallographically oriented cracks and fissures developed (Figures 1c,d and 2c,d).

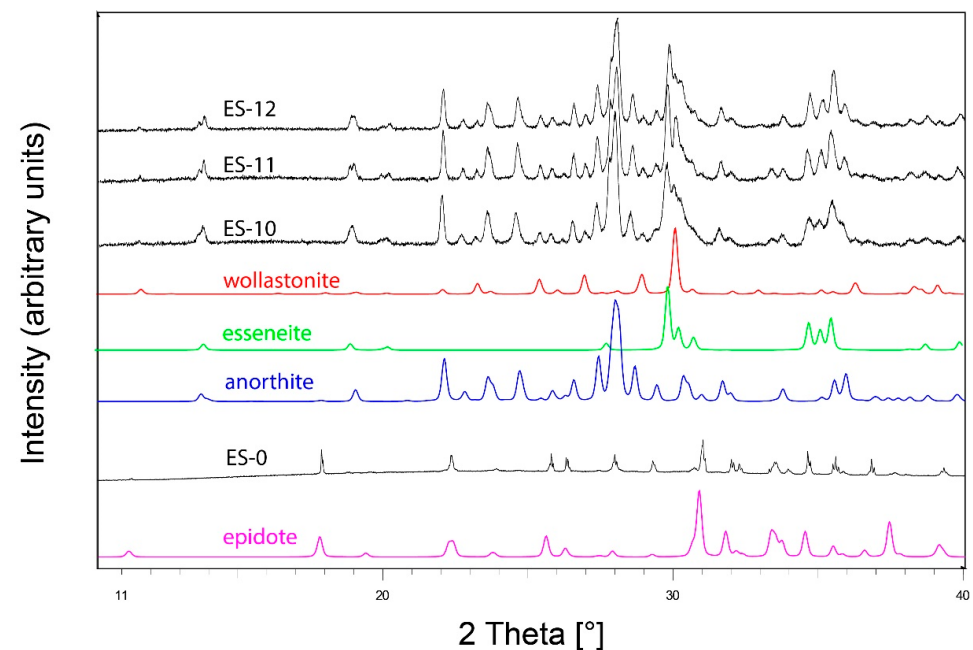
The formation of cracks was connected with volume changes after the transformation and dehydration with a visible increase in size with rising temperature. This phenomenon was probably related to structural changes in the transition of ES and CP to the breakdown products. The breakdown process is well documented in the XRD pattern (Figures 4 and 5) and Raman spectra (Figures 6 and 7). The unit-cell dimensions of breakdown products are provided in Tables 5 and 6. The Raman spectra of samples heated at 900 °C clearly show that at this temperature did not take place (Figure 6, Table 7); however, spectra measured from the matrix developed after heating at 1000–1200 °C could be interpreted as a composite of anorthite, pyroxene and wollastonite (Figure 7, Table 8), confirming the results from powder XRD.

Table 5. Unit-cell parameters of the main breakdown products after the heat treatment of epidote (ES) and clinozoisite (CP).

Anorthite	ES-10	ES-11	ES-12	CP-10	CP-11	CP-12
<i>a</i> (Å)	8.1832(4)	8.1847(4)	8.1872(4)	8.1819(4)	8.1809(4)	8.1820(4)
<i>b</i> (Å)	12.876(3)	12.8824(4)	12.8804(4)	12.778(3)	12.8789(4)	12.8774(4)
<i>c</i> (Å)	7.0869(4)	7.0879 (4)	7.0877(4)	7.033(3)	7.0857(4)	7.0887(4)
α (°)	93.223(3)	93.136(3)	93.153(3)	93.04(2)	93.094(3)	93.124(3)
β (°)	115.720(3)	115.769(3)	115.763(3)	115.59(2)	115.766(3)	115.803(3)
γ (°)	91.059(3)	91.188(3)	91.191(3)	91.147(3)	91.227(3)	91.232(3)
<i>V</i> (Å ³)	670.94(2)	671.2(1)	671.3(2)	656.4(1)	670.5(1)	670.6(1)
Wollastonite	ES-10	ES-11	ES-12	CP-10	CP-11	CP-12
<i>a</i> (Å)	8.011(3)	7.940 (3)	7.932 (3)	7.923(3)	7.945(3)	7.911(3)
<i>b</i> (Å)	7.309(3)	7.318(3)	7.317(3)	7.222(3)	7.341(3)	7.279(3)
<i>c</i> (Å)	6.753(3)	6.755(3)	7.058(3)	7.105(3)	7.051(3)	7.055(3)
α (°)	90.99(2)	91.98(2)	90.23(2)	91.21(2)	89.58 (2)	90.74(2)
β (°)	95.61(2)	95.11(2)	95.17(2)	94.92(2)	95.47 (2)	95.09(2)
γ (°)	103.49(2)	103.18(2)	103.36(2)	103.67(2)	103.33 (2)	102.62(2)
<i>V</i> (Å ³)	382.353(3)	380.05 (2)	396.811 (3)	393.233(3)	398.274(3)	394.7(1)

Table 6. Unit-cell parameters of pyroxene as a breakdown product after the heat treatment of epidote (ES) and clinozoisite (CP) compared to esseneite (Ess), diopside (Di), hedenbergite (Hd), aegirine (Aeg), and jadeite (Jd).

	ES-10	ES-11	ES-12	CP-10	CP-11	CP-12	Ess	Di	Hd	Aeg	Jd
Ref.	This Work						[35]	[36]	[37]	[37]	[38]
<i>a</i> (Å)	9.815(3)	9.8329(4)	9.809(3)	9.808(3)	9.606(3)	9.689 (3)	9.7610(12)	9.7470(7)	9.8357(8)	9.6554(8)	9.4278(3)
<i>b</i> (Å)	8.830(3)	8.8334(4)	8.8212(4)	8.690(3)	8.874(3)	8.923(3)	8.8223(8)	8.9235/4)	9.0078(8)	8.7998(8)	8.5651(4)
<i>c</i> (Å)	5.381(4)	5.3904(4)	5.3815(4)	5.293(3)	5.326(3)	5.289(3)	5.3360(5)	5.2524(4)	5.2408(5)	5.2900(6)	5.2262(2)
β (°)	105.99(2)	105.848(3)	105.909(3)	105.43(2)	104.96(2)	105.45(2)	105.918(13)	105.939(4)	104.664(6)	107.304	107.624(2)
<i>V</i> (Å ³)	448.363(3)	450.41(2)	447.81(2)	434.88(2)	438.534(3)	440.8(1)	441.89(8)	439.28(5)	449.2	429.12	402.21(2)

**Figure 4.** Powder X-ray diffraction patterns of epidote experimental samples (ES) compared to patterns of wollastonite [39], anorthite [40], esseneite [33], and epidote [41] (modeled from structural data using pseudo-Voigt function).

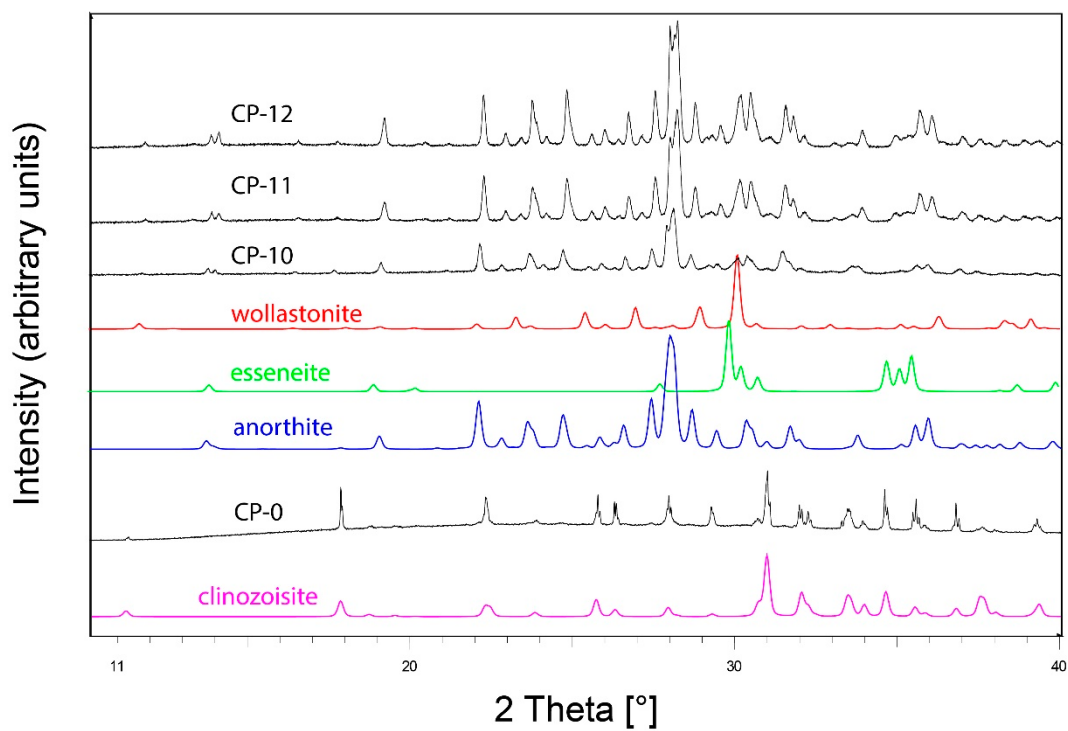


Figure 5. Powder X-ray diffraction patterns of clinozoisite experimental samples (CP) compared to patterns of wollastonite [39], anorthite [40], esseneite [33], and clinozoisite [14] (modeled from structural data using pseudo-Voigt function).

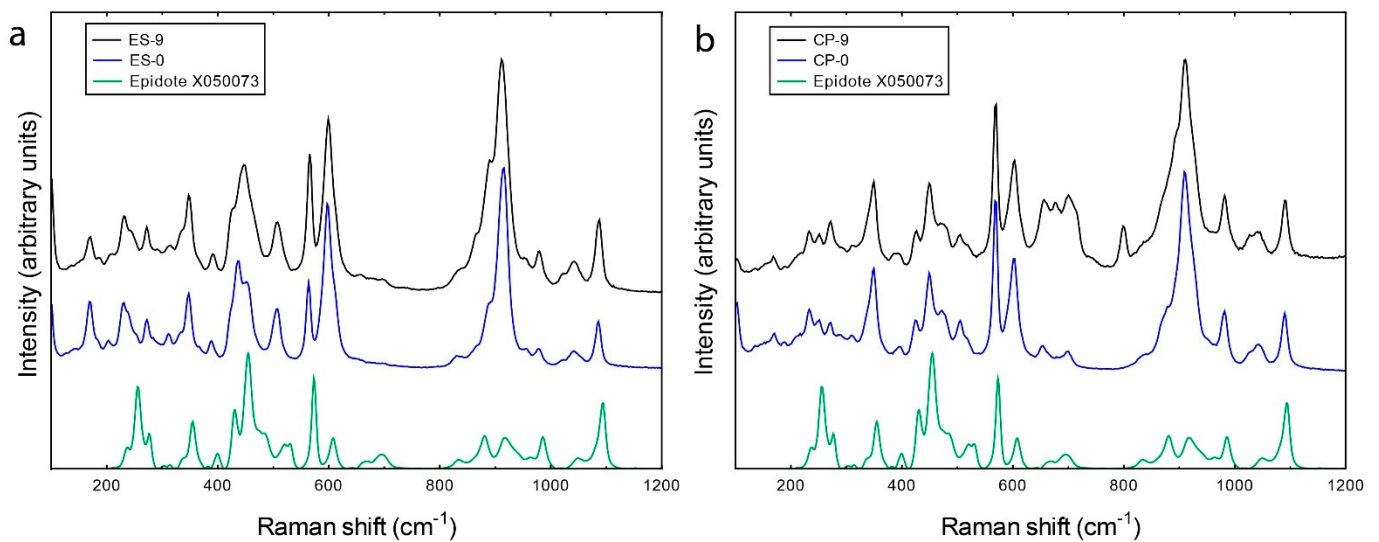


Figure 6. The Raman spectra of epidote (a) and clinozoisite (b), natural samples and heated at 900 °C in the 1200–100 cm⁻¹ region; our spectra were compared with the published spectrum of epidote [42].

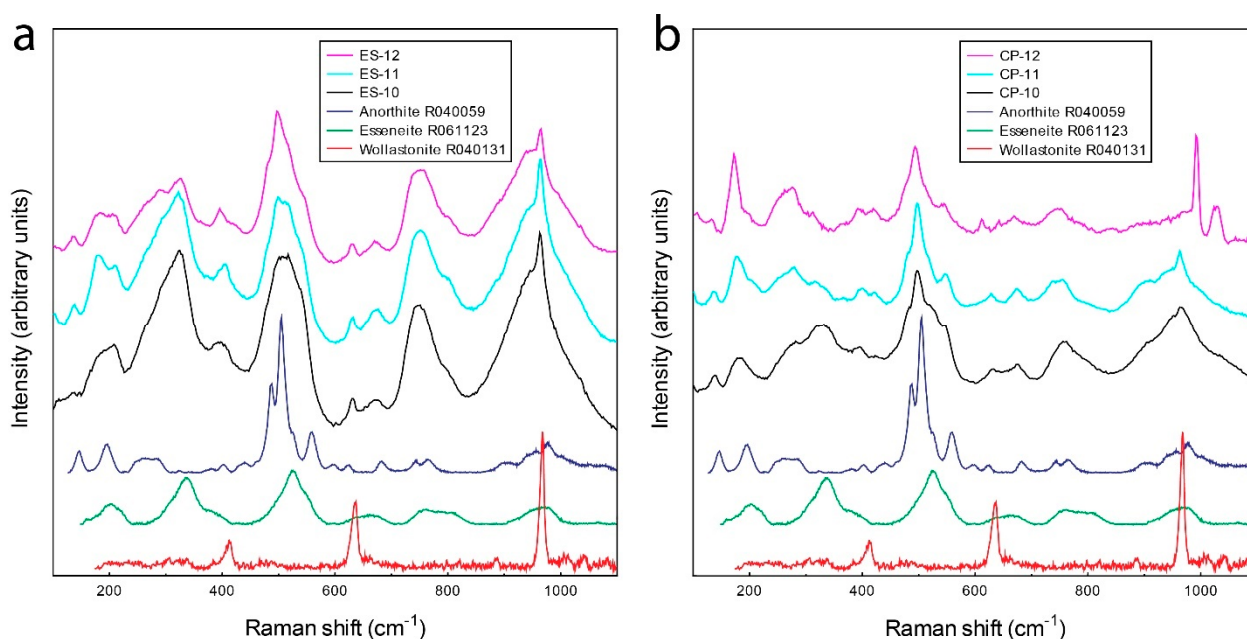


Figure 7. The Raman spectra of epidote (a) and clinozoisite (b) samples, heat-treated at temperatures higher than 1000 °C, compared with the published spectra of anorthite, esseneite, and wollastonite [42].

Table 7. Assignment of epidote and clinozoisite bands in the Raman spectra of studied samples.

ES-9	CP-9	Assignment	[43]	Assignment	[44]	Assignment
136		$\nu(\text{M-O})$	130		134	
170	166	$\nu(\text{M-O})$	165		168	
232	235	$\nu(\text{M-O})$	230		230	
273	272	$\nu(\text{M-O})$	275		276	
310		$\nu(\text{M-O})$	-		314	
345	347	$\nu(\text{M-O})$	350	$\nu(\text{M-O})$	350	$\nu(\text{M-O})$
398	390	$\nu(\text{Si-O}_b\text{-Si})$	390	$\nu(\text{M-O})$	390	$\nu(\text{M-O})$
	424	$\nu(\text{Si-O}_b)$	430	$\nu(\text{Si-O}_b\text{-Si})$	430	$\nu(\text{Si-O}_b\text{-Si})$
447	450	$\nu(\text{Si-O}_b)$	450	$\nu(\text{Si-O}_b\text{-Si})$	452	$\nu(\text{Si-O}_b\text{-Si})$
505	506	$\nu(\text{Si-O}_b)$	510	$\nu(\text{M-O})$	508	$\nu(\text{M-O})$
557	569	$\nu(\text{Si-O}_b)$	565	$\nu(\text{Si-O}_b\text{-Si})$	565	$\nu(\text{Si-O}_b\text{-Si})$
607	605	$\nu(\text{Si-O}_{nb})$	600	$\nu(\text{Si-O}_b)$	599	$\nu(\text{Si-O}_b)$
843		$\nu(\text{Si-O}_{nb})$	830	$\nu(\text{Si-O}_{nb})$	832	$\nu(\text{Si-O}_{nb})$
-	868		-	-	864	$\nu(\text{Si-O}_{nb})$
882	887	$\nu(\text{Si-O}_{nb})$	880	$\nu(\text{Si-O}_{nb})$	885	$\nu(\text{Si-O}_{nb})$
913	912	$\nu(\text{Si-O}_{nb})$	920	$\nu(\text{Si-O}_{nb})$	914	$\nu(\text{Si-O}_{nb})$
975	981	$\nu(\text{Si-O}_{nb})$	980	$\nu(\text{Si-O}_{nb})$	980	$\nu(\text{Si-O}_{nb})$
1038	1039	$\nu(\text{Si-O}_{nb})$	1040	$\nu(\text{Si-O}_{nb})$	1040	$\nu(\text{Si-O}_{nb})$
1087	1091	$\nu(\text{Si-O}_{nb})$	1085	$\nu(\text{Si-O}_{nb})$	1084	$\nu(\text{Si-O}_{nb})$

Both sets of samples heated at 1000 °C or more displayed significant changes in the Mössbauer spectra compared to original samples and samples heated at 900 °C (Tables 9 and 10, Figure 8). According to the mineral phases in breakdown products, it is most likely that Fe was incorporated into the pyroxene structure at both octahedral and tetrahedral sites according to isomer shift (IS) and quadrupole splitting (QS) of measured doublets. Doublets with QS above 0.97 mm/s were attributed to Fe^{3+} at the T site, whereas those with QS below 0.70 mm/s were interpreted as Fe^{3+} at the M1 site. Moreover, in the CP sample heated at 1200 °C, a magnetic component occurred, which could be interpreted as hematite.

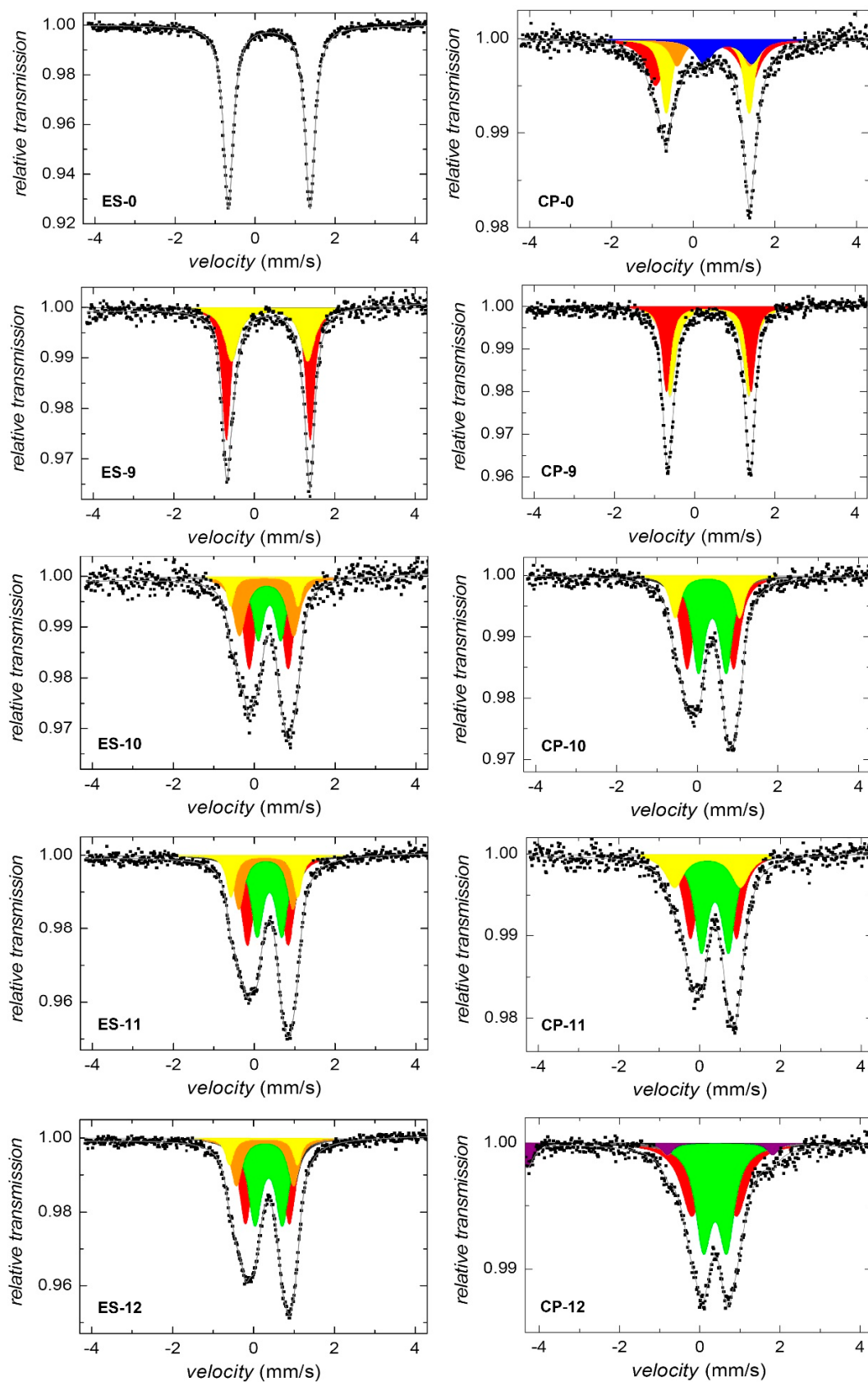


Figure 8. Room-temperature Mössbauer spectra of the ES and CP samples in their original state (ES-0, CP-0) and after annealing from 900 to 1200 °C. Experimental points are plotted as solid symbols. Fitting curves for all data points are gray. Decomposed peaks are also colored with different shades of gray. Shaded sub-spectra correspond in color to Fe^{3+} sites from Tables 7 and 8.

Table 8. Assignment of breakdown products bands in the Raman spectra of studied samples compared to anorthite (An), Ca-tschermakitic pyroxene (Ca-Tsch Px), aegirine (Aeg), and wollastonite (Wol).

ES-10	ES-11	ES-12	CP-10	CP-11	CP-12	An	[45]	Ca-Tsch Px	[45]	Aeg	[46]	Wol	[46]
			137	136	133	139	lattice mode	132	lattice mode				
183	182	181	178	178	176	182	lattice mode						
			199	199	202	200	lattice mode						
209	210	208						206	lattice mode				
		258	252	252	258	253	lattice mode						
286	282	289	275	279	282	273	lattice mode			273	M-O stretch/bend		
326	325	327	317	319	317	316	lattice mode						
		368	369	367	369	369	lattice mode	370	lattice mode				
400	405	396	397	400	396	400	lattice mode						
		423	426	423	423	427	ν_s (T-O-T)						
		480	478	479	481	484	ν_s (T-O-T)						
495	497	499	499	498	499					499	O-Si-O bend		
543	544	545	549	549	548	553		549		544	Si-O _{br} stretch		
	632	631			645			651	ν_s (T-O-T)			635	Si-O _{br} stretch
668	671	671	675	675	672	681		676		678	Si-O _{br} stretch		
			708										
737	736	735	736	733		741							
760	756	753	757	755	748	755							
		897	889	887								887	Si-O _{nbr} stretch
			909	906	915	908	ν_{as} (Si-O-Si)						
								922	ν_s (T-O ⁻)				
945	938	942	944	939		949	ν_{as} (Si-O-Si)	953	ν_s (T-O ⁻)	953	Si-O _{nbr} stretch		
965	965	966	970	964	973							968	Si-O _{nbr} stretch
		997	997	991	997	998	ν_{as} (Si-O-Si)						
1022	1008		1044		1032					1044	Si-O _{nbr} stretch	1042	Si-O _{nbr} stretch

Table 9. Parameters of ⁵⁷Mössbauer spectra for epidote samples. Color of dublets is for their identification in the Figure 8.

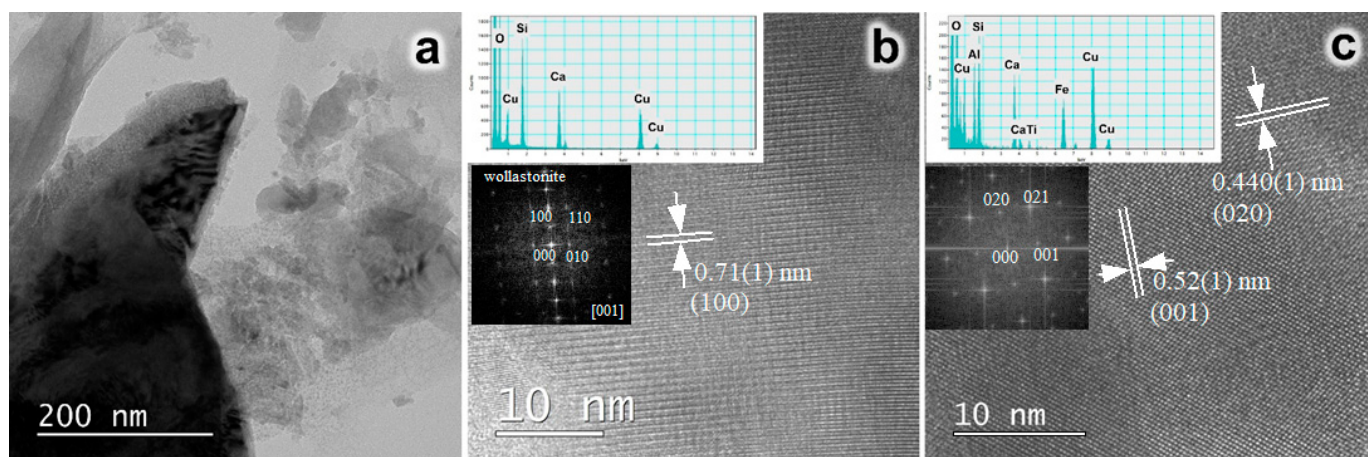
No.	Doublet		Area	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Mineral	Site
ES-0	D 1		1.00	0.36	2.04	0.30	epidote	Fe ³⁺ , M3
ES-9	D 1		0.60	0.35	2.09	0.26	epidote	Fe ³⁺ , M3
	D 2		0.40	0.38	1.90	0.42	epidote	Fe ³⁺ , unspecified
ES-10	D 1		0.08	0.25	1.67	0.22	pyroxene	Fe ³⁺ , T
	D 2		0.28	0.31	1.34	0.38	pyroxene	Fe ³⁺ , T
	D 3		0.40	0.36	0.97	0.35	pyroxene	Fe ³⁺ , T
	D 4		0.24	0.38	0.56	0.31	pyroxene	Fe ³⁺ M1
ES-11	D 1		0.12	0.25	1.65	0.26	pyroxene	Fe ³⁺ , T
	D 2		0.19	0.29	1.33	0.31	pyroxene	Fe ³⁺ , T
	D 3		0.38	0.34	1.01	0.37	pyroxene	Fe ³⁺ , T
	D 4		0.31	0.38	0.61	0.34	pyroxene	Fe ³⁺ M1
ES-12	D 1		0.08	0.25	1.68	0.25	pyroxene	Fe ³⁺ , T
	D 2		0.18	0.29	1.41	0.33	pyroxene	Fe ³⁺ , T
	D 3		0.36	0.35	1.09	0.37	pyroxene	Fe ³⁺ , T
	D 4		0.37	0.38	0.68	0.38	pyroxene	Fe ³⁺ M1

Table 10. Parameters of ^{57}Fe Mössbauer spectra for clinozoisite samples. Color of doublets is for their identification in the Figure 8.

No.	Doublet		Area	IS (mm/s)	QS (mm/s)	Γ (mm/s)	Mineral	Site
CP-0	D 1		0.37	0.23	2.32	0.56	epidote	Fe^{3+} , M3'
	D 2		0.31	0.36	2.03	0.29	epidote	Fe^{3+} , M3
	D 3		0.15	0.50	1.78	0.39	epidote	Fe^{3+} , M1
	D 4		0.17	0.84	1.17	0.50	epidote	Fe^{3+} , 6
CP-9	D 1		0.40	0.35	2.11	0.25	epidote	Fe^{3+} , M3
	D 2		0.60	0.37	1.96	0.35	epidote	Fe^{3+} , M1
CP-10	D 1		0.16	0.25	1.59	0.32	pyroxene	Fe^{3+} , T
	D 2		0.43	0.33	1.15	0.41	pyroxene	Fe^{3+} , T
	D 3		0.41	0.38	0.69	0.38	pyroxene	Fe^{3+} , M1
CP-11	D 1		0.20	0.19	1.63	0.54	pyroxene	Fe^{3+} , T
	D 2		0.38	0.34	1.14	0.41	pyroxene	Fe^{3+} , T
	D 3		0.42	0.38	0.67	0.39	pyroxene	Fe^{3+} , M1
CP-12	S 1 *		0.22	0.41	−0.20	0.34	hematite	Fe_2O_3
	D 1		0.38	0.36	1.12	0.63	pyroxene	Fe^{3+} , T
	D 2		0.40	0.38	0.58	0.48	pyroxene	Fe^{3+} , M1

* Hyperfine magnetic field, $B_{\text{hf}} = 51.6$ T.

Epidote-clinozoisite structural breakdown and breakdown products were documented on the nanoscale by HRTEM. Breakdown products formed particles several tens of nm (Figure 9a). It was also used to confirm the presence of both pyroxene and wollastonite, because these XRD peaks and Raman bands were partly overlapping (not in the case of well-evidenced anorthite); therefore, this observation could be taken as their definitive proof. The particle with O, Si, and Ca identified in the EDS spectrum was wollastonite (Figure 9b), whereas the nanocrystal with O, Si, Ca, Fe, Al, and Ti peaks was pyroxene (Figure 9c).

**Figure 9.** The HRTEM images of epidote breakdown products: (a) nanocrystals of breakdown products; (b) detailed view of wollastonite with its EDS spectrum; (c) detailed view of pyroxene with its EDS spectrum. Note that Cu in the EDS spectrum is from the Cu TEM grid.

4. Discussion

In the present experiment, the epidote-clinozoisite solid solution stability was studied under ambient conditions, atmospheric pressure, and without addition of any fluid phase. There was no evidence of phase transition or breakdown of epidote or clinozoisite at 900 °C; however, at $T > 1000$ °C, a breakdown of both epidote and clinozoisite was observed. The Raman spectra of samples heated at temperatures greater than 1000 °C contained relatively broad bands and were probably the composite of both anorthite and esseneite-like pyroxene

contributions. The broadness of the bands suggested a very low structural order of the breakdown product, which was supported by other analytical data.

All products were convincingly identified by the selected analytical methods. Anorthite and wollastonite presumably had low chemical variability. The original epidote and clinozoisite had low Na content, below the EMPA detection limit. This limited possible albite substitution.

Pyroxene was the most intriguing breakdown product. It had the largest compositional variability and could accommodate Si, Ca, and both Al and Fe. This composition indicates that pyroxene in our samples had QUAD composition [47]. The composition of hedenbergite proposed for epidote breakdown [28] was not very likely for our reaction because hedenbergite contains only divalent Fe, and, without Na, there is no substitution that could balance the increased charge of Fe^{3+} indicated by the Mössbauer study of our samples. However, a tschermakite-type substitution with trivalent cation substituting for Si^{4+} could charge-balance the exclusive Fe^{3+} content in studied pyroxene. The tschermakite-type substitution is the most probable mechanism allowing the incorporation of trivalent cations such as Fe^{3+} into Ca pyroxene, similarly to esseneite [33].

The doublets in the Mössbauer spectra of breakdown products could be divided into two groups. Both had an isomer shift below 0.40 mm/s, indicating that all Fe in pyroxene was ferric [37,48–50]. However, there were differences between both groups according to their quadrupole splitting. Doublets with quadrupole splitting between 0.60 and 0.70 mm/s were similar to those of octahedral Fe^{3+} at the M1 site of aegirine pyroxene [37,48,50], has albeit with slightly higher QS than in pyroxenes from a hedenbergite-aegirine solid solution (up to 0.49 mm/s [37]). This could have result from the different distortion level of M1 octahedron in the studied pyroxene.

The second group of doublets had distinctly higher quadrupole splitting than octahedral Fe^{3+} doublets. Their QS and IS values were similar to tetrahedral Fe^{3+} in Fe-esseneitic or Ca-Fe-tschermakitic pyroxenes [49,51,52]. The presence of Fe^{3+} at the tetrahedral site caused an expansion of the *T* tetrahedron. This expansion was anisotropic; the length of nonbridging *T*-O1 and *T*-O2 bonds was very similar in pyroxene with tetrahedral Al and Fe^{3+} , while the bridging bonds were larger by 0.02 Å in pyroxene with tetrahedral Fe^{3+} than those in CaTs [49].

The quadrupole splitting had a negative correlation to the area of tetrahedral Fe^{3+} doublets but was positively correlated for octahedral Fe^{3+} (Figure 10a,b). The decrease in tetrahedral Fe^{3+} quadrupole splitting could be attributed to the reduced distortion of the tetrahedra with increasing $^T\text{Fe}^{3+}$ or ^TAl occupancy due to $^{M1}\text{Fe}^{2+} + ^T\text{Si} \leftrightarrow ^{M1}\text{Fe}^{3+} + ^T\text{Fe}^{3+}$ substitution [49,53]. The positive correlation of octahedral Fe^{3+} in studied samples was unusual. The difference to the published data [49] could be explained by the different substitution. The electric field was more strongly perturbed by changing the valence of neighboring M1 or M2 ions, and the change in quadrupole splitting of $^{M1}\text{Fe}^{3+}$ was also influenced by a change in valence of the tetrahedral site ions [48]. In the synthetic Si-deficient pyroxenes of $\text{CaFe}^{3+}\text{AlSiO}_6$ – $\text{CaTiAl}_2\text{O}_6$ composition, the octahedral distortion and change in quadrupole splitting of $^{M1}\text{Fe}^{3+}$ were influenced by the $^{M1}\text{Fe}^{3+} \leftrightarrow ^{M1}\text{Ti}^{4+}$ and $^T\text{Si} \leftrightarrow ^T\text{Al}$ substitutions [49]. However, in the studied samples, the Ti content was low. Therefore, the accommodation of Fe^{3+} at the octahedral site was allowed by $^{M1}\text{R}^{2+} + ^T\text{Si} \leftrightarrow ^{M1}\text{R}^{3+} + ^T\text{R}^{3+}$, where R is either Fe or Al. Consequently, if a random distribution of Al and Fe^{3+} is assumed, an increase in the octahedral distortion and quadrupole splitting would have been in a linear dependence of the $^{M1}\text{Fe}^{3+}$ proportion. The evolution of quadrupole splitting values against the heating temperature is shown in Figure 10c,d.

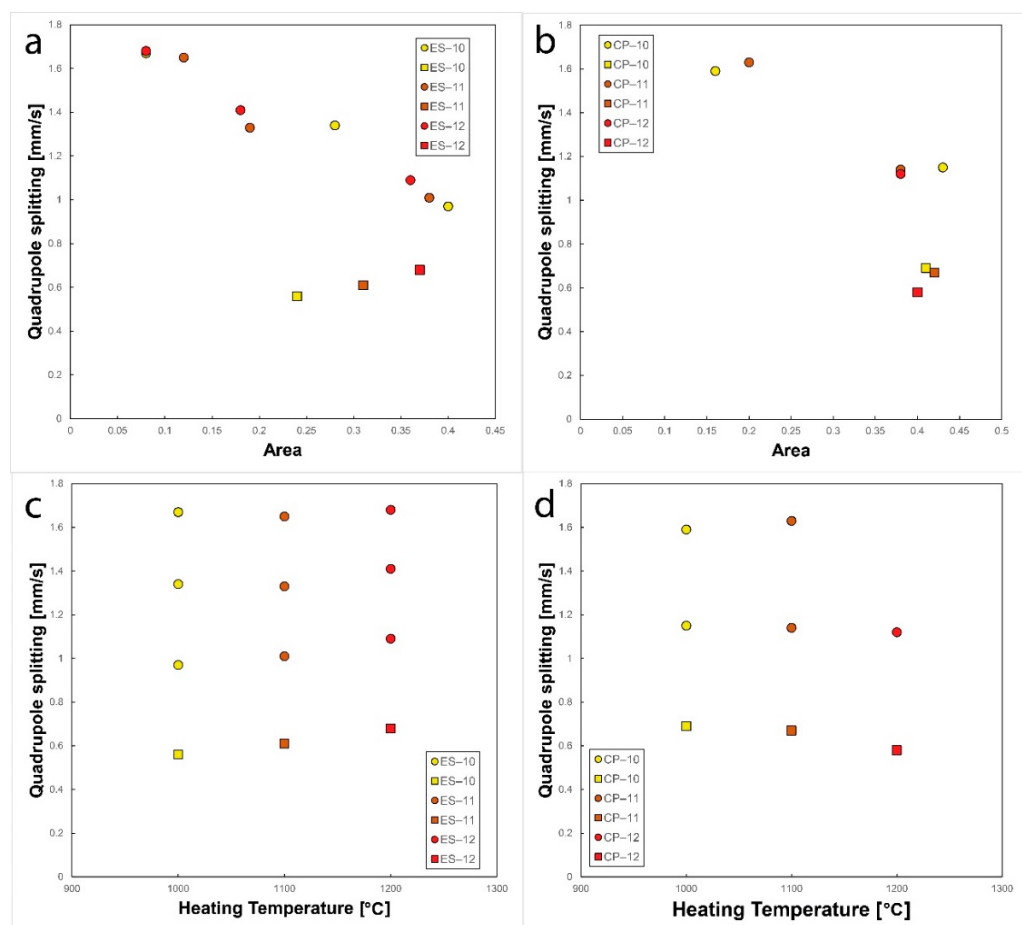


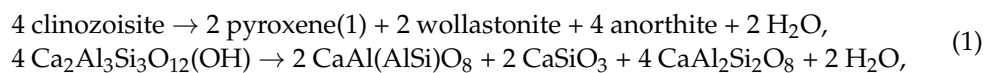
Figure 10. Comparison of quadrupole splitting and area of doublets for (a) ES and (b) CP samples and quadrupole splitting and heating temperature for (c) ES and (d) CP samples.

Pyroxenes in the studied samples showed some similarities, as well as some differences. The *a* size was similar to hedenbergite [37] in the ES samples, whereas, in the CP samples heated at >1100 °C, it was significantly smaller, even smaller than that of aegirine [37], shifting toward jadeite [38]. The *b* size of ES pyroxene was very similar to the published esseneite [35] and aegirine [37] data. The data for CP pyroxene were very variable, increasing with the temperature from a value similar to jadeite [38] for the sample heated at 1000 °C to a value approaching that of hedenbergite [37]. The *c* size in the CP samples was very similar to aegirine [37] or esseneite [35], whereas, in ES pyroxene, it was even larger than esseneite.

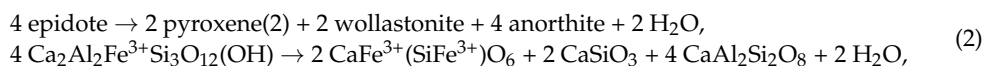
On the basis of the lattice parameters of studied samples, it can be concluded that *a* and *b* indicate variable Al³⁺ and Fe³⁺ occupancy at the *M* sites. Observed variations could result from the various degree of ordering of these cations. The *c* sizes in all samples clearly evidence a relatively high substitution of trivalent cations for Si⁴⁺ at the *T* site. The CP pyroxene likely had a composition close to esseneite. Esseneite was described with the composition of (Ca_{1.01}Na_{0.01}) (Fe³⁺_{0.72}Mg_{0.16}Al_{0.04}Ti_{0.03}Fe²⁺_{0.02}) Si_{1.19}Al_{0.81}O_{6.00} [33] and end-member formula CaFe³⁺AlSiO₆. However, the ES pyroxene with the *c* size larger than esseneite very likely had Fe³⁺ at the *T* site, expanding the tetrahedra and, as the result of its larger ionic radius (0.49 Å, [54]) than Si (0.26 Å, [54]) and Al (0.39 Å, [54]), extending the tetrahedral chain. There was no detectable Fe³⁺ in the tetrahedra of natural esseneite, but experimentally synthesized CaFe³⁺AlSiO₆ contained tetrahedral Fe³⁺, implying a cooling rate dependence of Fe³⁺ and Al ordering at the M1 and T sites [33]. Consequently, the proportion of Fe³⁺ and Al in pyroxene varied to replicate the composition of original epidote and clinozoisite. On the basis of the Fe³⁺ content in the original samples and with

regard to proposed reactions, there was ca. 0.60 apfu and 0.20 apfu of tetrahedral Fe³⁺ in ES and CP samples, respectively.

Taking into account the observed associations of breakdown products, we can propose variable temperature-induced transformation reactions of the epidote-clinozoisite solid solution:



for clinozoisite, and

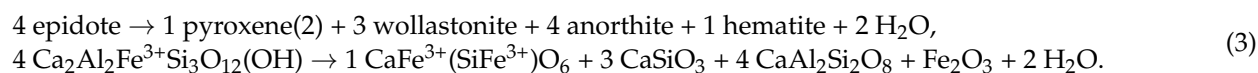


for epidote.

It is important to stress that these reactions were calculated for ideal end-member compositions; the composition of products was also ideal. However, the variations in Al:Fe ratio could be balanced not only by the different proportion of breakdown products in each reaction but also by the change in the composition of breakdown products.

Moreover, hematite was observed in the Mössbauer spectrum of the CP sample heated at 1200 °C, although it was not clearly identified in powder XRD. This can be explained by the large peak broadening induced by the small size of particles observed in the studied sample. In contrast, in the Mössbauer spectroscopy, the proportion of phases was determined by the proportion of Fe contained in them. Consequently, hematite was more significantly reflected in the Mössbauer spectrum than in the powder XRD pattern when associated with a large volume of Fe-poorer (pyroxene) or even almost Fe-free (anorthite, wollastonite) minerals.

The breakdown of the epidote component in the CP sample at 1200 °C with the production of hematite can be driven by following reaction:



This reaction is similar to the previous one; the production of hematite is managed by the partial transformation of Fe-bearing clinozoisite through pyroxene(2) resulting in hematite and wollastonite formation at 1200 °C. Hematite is the final product of high-temperature heating of all Fe-oxidic compounds under oxidizing conditions [55]. This also includes Fe-bearing silicates such as tourmalines, which, when heated at a temperature of 900 °C, break down producing a mass containing mullite and hematite [56]. However, at temperatures below 1200 °C, pyroxene(2) seems to be stable, and no hematite is produced.

Breakdown of epidote probably had a subsolidus character with recrystallization of primary mineral with deformation mechanism induced by crystal-structural changes resulting in grain-size reduction. The texture of samples was maintained and contained decomposed minerals. Samples were without signs of any differentiation or partial melting. The temperature of 1200 °C allowed partial chemical diffusion as a result of the reaction of product division. This could also indicate a subsolidus character of the reaction.

The resulting breakdown association with anorthite, wollastonite, and esseneitic pyroxene also has implications for natural processes. Esseneite is a product of either high-temperature recrystallization of silicate-bearing rocks in strongly oxidizing conditions usually induced by coal burning [33,57] or high-temperature metamorphic and metasomatic processes connected with volcanic extrusions and magmatic intrusions in form of skarns and skarnoids [35,58,59]. Wollastonite and anorthite occur in very high-temperature parageneses, such as at Nanga Parbat, India, where this association replaces grossular and quartz [60]. Associations with clinopyroxene (En₁₅₋₄₃Fs₁₄₋₃₆Wo₄₁₋₅₁) + plagioclase (An₃₇₋₁₀₀) ± magnetite and with wollastonite ± clinopyroxene (En₁₇₋₃₈Fs₈₋₃₄Wo₄₉₋₅₉) ± plagioclase (An₄₆₋₁₀₀) ± garnet (Grs₀₋₆₅Adr₂₄₋₇₅Sch₀₋₇₆) ± quartz were observed in calc-silicate xenoliths from Merapi Volcano, Indonesia upon contact of lava with limestones [61]. Therefore,

it is possible to assume that epidote-group minerals can also be precursors for tschermakitic pyroxenes and pyroxenoids, if the temperature exceeds their stability.

5. Conclusions

In the present experiment, the epidote-clinozoisite solid solution stability was studied under ambient conditions, atmospheric pressure and without addition of any fluid. The structural breakdown was observed in samples heated at 1000–1200 °C. The breakdown mineral association comprised anorthite, pyroxene, and wollastonite with additional hematite occurring after heating at 1200 °C. The XRD and Mössbauer spectroscopy data suggest that pyroxene contained a significant proportion of Ca-tschermakitic molecules, resulting in a composition similar to esseneite but with the substitution of Al^{3+} and Fe^{3+} at both tetrahedral and octahedral sites depending on their proportion in the original epidote and clinozoisite sample. The high-temperature and low-pressure breakdown of epidote to the specific mineral association suggests that a similar process could also take place naturally.

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