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Ghiaraite: a new mineral from Vesuvius volcano, Naples (Italy)

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Abstract

In this work we report the first finding of $CaCl_2 \cdot 4H_2O$, long known as a synthetic phase. The mineral, called ghiaraite, was discovered in 2011 in a sample belonging to the Real Museo Mineralogico di Napoli (Italy), that had been collected in 1872 at Vesuvius volcano and stored in a glass sealed vial. It is associated with chlorocalcite ($KCaCl_3$), hematite, sylvite and halite. The mineral was found inside an ejecta of 5 m in size transported by a lava flow to the locality of Massa di Somma. Here with the ejecta still hot the sample was collected and rapidly stored in a sealed glass vial in order to preserve it from the atmospheric conditions. Ghiaraite is triclinic, space group $P\text{-}1$, with unit-cell parameters: a = 6.3660(5), b = 6.5914(5), c = 8.5568(6) Å, α = 93.504(6)°, β = 97.778(7)°, γ = 110.557(6)°, V = 330.802(9) Å^3, Z = 2. The calculated density is 1.838 g cm^{-3} using the ideal formula and the powder X-ray diffraction data. It occurs as euhedral isometric grains up to 5-6 μm long intimately intermixed with chlorocalcite. The eight strongest reflections in the X-ray powder diffraction pattern [listed as d(Å)(I)(hkl)] are: 2.628(100)(02-2); 2.717(88)(10-3); 4.600(88)(1-1-1); 2.939(77)(200); 2.204(75)(121), 5.874(73)(100), 6.124(47)(010); 3.569(46)(11-1).

Ghiaraite was approved by the Commission on New Minerals, Nomenclature and Classification with IMA number 2012-072. The mineral was named in honour of Prof. Maria

Rosaria Ghiara (b. 1948), Head of Real Museo Mineralogico of Napoli and Centro Musei delle Scienze Fisiche e Naturali dell'Università degli Studi di Napoli Federico II for her important work in promoting the scientific research focused on the mineralogy of Vesuvius volcano.

Keywords: ghiaraite, new mineral, X-ray diffraction, EDS, Vesuvius volcano, calcium tetrahydrate chloride

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Introduction

The new mineral described in this work, named ghiaraite, appears to be extremely rare and was found by one of the authors (MR) in association with chlorocalcite ($KCaCl_3$), hematite, sylvite and halite in the mineral collection "Vesuviana" of the Real Museo Mineralogico di Napoli in 2011. Ghiaraite occurs in voids in the ejecta surface that were exposed to volcanic vapors. The sample was collected at the Vesuvius volcano, stored in a sealed glass vial and deposited at the Real Museo di Napoli in 1872 by Arcangelo Scacchi (1810-1894), a member of the “Reale Accademia delle Scienze Fisiche e Matematiche”, see Fig. 1. More in detail, it was found inside an ejecta of 5 m in size transported by a lava flow to the locality of Massa di Somma (Fig. 2, coordinates: 40.5° N, 14.22 E). Here, with the ejecta still hot (Scacchi 1874), the sample was collected and within a few minutes stored in a sealed glass vial in order to preserve it from the atmospheric conditions. Arcangelo Scacchi reported the description of the ejecta finding on a note published on October 1872 right after the Vesuvius eruption of April 26th, 1872 (Scacchi 1872). The note was published by the “Società Reale di Napoli” in the “Rendiconto dell’Accademia delle Scienze Fisiche e Matematiche” (year XII). In the note of 1872 Scacchi described chlorocalcite with the wrong chemical formula CaCl; however, he reported a chemical analysis in which the CaCl compound represented the 58.76% with the remaining 32.24% constituted by potassium chloride, sodium chlorides and manganese chloride. At that time the microprobe analysis was not an available technique and the data reported by Scacchi were clearly a bulk chemical analysis on a mixed sample. Therefore, Scacchi could not identify ghiaraite by its chemical composition, and could not realize that "chlorocalcite" was actually $KCaCl_3$ (Zambonini 1935). Chlorocalcite is also obtained a synthetic compound by melting a 1:1 mixture (molar ratios) of KCl and $CaCl_2$ at 750 °C (Korshunov et al. 1984). Similarly, the synthetic analogue of ghiaraite was first reported in 1875 to be obtained while melting $CaCl_2{\cdot}6H_2O$ (Gmelin 1957).

In this work we report the first natural finding of $CaCl_2{\cdot}4H_2O$, which has been named ghiaraite in honour of Prof. Maria Rosaria Ghiara (b. 1948) who is Head of Real Museo Mineralogico of Napoli and Centro Musei delle Scienze Fisiche e Naturali dell'Università degli Studi di Napoli Federico II. Several years ago Prof. Ghiara began a program to promote scientific collaborations to obtain new information about the stored minerals from the Vesuvius volcano in the last two hundred years.

Ghiaraite was approved by the Commission on New Minerals, Nomenclature and Classification with IMA number 2012-072. The type specimen is deposited in the collections of the Real Museo of Napoli with registration number 16986-E5525.

Appearance, morphology, physical and optical properties

Ghiaraite occurs as euhedral isometric very small grains (up to 5-6 μm long) intimately intermixed with chlorocalcite (Fig. 3 and 4). The bulk sample chlorocalcite – ghiaraite appears milky white toward light grey in color. The forms cannot be easily determined as ghiaraite appears as intergrown crystals. The association chlorocalcite – ghiaraite is strongly deliquescent when exposed to the air.

The combination of small grain size plus sensitivity to the moisture did not allow us to obtain a better physical or optical characterization, with the exception of the calculated density, which is 1.838 g cm^{-3} using the ideal formula and the unit-cell volume obtained from powder X-ray diffraction data. For the synthetic α-$CaCl_2{\cdot}4H_2O$ analogue, the measured densities are 1.826(3) $g{\cdot}cm^{-3}$ at 25°C (Wulff and Schaller 1934), and 1.837 $g{\cdot}cm^{-3}$ (Thewalt and Bugg 1973). These data are in perfect agreement with the calculated density of our sample..

From the data obtained on the synthetic α-$CaCl_2{\cdot}4H_2O$ analogue, Bunn et al. (1935) deduced that the compound is biaxial negative, not pleochroic, and with refractive indexes $\alpha = 1.530$, $\beta = 1.557$, $\gamma = 1.567$. The only available data, even if of poor quality, are those from Wulff and Schaller (1934) who reported $n_{min} = 1.54(8)$, $n_{max} = 1.56(6)$. No optical properties were measured on ghiaraite as the typical crystal size did not allow any optical experimental measurement.

Experimental methods

X-ray powder diffraction

X-ray powder diffraction (XRPD) data were recorded on a PANalytical θ-θ diffractometer (Cu radiation) equipped with a long fine focus Cu X-ray tube operating at 40kV and 40mA and a Real Time Multi STRIP (RTMS) detector (X'Celerator). The active length (detector aperture) of the X'Celerator (RTMS detector) is 2.122° and this leads to collect the signal over a large angular range at the same time, reducing the total time of the scan. The data collection time is about 100 times shorter with respect to an identical scan performed using the traditional proportional detector (Reiss 2002). The data were collected in the angular range 3-67° in 2θ in continuous mode with an integrated step scan of 0.033° in 2θ and a total time for the data acquisition of about 8 minutes (angular speed 0.14°/s). This corresponds to a scan with a virtual counting statistic of 30s/step. The program High Score Plus (PANalytical) was used for phase identification and Rietveld refinement (Rietveld 1967). The structural model of synthetic $CaCl_2 \cdot 4H_2O$ (ICSD code 8061, PDF 01-070-2220), determined by Leclaire and Borel (1979) was used as starting structural model of ghiaraite. A pseudo-Voigt function was employed for the profile shapes. Refined parameters were scale factors, zero-shift, background, lattice constants, and profile parameters (Gaussian and Lorentzian coefficients).

SEM and EDS

The SEM-EDS investigation was carried out using a CamScan MX2500 scanning electron microscope, equipped with a LaB_6 cathode, four quadrant solid-state BSE detector and a EDAX EDS system for micro-analysis. The analytical conditions were: accelerating voltage of 20 kV, filament emission of ~130 μA and working distance of 27 mm.

Results and discussion

Ghiaraite was found during an X-ray diffraction investigation in collaboration between the Real Museo Mineralogico di Napoli, the Department of Geosciences of University of Padova and the Museo of Mineralogy of University of Padova, with the aim to identify the rare minerals collected at the end of 1800 at Vesuvius volcano. In detail, the aim of this collaboration was initially that to identify the chlorocalcite phase. The original glass vial (Fig. 1) containing ghiaraite and chlorocalcite was cut and a small fraction of the sample was collected extremely quickly in order to avoid the deliquescence phenomenon occurring for such phases. X-ray diffraction data were measured very fast thanks to the use of the highly sensitive detector available and by SEM-EDS under vacuum. The results of the study are reported below.

X-ray diffraction

The sample analyzed by X-ray diffraction is constituted by chlorocalcite, ghiaraite and sylvite (Fig. 5) (the fourth associated phase is hematite, but this mineral was found inside the vial as separate crystals not intermixed with chlorocalcite, ghiaraite and sylvite). Patterns of synthetic α-$CaCl_2{\cdot}4H_2O$ strongly agreed with the peaks of natural ghiaraite. Ghiaraite is triclinic with space group *P*-1. The Rietveld refinement using the structural data of the synthetic compound gives the following results: the agreement indices were R_p = 5.09% and R_{wp} = 6.68%. For ghiaraite, R_{Bragg} = 1.22%. Data of *d*-spacing (in Å for Cu*K*α) are provided in Table 1, whereas the refined unit-cell parameters are the following: *a* = 6.3660(5), *b* = 6.5914(5), *c* = 8.5568(6) Å, *α* = 93.504(6)°, *β* = 97.778(7)°, *γ* = 110.557(6)°, *V* = 330.802(9) $Å^3$, *Z* = 2. Leclaire and Borel (1979) report for their synthetic sample the following cell parameters: *a* = 6.3673(8) Å, *b* = 6.5932(6) Å, *c* = 8.5606(15) Å, *α* = 93.50(1)°, *β* = 97.83(1)°, *γ* = 110.58(1)°. Thewalt and Bugg (1973) report: *a* = 6.364(5) Å, *b* = 6.593(2) Å, *c* = 8.557(3) Å, *α* = 93.52(4)°, *β* = 97.77(5)°, *γ* = 110.56(3)°. Such excellent match between ghiaraite and the synthetic $CaCl_2{\cdot}4H_2O$ samples, not only demonstrates that ghiaraite is the natural analogue of the calcium-chloride tetrahydrated, but also that the major element chemistry of the natural and synthetic samples coincide.

Chemistry

Due to the impossibility of preparing a suitable sample for WDS analyses we could only qualitatively analyse the sample of Fig. 3 and 4 by SEM-EDS. The EDS spectra are shown in Fig. 6. It can be noted that for ghiaraite we nearly could not measure the water oxygen as the vacuum under which the measurements were performed is in the order of the 10^{-5} mbar. Under such vacuum conditions the coordinated water of a compound like $CaCl_2{\cdot}4H_2O$ is totally lost. In addition, the limited amount of potassium visible in the spectra for ghiaraite must belong to chlorocalcite, this is quite evident by the X-ray diffraction data: in fact the unit-cell volume of ghiaraite only differs from the synthetic calcium-chloride tetrahydrated by less than 0.1%; this is in agreement with the total absence of a large cation like K^+, which would strongly affect the unit-cell volume. Consequently, the combined study of ghiaraite by EDS and X-ray diffraction definitively prove that ghiaraite is the natural analogue of the tetrahydrated calcium chloride, $CaCl_2 \cdot 4H_2O$, for which the crystal structure has been well known for about forty years (i.e. Thewalt and Bugg 1973).

Relation to other species

Ghiaraite has the synthetic analogue α-$CaCl_2 \cdot 4H_2O$, which can be obtained during the melting of $CaCl_2 \cdot 6H_2O$ as well as by crystallization from aqueous solutions. However, it can be formed by simple hydration of anhydrous $CaCl_2$ or $CaCl_2 \cdot 2H_2O$. It is also formed by interconversion of other polymorphs (β- and γ-$CaCl_2 \cdot 4H_2O$, both showing $P2_1/c$ space group), as it appears to be the most stable tetrahydrated form (Gmelin 1957). It is itself a hygroscopic compound and its occurrence and role in the system $CaCl_2 - H_2O$ has been thoroughly studied by Basset et al. (1933, 1937) and Lannung (1936).

The analogue of ghiaraite was found by Chesnokov in a burning coal dump at mine #45 in Kopeisk, Chelyabinsk Oblast, Southern Ural, Russia and described as unnamed “tetrahydrated calcium chloride” (Chesnokov et al. 1987) and then under the name “mesohydrite” (Chesnokov et al. 1994). “Mesohydrite” was described as a product of dehydration of antarcticite; physical properties and X-ray powder data identical to synthetic $CaCl_2 \cdot 4H_2O$ were reported (Chesnokov et al. 1994). However, the above locality has a clearly technogenic character and “mesohydrite”, thus, was considered as a substance of anthropogenic origin and never approved as a valid mineral species by the IMA. On the contrary ghiaraite described in this work has undoubtedly a natural origin.

The structure of the synthetic analogue of ghiaraite by Thewalt and Bugg (1973) shows Ca^{2+} be coordinated by $3Cl^{-} + 4H_2O$, forming $Ca_2Cl_4(H_2O)_8$ molecular moieties that are held together by only weak H-bonds and van der Waals forces. This is quite different from the structures of antarcticite ($CaCl_2 \cdot 6H_2O$) (Torii and Ossaka 1965), in which columns of face-sharing $Ca(H_2O)_9$ polyhedra are linked through Cl^- ions, or sinjarite (Aljbouri and Aldabbagh 1980), in which $CaCl_4(H_2O)_2$ octahedra share corners to form $CaCl_2(H_2O)_2$ sheets, linked via H-bonds. Ghiaraite can be considered an intermediate hydrate of $CaCl_2$, between sinjarite and antarcticite. There does not appear to be any isostructural minerals.

Sonnenfeld and Kühn (1993) noted the presence of a mineral with this formula in an evaporite from Sergipe, Brazil, and introduced the name sergipite for it. But no mineralogical data were presented.

The natural origin of ghiaraite: monitoring the $CaCl_2$ and chlorocalcite ($KCaCl_3$) kinetics

In order to definitively demonstrate that ghiaraite has a natural origin we investigated the kinetic behavior of a synthetic $CaCl_2$ crystalline compound under the same temperature and humidity conditions usually present in laboratory (23 °C and 30% of relative humidity). About 150 mg of powder $CaCl_2$ were deposited above a zero-background sample holder (in pure silicon) and kept for five hours at 300 °C in order to have an anhydrous starting material. The temperature and the relative humidity were monitored observing fluctuations of about 1 °C and 1% of relative humidity.

Very fast X-ray powder diffraction analyses were carried out, with each diffractogram collected over 3 minutes between 10 and 46° in 2θ. The measurements were performed in a continuous mode over five hours. Considering the "zero minute" the exact instant when the sample was extracted from the furnace, the first X-ray measurement was performed after 3 minutes: after only 3 minutes the sample resulted to be constituted by about 70% of $CaCl_2$ and 30% of $CaCl_2 \cdot 2H_2O$ (the quantitative analyses were performed by method). The natural analogue of $CaCl_2 \cdot 2H_2O$ is called sinjarite (Aljbouri and Aldabbagh 1980). The diffractograms showing the kinetics investigated are plotted in Fig. 7a: it is possible to note that $CaCl_2$ (indicated with symbol A) decreases gradually to disappear after 36 minutes, completely transforming to sinjarite (indicated with symbol B). After 39 minutes sinjarite starts to transform to ghiaraite [$CaCl_2 \cdot 4H_2O$], indicated with symbol T in Fig. 7b. After 1 hour and 3 minutes sinjarite and ghiaraite are present at 50% and only after 1 hour and 51 minutes sinjarite completely disappears (Fig. 7c). From 1 hour and 51 minutes on, only ghiaraite remains but it starts to become amorphous..

The second step of our kinetic analysis was focused on the possibility that ghiaraite could be originated by the chlorocalcite decomposition after the extraction of the sample from the ejecta by Scacchi in 1872. Therefore, we synthesized a sample of chlorocalcite (prepared by melting a 1:1 mixture of KCl and $CaCl_2$ at 750 °C for 2 hours). As done for the above experiments, the X-ray measurements were performed very quickly with single measurements of 3 minutes each. After 1 hour and 5 minutes chlorocalcite was totally decomposed to KCl and an amorphous compound and sinjarite and/or ghiaraite never crystallized.

Concerning ghiaraite, we should recall (see experimental method section at X-ray powder diffraction) that after the opening of the vial in which the original sample was kept and the preparation of the X-ray experiment the total time necessary to obtain the diffractogram was 8 minutes. Vial opening, sample preparation and X-ray analysis were performed under the same identical conditions described above (23 °C and 30% of relative humidity). Our kinetics studies clearly indicate that ghiaraite in 8 minutes could not be formed by hydration of $CaCl_2$ or sinjarite.

Scacchi described that he stored the ghiaraite-bearing sample extracted from the ejecta very quickly (a few minutes or even less) and even if a small amount of air remained trapped in the vial it was not sufficient to hydrate sinjarite to from ghiaraite as chlorocalcite, the strongly dominant phase, acted as a very strong buffer as demonstrated by our kinetic experiments.

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Table 1. X-ray powder-diffraction data for ghiaraite including the *d*-spacings calculated using the crystal structure data by Thewalt and Bugg (1973).

h	***k***	***l***	$d_{obs.}$	$I_{rel.}$	$d_{calc.}$	$d_{calc.}$	$I_{rel.}$
			ghiaraite	ghiaraite	ghiaraite	Thewalt and Bugg (1973)	Thewalt and Bugg (1973)
0	**1**	**0**	**6.124**	**47**	**6.130**	**6.130**	**53**
1	**0**	**0**	**5.874**	**73**	**5.875**	**5.874**	**99**
1	-1	0	5.315	29	5.317	5.315	31
1	**-1**	**-1**	**4.600**	**88**	**4.603**	**4.599**	**100**
1	**1**	**-1**	**3.569**	**46**	**3.568**	**3.568**	**56**
0	1	2	3.296	38	3.295	3.295	42
1	-2	-1	2.998	44	2.996	2.996	40
2	**0**	**0**	**2.939**	**77**	**2.938**	**2.937**	**64**
1	**0**	**-3**	**2.717**	**88**	**2.719**	**2.716**	**78**
0	**2**	**-2**	**2.628**	**100**	**2.629**	**2.629**	**84**
2	-2	-1	2.574	29	2.573	2.571	21
2	-2	1	2.499	20	2.499	2.499	16
1	2	-1	2.396	36	2.397	2.397	33
0	**2**	**2**	**2.350**	**25**	**2.350**	**2.350**	**20**
2	**-2**	**-2**	**2.300**	**24**	**2.301**	**2.300**	**19**
1	**2**	**1**	**2.204**	**75**	**2.204**	**2.204**	**76**
1	-3	-1	2.090	33	2.090	2.090	31
0	1	-4	2.067	23	2.067	2.067	20

Figure captions

Figure 1. Original sealed glass vial deposited by Scacchi in 1872 at Real Museo di Napoli. The vial is about 5 cm long.

Figure 2. Satellite view of the Vesuvio volcano showing the locality where the projectile containing ghiaraite was found (from: Immagini©2012 Cnes/Spot Image, DigitalGlobe, GeoEye, Map data©2012 Google).

Figure 3. SEM image of the intermixed sample of chlorocalcite, ghiaraite, sylvite and hematite (large single crystal at the bottom of the sample).

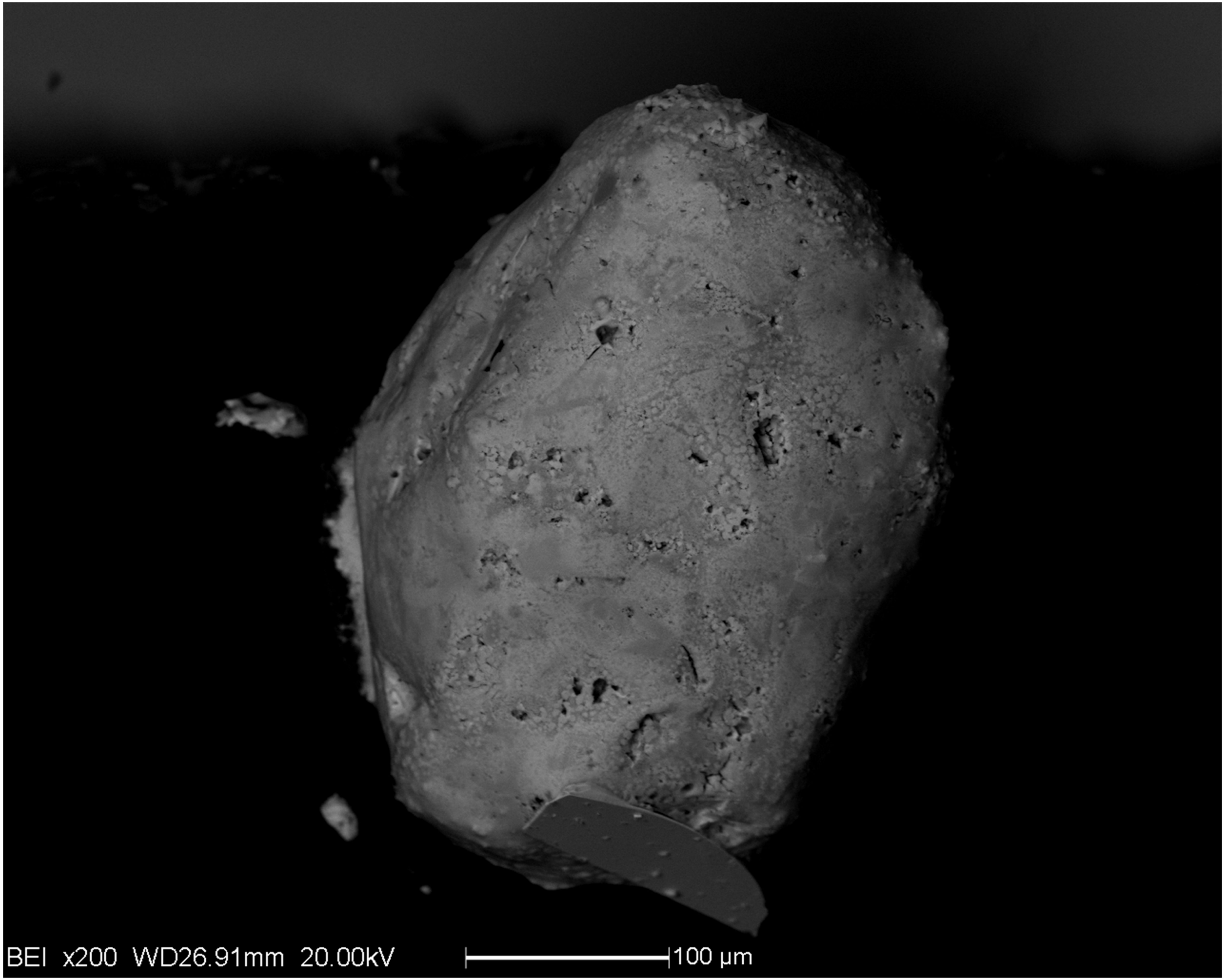
Figure 4. Enlargement of Fig. 2 with evident ghiaraite (isometric and euhedral grains) and chlorocalcite (surrounding matrix).

Figure 5. Diffractogram of the sample containing ghiaraite (indicated with symbol G) (reference diffractogram: ICSD card n° 8061). In green and in brown chlorocalcite (ICSD card n° 00-021-1170) and sylvite (ICSD card n° 98-009-9788) are shown.

Figure 6. Qualitative analysis by EDS of chlorocalcite and ghiaraite performed on the sample shown in Fig. 2.

Figure 7. X-ray powder diffractograms relative to the kinetics of anhydrous $CaCl_2$ (symbol A), sinjarite (symbol B) and ghiaraite (symbol T).


Massa di Somma
Comune di San Sebastiano Al Vesuvio
Municipio
Via Panoramica Fellapane
Massa di Somma
Locality where the ejecta containing ghiaraite was found
Via S. Vito
Via Sac Benedetto Cozzolino
Ottaviano
Vesuvio
Parco Nazionale del Vesuvio
Santa Maria la Scala
500 m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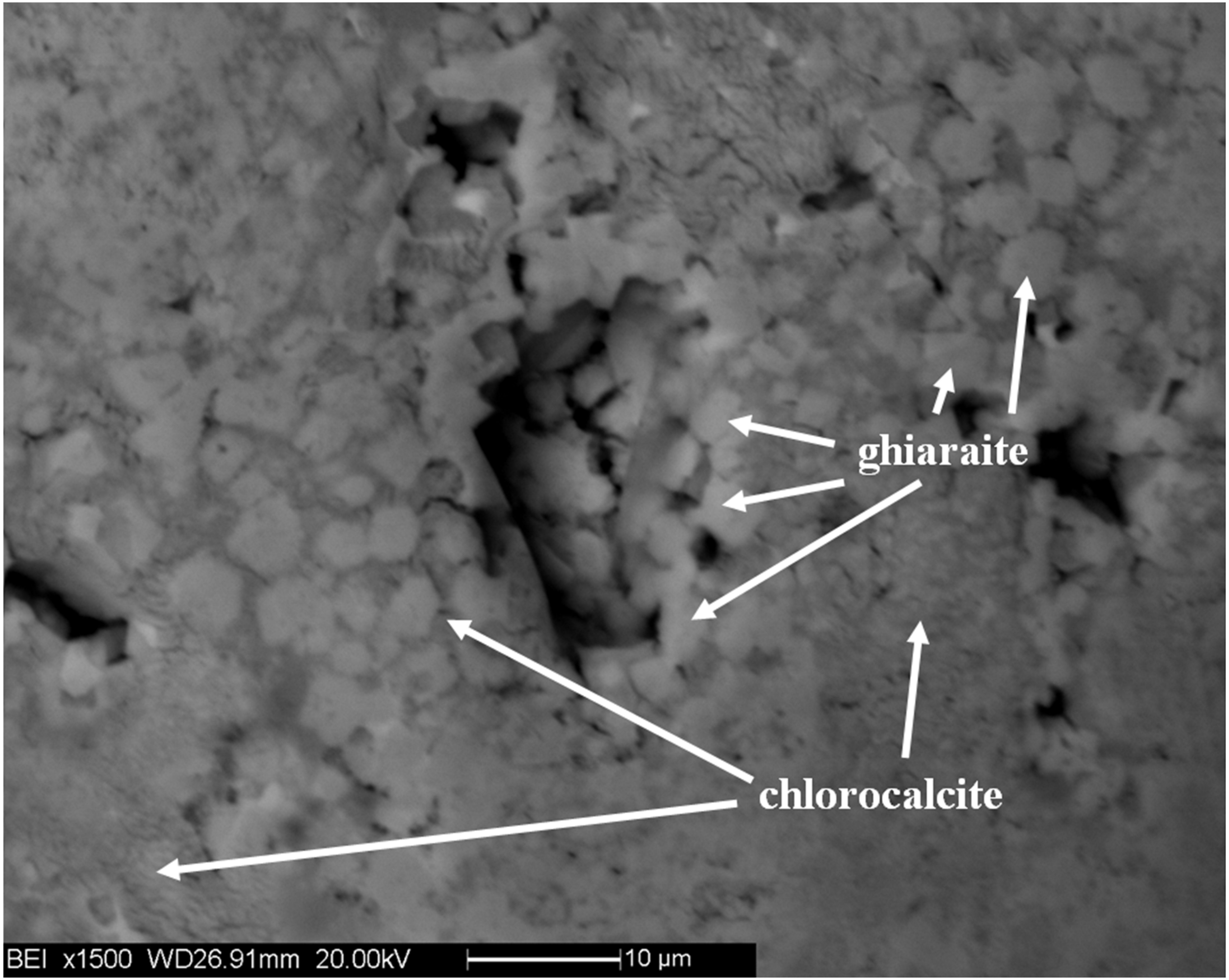
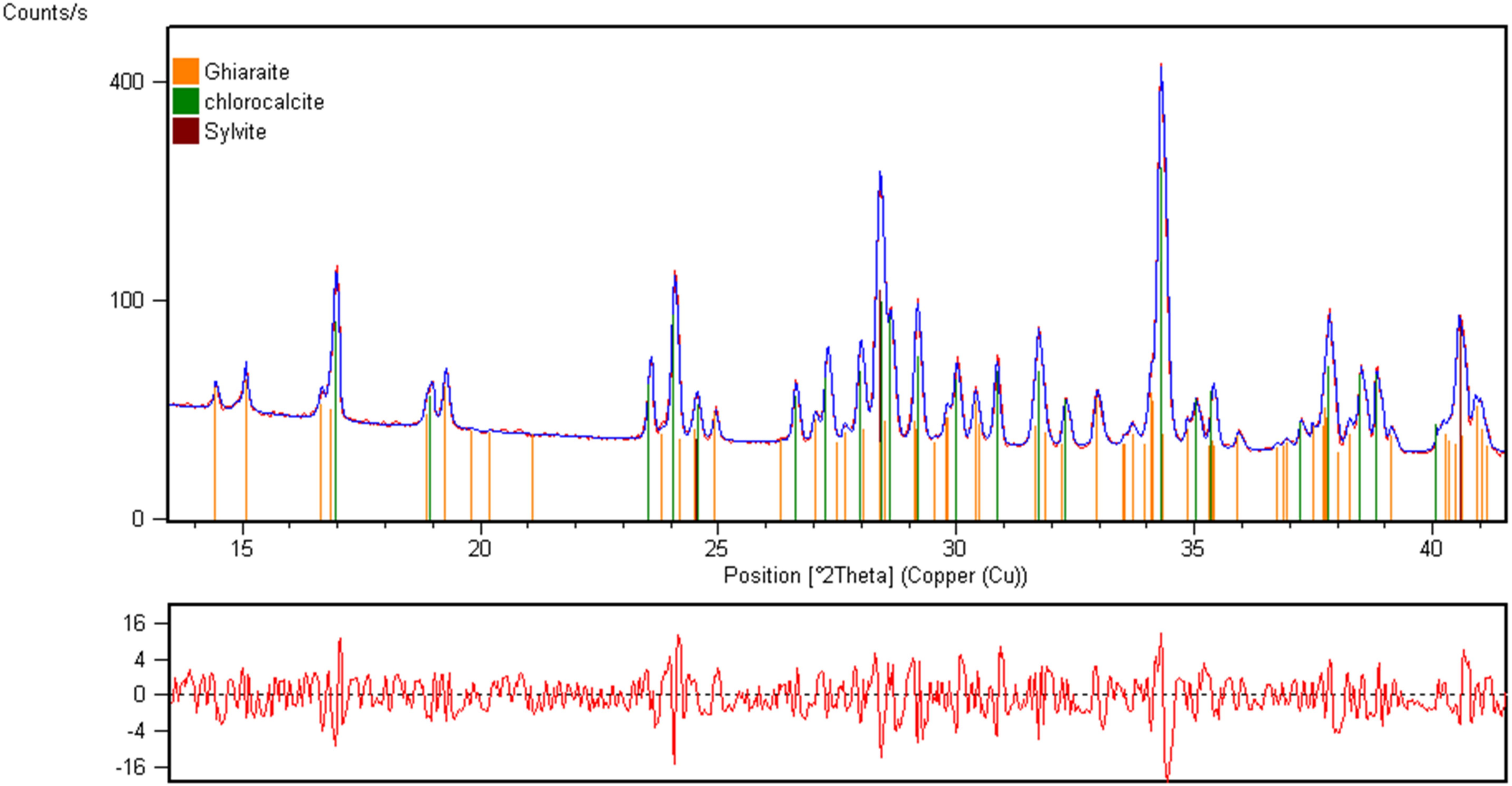
100 µm


ghiaraite
chlorocalcite
BEI x1500 WD26.91mm 20.00kV
10 µm


Counts/s
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100
0
Ghiaraite
chlorocalcite
Sylvite
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20
25
30
35
40
Position [°2Theta] (Copper (Cu))
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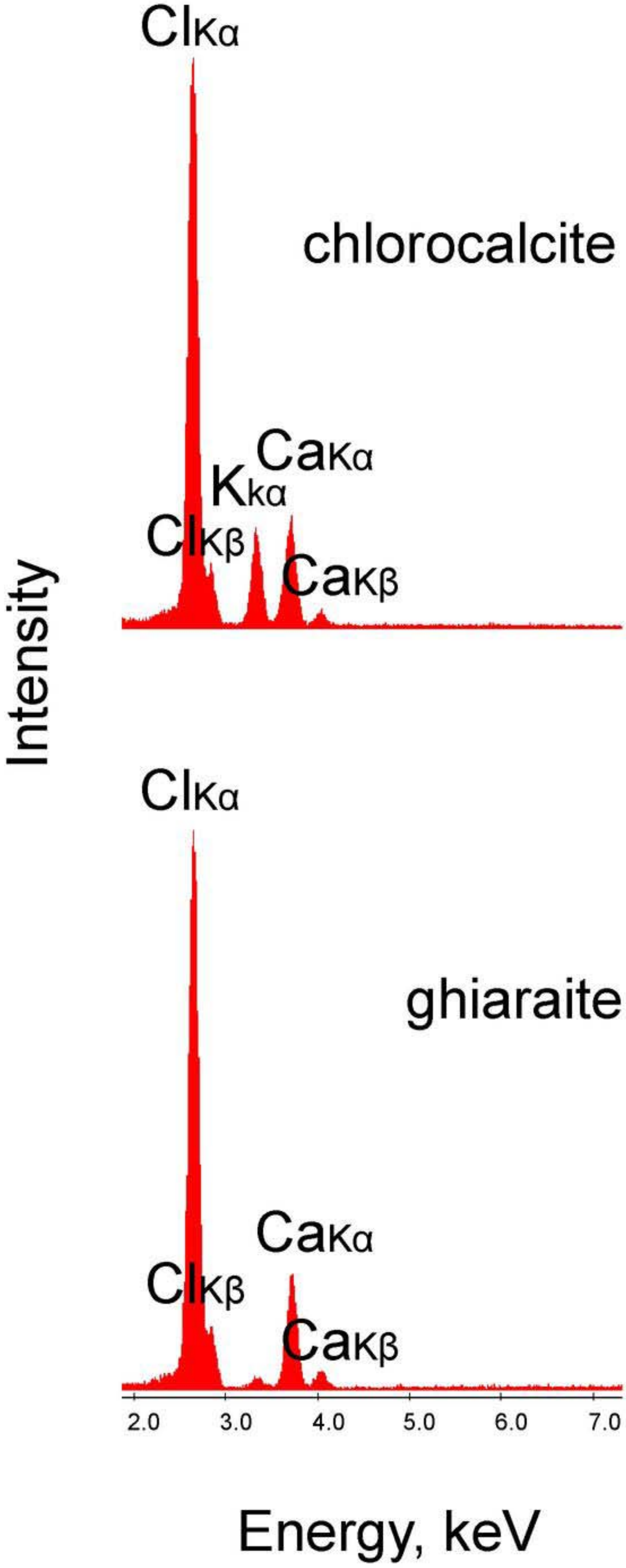
4
0
-4
-16


ClKα
chlorocalcite
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CaKβ
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ClKα
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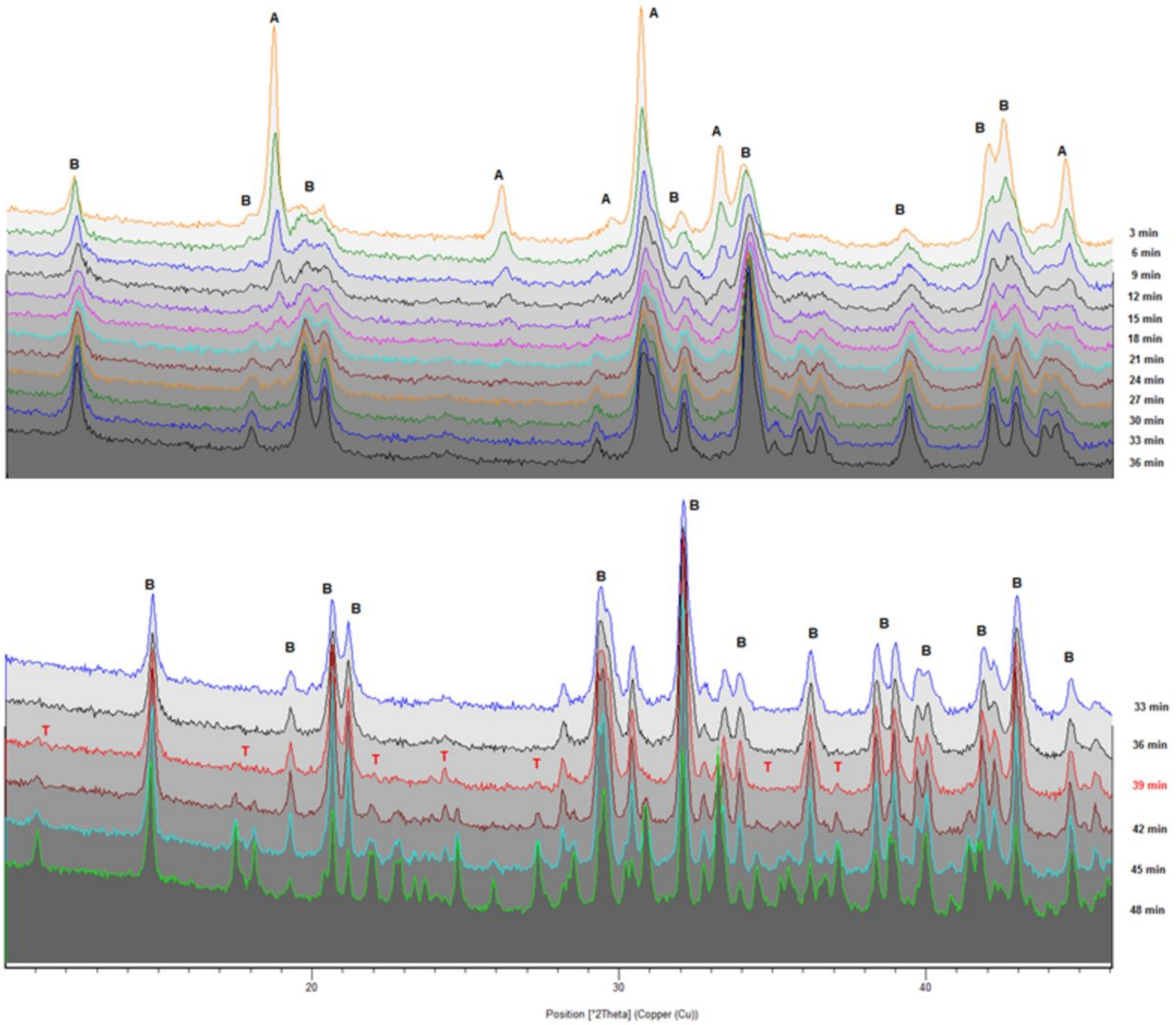
5.0
6.0
7.0
Energy, keV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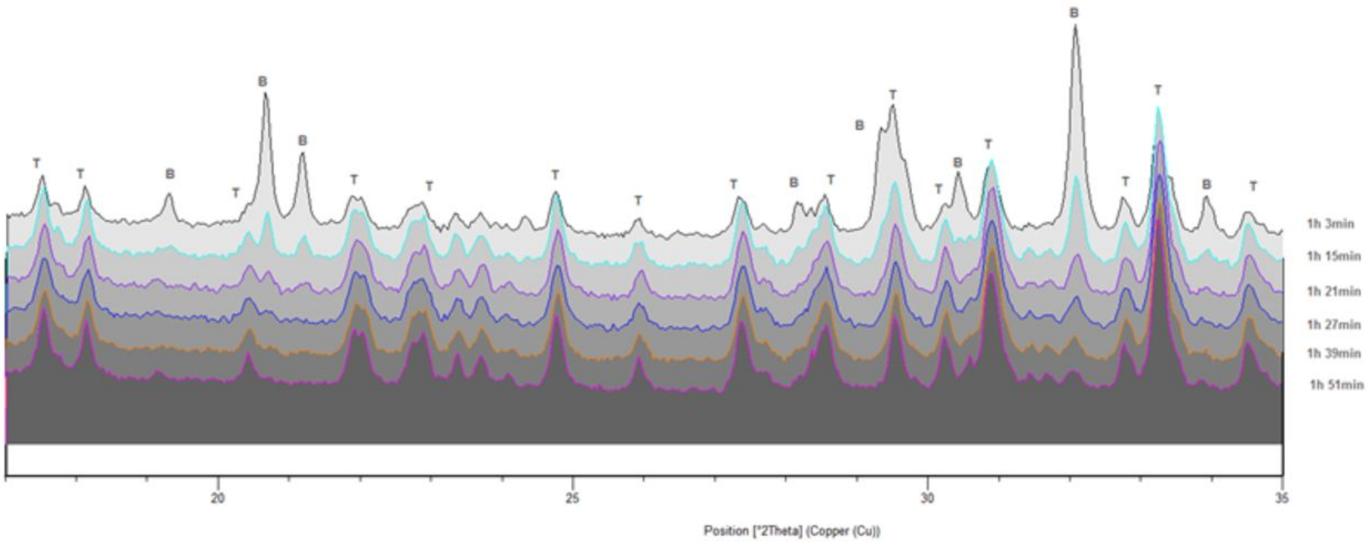
B
B
B
B
B
B
T
T
T
T
T
T
T
33 min
36 min
39 min
42 min
45 min
48 min
20
30
40
Position [°2Theta] (Copper (Cu))


T
T
B
T
B
B
T
T
T
T
T
B
T
B
T
T
B
T
B
T
T
B
T
1h 3min
1h 15min
1h 21min
1h 27min
1h 39min
1h 51min
20
25
30
35
Position [°2Theta] (Copper (Cu))