

MINERALS FROM MACEDONIA**IX. DISTINCTION BETWEEN SOME RHOMBOHEDRAL CARBONATES BY FT IR SPECTROSCOPY****Petre Makreski, Gligor Jovanovski**

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The FT IR spectroscopy is used in order to discriminate between the calcite group (calcite, CaCO_3 ; magnesite, MgCO_3 ; siderite, FeCO_3) as well as the dolomite group (dolomite, $\text{CaMg}(\text{CO}_3)_2$; kutnahorite, $\text{CaMn}(\text{CO}_3)_2$) of rhombohedral carbonate minerals originating from Macedonia. Although both groups of the studied minerals share essentially the same structure, being collectively called rhombohedral carbonates, significant frequency differences between the corresponding ν_3 , ν_2 and ν_4 active modes in their FT IR spectra are observed. The frequency variation is particularly expressed in the case of the ν_4 mode. It enables to distinguish the studied five geologically important carbonate minerals from one another as well as to determine the presence of impurities of some minerals in the corresponding two-component mixtures. It is (e.g.) shown that the low limit of detection of impurities of calcite in dolomite and vice versa amounts about 1 wt %. The effect of the sample powdering extent on the spectral appearance is studied as well. An elemental analysis on three morphologically different siderite mineral species with identical infrared spectra as well as for two kutnahorite samples whose infrared spectra are also identical is performed.

Keywords: minerals; Macedonia; discrimination; rhombohedral carbonates; FT IR spectroscopy; atomic absorption spectrometry

INTRODUCTION

The need to develop rapid and simple but at the same time effective methods for mineral identification as well as confirmation of their purity using different techniques (analytical, spectroscopic etc.) is continual. Although it is recommendable the mineral identification and characterization to be followed by the complementary rather than the competitive use of various techniques, sometimes it is particularly valuable and gratefully encouraged to develop the new simple methods to distinguish or determine the presence of impurities in the mineral samples which share the same structure (as it is the case with the studied rhombohedral carbonate minerals) using only one technique (e.g., FT IR spectroscopy, Raman spectroscopy, X-ray diffraction etc.).

A higher local symmetry of the CO_3^{2-} ions (D_3) in the structure of the studied rhombohedral carbonate minerals (calcite and dolomite type)

compared to the symmetry of the same present anion in aragonite type (C_s) is manifested by the absence of ν_1 mode in their FT IR spectra [1–4]. Therefore, IR spectroscopy enables relatively easy to discriminate between the calcite and dolomite type, on the one hand, and the aragonite type of carbonate minerals, on the other hand [5]. IR spectroscopy can also be used to perform a semi-quantitative analysis in order to calculate the content of impurities of aragonite in calcite and vice versa and to determine the lower limit of detection [5, 6]. The detection of impurities in aragonite-calcite mineral mixtures can also be performed by a powder X-ray diffraction [7].

On the other hand, the distinction between the rhombohedral carbonate (calcite and dolomite type) minerals using IR spectroscopy is expected to be more complex or sometimes impossible because they share the same structure. Consequently,

the D_3 symmetry of the CO_3^{2-} ions in their structures is expected to cause the appearance of corresponding ν_2 , ν_3 and ν_4 modes with very similar IR frequencies. Their discrimination by IR spectroscopy is additionally complicated by the common appearance of these minerals in the nature [8].

Continuing our broad spectroscopic and analytical research on carbonate minerals from Macedonia, in the current paper we present the results of

the application of FT IR spectroscopy for discrimination between the carbonate minerals with the rhombohedral symmetry as well as the detection of very low content of impurities of magnesite in calcite and vice versa in their two-component mixtures including the determination of the low limit of detection. The results of the identification of the collected samples of kutnahorite ($\text{CaMn}(\text{CO}_3)_2$) using FT IR spectroscopy are also presented.

EXPERIMENTAL

Samples and reagents

The studied calcite type minerals were collected from various localities: calcite (Mrzen, Damjan, Alšar, Trojaci), siderite (Zletovo), magnesite (Pčinja), while dolomite type minerals, dolomite and kutnahorite, were taken from Prilep and Sasa, respectively. The investigated minerals were carefully picked up under a microscope from the ore samples and then powdered.

All reagents and standards used for the elemental analysis were of analytical grade.

Instrumentation

The Perkin-Elmer FT IR system 2000 interferometer was employed for recording the spectra using the KBr pellet method.

A Varian SpectrAA 640Z Zeeman electrothermal atomic absorption spectrophotometer with a Varian PSD-100 Autosampler and a Varian SpectrAA 880 with deuterium correction (for flame determination) were used for determination of the

trace elements in three morphologically different samples of siderite. The flame spectrophotometer was also employed for elemental analysis of two kutnahorite samples.

Procedures

The quantitative FT IR analyses were carried out taking exactly 1 mg of the minerals (and mineral mixtures) in 250 mg KBr.

The powdered siderite (0.1–0.2 g) was dissolved in 5 ml conc. HCl, 1 ml HNO_3 and 1 ml H_2O_2 . The solution was evaporated to dryness and residue dissolved with 50 ml of 8 mol/l HCl. Then solution was transferred into a separatory funnel, adding 5 ml isoamyl acetate and shaking for 1 min. This operation was repeated 4 times. To avoid interference of chlorides, an inorganic layer was evaporated and the residue was dissolved in 5 ml of 2 mol/l HNO_3 .

Dissolution of the powdered kutnahorite samples (0.1 g) was performed in 1.5 ml conc. HCl.

STRUCTURAL CHARACTERISTICS OF RHOMBOHEDRAL CARBONATES

The structure of all rhombohedral carbonates belongs to the *halite type*, being consisted of CO_3^{2-} groups instead of Cl^- anions and M^{2+} replacing Na^+ cations [9]. The plane of the triangular CO_3^{2-} groups as well as the formed (by CO_3^{2-} groups) layers are perpendicular to the one of the shortened 3-fold axes of the previous cube which becomes the c axis of the transformed cube into rhombohedron. The carbon atom within the formed CO_3 layers occupies the selected triangular sites of the layer formed by close-packed layers of oxygen atoms. Consequently, the position of the C atom is equivalent to the cubic close packing being re-

peated in every third layer, whereas an exact duplicate layer of CO_3 groups is repeated only every sixth sheet. Therefore, the unit cell is six CO_3 layers along the c axis.

Octahedral positions between CO_3 layers are occupied by the divalent cations. In this type of structure each oxygen anion is coordinated by three cations: carbon cation within the CO_3 layer and divalent cations above and below the CO_3 sheets. Compared to the calcite group of minerals where all octahedral sites are occupied by the same cation, two significantly different-sized atoms are accommodated in the dolomite group of minerals

(one of them being Ca and the the smaller Mg, Fe or Mn).

The formation of the solid solution among the studied calcite group minerals is strongly depended on the size of the cations (ionic radii). Thus, Ca^{2+} as a largest cation (1.00 Å), causes formation of a limited solid solution of calcite with other calcite type minerals where the ionic radii is smaller: magnesite (Mg^{2+} , 0.72 Å) and siderite (Fe^{2+} , 0.78 Å) (see Table 1). On the other hand, the solid solution between the minerals siderite and magnesite (consisting of similar-sized cations) is complete. The solid solution between the studied representa-

tives of the dolomite group, kutnahorite and dolomite, is somewhat limited. According to Bermanec [8], a solid solution between the members of the calcite group, on the one hand, and the dolomite group, on the other hand, is also possible.

The cations of the studied rhombohedral carbonates are six coordinated (except the polymorph of calcite – aragonite, where Ca is nine coordinated) and their ionic radii do not exceed 1 Å. All divalent cations included in formation of known carbonates which are characterized by larger ionic radii do not fit into this group.

Table 1

The most important crystallographic data for the studied rhombohedral carbonates [9]

Mineral	Crystal system	Space group	Unit cell parameters Å	Unit cell volume Å ³	Z	Cation properties ^a	
						Ionic radii Å	CN
Calcite, CaCO_3	Hexagonal (rhombohedral)	$R\bar{3}c$	$a = 4.99; c = 17.06$	367.9	6	1.00	6
Siderite, FeCO_3	Hexagonal (rhombohedral)	$R\bar{3}c$	$a = 4.69; c = 15.38$	293.0	6	0.78	6
Magnesite, MgCO_3	Hexagonal (rhombohedral)	$R\bar{3}c$	$a = 4.63; c = 15.01$	278.7	6	0.72	6
Kutnahorite, $\text{CaMn}(\text{CO}_3)_2$	Hexagonal (rhombohedral)	$R\bar{3}$	$a = 4.85; c = 16.34$	332.9	3	(0.91) _{av}	6
Dolomite, $\text{CaMg}(\text{CO}_3)_2$	Hexagonal (rhombohedral)	$R\bar{3}$	$a = 4.80; c = 15.98$	318.9	3	(0.86) _{av}	6

^aAccording to Shannon [10].

RESULTS AND DISCUSSION

The effect of powdering of the mineral samples

As known, in the case of compounds with high refractive index (e. g. rutile with $n = 2.605$), the IR spectra of minerals using KBr discs are strongly dependent on the particle size and other conditions of the particular specimen preparation [11]. Consequently, the spectra of the studied samples belonging to the same mineral species are often rather different. Having in mind the relatively small values of the refractive index for calcite ($n = 1.658$) and kutnahorite ($n = 1.727$) [9], the appearance of unexpected bands [1–5, 12–15] at 1703, 1084, 975 and 585 cm^{-1} in the infrared spectra of their handly powdered samples (Fig. 1) was firstly prescribed to the presence of some type of impurities rather than to the sample particle size.

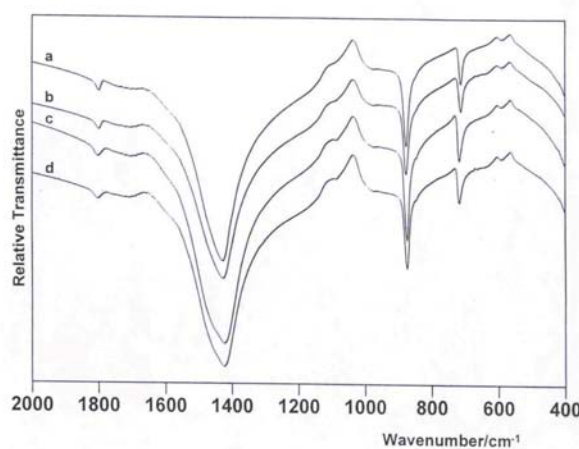


Fig. 1. FT IR spectra of hand-powdered samples of calcite from Mrzen and Trojaci (a, b), kutnahorite („otavite”) from Sasa (c) and kutnahorite from Sasa (d)

The additional powdering of the samples in special steel mills has, however, shown that the unexpected bands are eliminated, and only the expected bands due to ν_3 (antisymmetric stretching mode), ν_2 (out-of-plane bending mode), and ν_4 (in plane bending mode) appear in their infrared spectra (Fig. 2). Although the ν_1 mode for rhombohedral carbonates is forbidden, its appearance as a very small band in the infrared spectra of the studied minerals at 1084 cm^{-1} (Fig. 2) is the result of the relaxation of the selection rules due to distortions in the structure caused by structural damage during grinding [16].

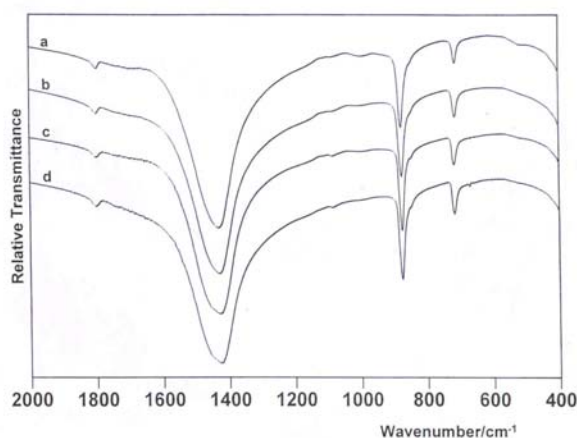


Fig. 2. FT IR spectra of additionally powdered samples of calcite from Mrzen and Trojaci (a, b), kutnahorite („otavite”) from Sasa (c) and kutnahorite from Sasa (d)

Kutnahorite or otavite?

The appearance of some frequency differences between the spectrum of the third sample supposed to be otavite, CdCO_3 (Fig. 2c) and the spectrum of the fourth sample representing kutnahorite, $\text{CaMn}(\text{CO}_3)_2$ (Fig. 2d) was expected after the additional powdering of the samples. It was shown, however, that the spectra of both samples

are identical. This was taken as a strong indication that the studied mineral samples belong to the same mineral type. Namely, the bands due to the ν_3 and ν_2 modes in the spectra of both (kutnahorite) samples are registered at 1425 and 873 cm^{-1} , respectively, whereas, the ν_4 mode appears at 716 cm^{-1} (Fig. 2 and Table 2). All mentioned frequencies are very similar to those reported in the literature [17].

Table 2

The spectroscopic data of the studied rhombohedral carbonates

Mineral	Vibrational frequencies / cm^{-1}		
	ν_3	ν_2	ν_4
Calcite – CaCO_3	1427	876, 875 ^a	712, 725 ^a
Kutnahorite ^b – $\text{CaMn}(\text{CO}_3)_2$	1425	873	716
Dolomite – $\text{CaMg}(\text{CO}_3)_2$	1443	881	728
Siderite ^c – FeCO_3	1421	866	731
Magnesite – MgCO_3	1450	887	748

^aCalcite sample from Damjan.

^bBoth kutnahorite species have the same frequency values.

^cAll three siderite species have the same frequency values.

Since the discrimination between kutnahorite and otavite based on their morphology (crystal shape, color etc.) is practically impossible [8, 9], the quantitative elemental analysis was undertaken and the content of the Ca, Mn, Cd as well as Fe and Mg in these two samples was determined in order to confirm the above presumption. The results have undoubtedly shown (see Table 3) that both mineral samples belong to kutnahorite, containing about 94 wt % Ca and Mn (expressed in carbonates) instead of Cd which appears as a trace element rather than as a major constituent. It agrees well with the IR spectral data.

Table 3

Determined content of some elements (expressed in carbonates) in kutnahorite samples taken from the Sasa locality using flame atomic absorption spectrometry

Mineral	w(CaCO_3) %	w(MnCO_3) %	w(FeCO_3) %	w(MgCO_3) %	w(CdCO_3) %	Total %
Kutnahorite („otavite”), $\text{CaMn}(\text{CO}_3)_2$	68.83	25.19	2.15	0.69	$18.91 \cdot 10^{-3}$	96.88
Kutnahorite, $\text{CaMn}(\text{CO}_3)_2$	70.45	23.60	1.79	0.67	$4.55 \cdot 10^{-3}$	96.51

Calcite samples from Trojaci, Mrzen and Alšar vs the specimen from Damjan

Continuing our spectroscopic study of the minerals collected from various localities in the Republic of Macedonia, our attention was focused on the specimens considered as calcite, one of the most widely spread mineral in the nature. The infrared spectra of the calcite samples from Trojaci, Mrzen, Alšar and Damjan, in the spectral region between 2000 and 400 cm^{-1} are shown on Fig. 3.

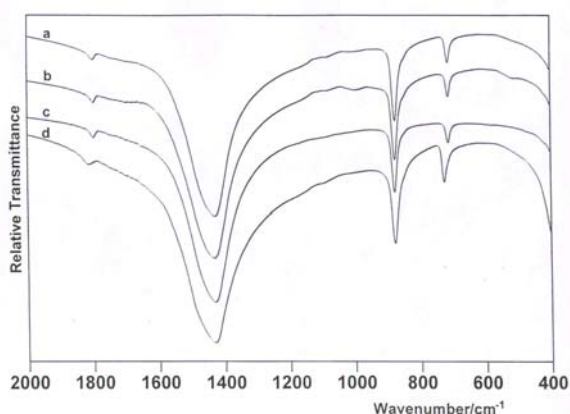


Fig. 3. FT IR spectra of calcite from Trojaci (a), Mrzen (b), Alšar (c) and Damjan (d).

As expected, three IR active modes are registered in each spectrum. As it can be seen, the frequencies of the ν_3 and ν_2 bands are practically the same for all calcite samples, being 1427 and 876 cm^{-1} (875 cm^{-1} in Damjan sample), respectively. The blue shifting of 13 cm^{-1} (much larger than the instrument resolution of 4 cm^{-1}) for ν_4 mode in the spectrum of the calcite sample originating from Damjan (725 cm^{-1}), compared to the corresponding band in the spectra of other three calcite specimens (712 cm^{-1}) is observed. The significantly higher frequency for ν_4 mode is not in accordance with the reported data in the literature (710–713 cm^{-1}) [1–5, 12–15, 18]. The above mentioned blue shifting of the ν_4 mode (approaching the frequency of the ν_4 mode around 730 cm^{-1} in siderite, FeCO_3 , specimen) could be considered as a significant evidence about the high contamination of Damjan calcite sample with isomorphous siderite [4, 5, 11]. This corresponds with the evident oxidation on the surface of the Damjan calcite sample. The presence of the siderite impurities in the calcite sample from Damjan does not cause significant shifting of the frequency of other two broader bands because the frequency gap between the corresponding ν_3 and ν_2

modes in calcite and siderite is smaller and does not exceed 9 cm^{-1} (see Table 2).

The influence of the cation size and unit cell volume

The spectral differences (discrepancies between the IR active vibrational modes) for the series of five studied rhombohedral carbonates which share the same structure are shown on Fig. 4 and Table 2. The discrepancy is particularly pronounced for the weakest band due to the ν_4 mode. It is evident that the frequency of the ν_4 mode is the most sensitive to the change of the divalent cation size [$r(\text{Ca}^{2+}) > r(\text{Fe}^{2+}) > r(\text{Mg}^{2+})$], being shifted to the higher frequencies [$\nu_4(\text{calcite}) < \nu_4(\text{siderite}) < \nu_4(\text{magnesite})$] for the smaller cations and a smaller unit cell volume [$V(\text{calcite}) > V(\text{siderite}) > V(\text{magnesite})$] of the studied mineral (see Tables 1 and 2). The smaller the cation is, the stronger the bending force constants are and cause closer stacking of the anions around it. The frequency of the ν_4 mode in kutnahorite, $\text{CaMn}(\text{CO}_3)_2$, (716 cm^{-1}) follows this trend and lies between the values of the corresponding modes in the infrared spectra of calcite (712 cm^{-1}) and rhodochrosite (722 cm^{-1}) [4] (Table 2). The corresponding cationic radii of Ca^{2+} and Mn^{2+} in calcite and rhodochrosite are 1.00 and 0.83 Å, respectively [10].

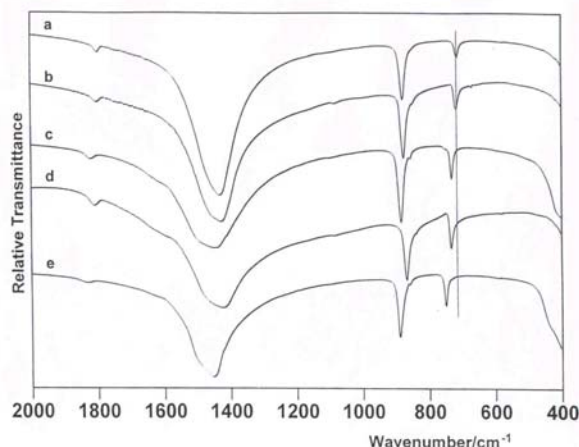


Fig. 4. FT IR spectra of studied rhombohedral carbonates: calcite (a), kutnahorite (b), dolomite (c), siderite (d) and magnesite (e)

Contrary to the ν_4 mode, the observed discrepancies between the corresponding ν_3 and ν_2 modes in the spectra of the series of the studied rhombohedral carbonates do not strictly correlate

with the values for the ionic radii size as well as with the unit cell volume values (Fig. 4, Table 2).

It is worth mentioning that the frequencies of the Raman active vibrational modes of the studied rhombohedral carbonates do not correlate with the corresponding cation radii [19].

Detection of the impurities in mineral samples

The appearance of ν_1 mode in the infrared spectra of the aragonite type of minerals (due to the lower (C_s) symmetry of the CO_3^{2-} anion compared to the D_3 symmetry in the rhombohedral calcite type) enables to determine the presence of rather low quantities of aragonite impurities in calcite [5]. Having in mind the previous discussion about the shifting of the band due to the ν_4 mode, it is interesting to see whether it can be used as an analytical band to detect the impurities in the two-component solid mixtures consisted of the rhombohedral carbonates. Determination of the present impurities is especially interesting and valuable in the cases when the minerals appear in common mixtures in the nature.

Two types of mixtures (magnesite–dolomite and magnesite–calcite) where the frequency of the corresponding ν_4 modes differs about 20 cm^{-1} in the former and 36 cm^{-1} in the latter case (Table 2) were selected. In the first case a series of mixtures of dolomite in magnesite where the content of dolomite ranges from 1 wt % to 10 wt % (1, 2, 5, 10 wt %) was prepared. The infrared spectra of the above mentioned mixtures as well as the spectra of the pure dolomite and magnesite in the ν_4 region are given in Fig. 5. As seen, a rather small frequency difference between the corresponding ν_4 modes (20 cm^{-1}) hardly allows detecting about 5 unsatisfactory wt % of dolomite in magnesite. The smaller frequency difference (16 cm^{-1}) between the corresponding Raman active ν_4 mode in the spectra of magnesite and dolomite does not promise more satisfactory results for detection of the impurities of dolomite in magnesite and vice versa [19].

The study was continued by preparing mixtures of calcite in magnesite (1, 2, 3, 5 and 10 wt %) and magnesite in calcite (1, 2, 5 and 10 wt %), where the ν_4 mode is found at 712 cm^{-1} and at 748 cm^{-1} , respectively (Table 2). The largest registered frequency difference among all five studied rhombohedral carbonate minerals of 36 cm^{-1} makes possible to detect the presence of about 1 wt % of calcite in magnesite (Fig. 6) and vice versa (Fig. 7). It should be mentioned that the lower limit of detec-

tion of the impurities of magnesite in calcite (amounting about 1 wt %) is more convincing due to the better baseline in the region where the higher frequency magnesite analytical band of the ν_4 mode appears (Fig. 7). On the other hand, the frequency difference between the Raman active ν_4 modes for calcite and magnesite amounts 22 cm^{-1} [19]. The closer appearance of the corresponding bands in the Raman spectra (compared to infrared ones) for both mineral forms could not provide lower limit of detection of impurities than 1 wt %.

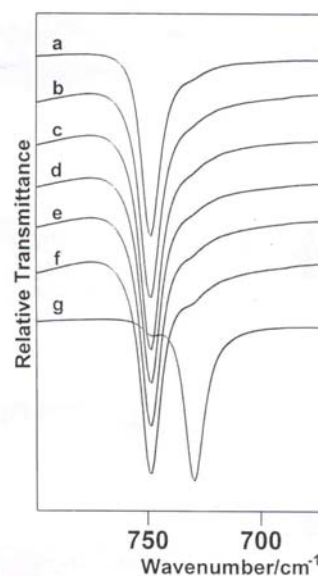


Fig. 5. FT IR spectra of magnesite (a) and dolomite (g) and mixtures of 1, 2, 3, 5 and 10 wt % dolomite in magnesite (b–f).

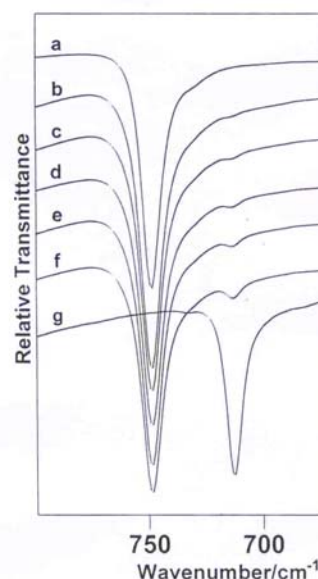


Fig. 6. FT IR spectra of magnesite (a) and calcite (g) and mixtures of 1, 2, 3, 5 and 10 wt % calcite in magnesite (b–f).

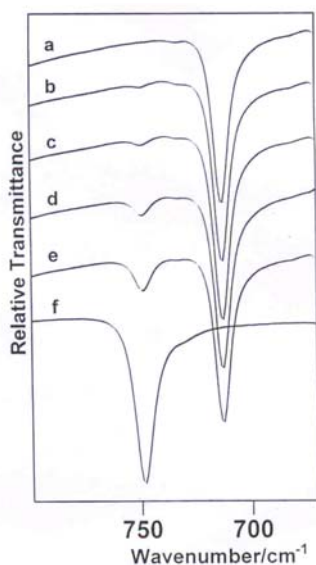


Fig. 7. FT IR spectra of calcite (a) and magnesite (f) and mixtures of 1, 2, 5 and 10 wt % magnesite in calcite (b–e).

Elemental analysis on siderite minerals

The studied three siderite samples from Zletovo exhibit morphological discrepancies. Two of them are shell-like being white and brown colored, whereas the third one is white colored with the kidney-like form of the crystals. In spite of that, their FT IR spectra (see Fig. 8) are practically identical, with observed maxima at 1421, 866 and 731 cm^{-1} for ν_3 , ν_2 and ν_4 modes, respectively. The above mentioned morphological discrepancies of the three siderite samples followed by the identity of their infrared spectra was the reason to undertake the quantitative analysis for the presence of

Mn, Zn, Ag, Cd, Co, Cr, Ni and Pb. The determined content of the investigated elements is given in Table 4. As it can be seen, a larger content of Zn and Cd in the kidney-like siderite specimen compared to other two shell-like samples is found.

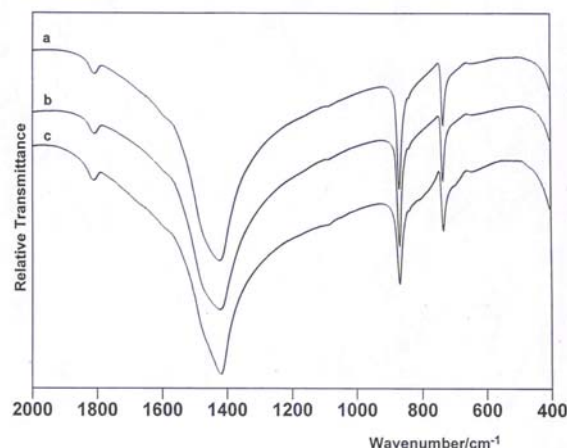


Fig. 8. FT IR spectra of brown shell-like (a), white shell-like (b) and white kidney-like (c) crystal forms of siderite from Zletovo

Their content, however, is still too small to influence the view of the infrared spectrum. It was also found that the content of Mn, compared to the presence of other metals is very high, but similar in all samples from Zletovo deposit, which is in accordance with the previous data about the presence of Mn minerals in Fe minerals [20–22]. Some other (for the appearance of the infrared spectra negligible) discrepancies for the content of Cr and Ni in various samples are also found.

Table 4

The content of investigated elements in siderite mineral samples from Zletovo

Studied samples	Locality (mine)	Mn mg/g	Zn mg/g	Ag $\mu\text{g/g}$	Cd $\mu\text{g/g}$	Co $\mu\text{g/g}$	Cr $\mu\text{g/g}$	Ni $\mu\text{g/g}$	Pb $\mu\text{g/g}$
Siderite ^a -1	Zletovo	139.0	0.990	31.0	2.33	< 0.01	12.0	0.87	0.181
Siderite ^b -2	Zletovo	157.8	1.105	42.5	2.92	< 0.01	5.04	9.46	0.235
Siderite ^c -3	Zletovo	138.6	7.728	34.7	11.5	< 0.01	0.93	8.54	1.135

^aWhite colored shell-like form. ^bBrown colored shell-like form. ^cWhite colored kidney-like form.

CONCLUSION

It was shown that the FT IR spectroscopy enables to distinguish between some rhombohedral calcite type minerals which essentially share the same structure. It is mainly due to the rather ex-

pressed sensitivity of the ν_4 vibrational mode to the change of the divalent cation size [$r(\text{Ca}^{2+}) > r(\text{Fe}^{2+}) > r(\text{Mg}^{2+})$]. It was also shown that the most pronounced frequency difference between the corre-

sponding ν_4 modes in dolomite and calcite is large enough and makes it possible to detect the presence of very low content (1 wt %) of magnesite in calcite and vice versa.

In spite of the morphological differences (in shape and color) between the three studied siderite samples, their infrared spectra are found to be identi-

cal. The performed atomic absorption elemental analysis revealed the extremely high presence of rhodochrosite (MnCO_3) in all siderite samples.

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Резиме

МИНЕРАЛИ ОД МАКЕДОНИЈА

IX. РАЗЛИКУВАЊЕ НА НЕКОИ РОМБОЕДАРСКИ КАРБОНАТИ СО FT IR СПЕКТРОСКОПИЈА

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Клучни зборови: минерали; Македонија; разликување; ромбодарски карбонати;
FT IR спектроскопија; атомска апсорпциона спектрометрија

Фуриеовата трансформна инфрацрвена спектроскопија (FT IR) е ползувана за разликување на некои минерали од калцитен (калцит, CaCO_3 ; магнезит, MgCO_3 ; сидерит, FeCO_3) и од доломитен тип (доломит, $\text{CaMg}(\text{CO}_3)_2$; кутнахорит, $\text{CaMn}(\text{CO}_3)_2$) со потекло од Република Македонија. И покрај фактот што двете групи кристализираат во хексагоналниот (ромбодарски) кристален систем и поседуваат иста структура (поради што се наречени ромбодарски карбонати), забележани се значителни фреквенциски разлики меѓу активните модови ν_3 , ν_2 и ν_4 во нивните FT IR спектри. Фреквенциската разлика е најизразена кај модот ν_4 . Тоа овозможува спомнатите геолошки важни кар-

бонати да бидат разликувани еден од друг, како и да се определува присуството на нечистотии на една компонента во друга. Така, најниската граница за детекција на нечистотии од калцит во доломит и обратно изнесува околу еден масен процент. Дискутирано е и влијанието на степенот на иситнетоста на пробата врз појавувањето на дополнителни спектрални ленти. Исто така е направена елементарна анализа на три сидеритни примероци кои, и покрај значителни морфолошки разлики, имаат идентични инфрацрвени спектри. Истото е направено и за двата кутнахоритни примероци.