

K'titel rechts:  
Minerals from Macedonia  
K'titel links:  
G. Jovanovski et al.

N. Jb. Miner. Abh.

Stuttgart, ● 2002

## Minerals from Macedonia. IV. Discrimination between some carbonate minerals by FTIR spectroscopy

Gligor Jovanovski, Viktor Stefov, Bojan Šoptrajanov, Skopje, and Blažo Boev, Štip, Macedonia

With 4 figures and 1 table

JOVANOVSKI, G., STEFOV, V., ŠOPTRAJANOV, B. & BOEV, B. (2002): Minerals from Macedonia. IV. Discrimination between some carbonate minerals by FTIR spectroscopy. – N. Jb. Miner. Abh. (●): 000–000; Stuttgart.

**Abstract:** The use of FTIR spectroscopy to distinguish between some geologically important carbonate minerals (calcite –  $\text{CaCO}_3$ , aragonite –  $\text{CaCO}_3$ , siderite –  $\text{FeCO}_3$ , magnesite –  $\text{MgCO}_3$  and dolomite –  $\text{CaMg}(\text{CO}_3)_2$ ) originating from Macedonia and to detect mineral impurities in them is considered. It was shown that the series of the studied isomorphous calcite type minerals is an ideal test case for the evaluating the influence of the corresponding cation upon the band frequencies of the carbonate  $\nu_3$ ,  $\nu_2$  and  $\nu_4$  modes in their infrared spectra. It enables to distinguish the isomorphous calcite type carbonates from one another. In the course of the quantitative determination of the composition of mixtures it is shown that the limit of detection of impurities of aragonite in the mixtures with calcite (or other calcite type minerals) is around 1 wt%. The spectra of natural calcite and siderite were compared to those of their synthetic analogues.

**Key words:** Carbonate minerals, Macedonia, detection, discrimination, FTIR spectroscopy.

### 1. Introduction

Various instrumental techniques and procedures for mineral detection, identification, discrimination and quantitative determination have been developed during the last few decades. The most frequently used among them are X-ray diffraction (BISH & POST 1993), thermal analysis (MOLDOWSKI & MORGAN 1980), optical diffuse reflectance (GAFFEY 1986), Raman (GRIFFITH 1974) and infrared (FARMER 1979) spectroscopy (only a selection of the relevant references is given above). Since all these techniques have their own advantages

and shortcomings, it is strongly recommendable (especially in the case of mineral characterization) to use as many of them as possible in a complementary rather than competitive manner. The importance of classical chemical analysis cannot be overemphasized.

Very often, however, it is advantageous to use (or to develop) rapid and simple methods for mineral discrimination as well as for detection of impurities in mineral mixtures using *only one* of the above-mentioned techniques, e.g., Fourier transform infrared (FTIR) spectroscopy or X-ray powder diffraction. Both techniques, namely, yield results quickly and provide a rapid indication about the presence of impurities.

As a part of a broader study of the structural and spectroscopic characteristics of minerals originating from Macedonia, we have previously studied the vibrational (IR and Raman) spectra of some sulfide minerals from Alšar (TRAJKOVSKA et al. 1992, ŠOPTRAJANOV et al. 1993, TRAJKOVSKA et al. 1993, ŠOPTRAJANOV et al. 1994, ŠOPTRAJANOV et al. 1997) as well as the analytical application of the FTIR spectra and X-ray diffraction patterns in the case of the carbonate minerals calcite and aragonite (JOVANOVSki et al. 1999a, 1999b, 1999c). Later the minerals siderite, magnesite and dolomite as well as calcite specimens from various localities in Macedonia were included in the study. Some sulfate minerals (gypsum, barite and their synthetic analogues) by FTIR and Raman spectroscopy were in the meantime characterized as well (STEFov et al. 1999, 2001).

In the current paper we present the results of our study on the application of FTIR spectroscopy for identification of various carbonate minerals from Macedonia and the determination of the low detection limit for aragonite in mixtures with calcite-type minerals.

## 2. Experimental

The mineral samples were collected from various localities in Macedonia (calcite: Sivec, Bešište, Bučim, Prilep, Sasa, Bela Pola – Nebregovo, Zletovo; aragonite: Ržanovo; siderite: Zletovo; magnesite: Pčinja; dolomite: Sivec). They were picked under a microscope from the ore samples. The synthetic analogues of calcite and siderite of p.a. quality were used for the analysis.

The infrared spectra of the studied samples were recorded on a Perkin-Elmer FTIR system 2000 interferometer using the KBr pellet method. The acquisition of the spectra was done using the GRAMS ANALYST 2000 package (1991–1993). The GRAMS32 package (1991–1996) was employed for manipulations on the recorded spectra.

### 3. Mineral associations of the studied calcite, siderite, dolomite, magnesite and aragonite

Details about the carbonate mineral deposits in Macedonia are previously published in many papers. Some of them are mentioned below where a brief summary of the main characteristics of the mineral associations of the studied calcite, siderite, dolomite, magnesite and aragonite is given.

#### 3.1. The Sivec – Bela Pola deposit

The mineralogical, structural and textural composition of the Sivec – Bela Pola marble mass is made up of dolomite sugary-white marbles with jets, stripes and nests of calcite and striped calcite marbles (BARIC 1967, DUMURGANOV & STEFKOV 1994). The dolomite sugary-white marbles developed in the lowest levels are white, fine-grained (grain size 0.1 to 0.5 mm) homogenized, massive and rather compact. Their dolomite composition is partially related to their genesis because the lowest levels of the marble series of the Pelagonian massif are made up of dolomite and dolomite–calcite marbles. However, the whiteness, the homogeneity and the compactness, typical of this site, are largely related to the thermal influence and the metamorphic processes of the Pelagonian granitoids. The granitoid influence of the marbles is also proved by the occurrence of corundum, fluorite, paragonite, phengite, titanite, epidote minerals which have not been determined in other sites. The carbonate minerals such as calcite and dolomite are very common at these localities. The dolomite as well as calcite occurs in crystal forms incorporated in the dolomite marbles. The crystals almost always represent the basic rhombohedron.

#### 3.2. The Zletovo deposit

This lead-zinc vein type hydrothermal deposit is genetically associated with the processes of Tertiary magmatic activity. Several major types of ore parageneses are established at this deposit including the *low temperature oxide carbonate paragenesis* (siderite, rhodochrosite, calcite, barite, quartz, chalcedony) where the studied calcite and siderite samples were taken from (DENKOVSKI 1974, BOEV et al. 1992, SERAFIMOVSKI 1993). Calcite occurs in clear, occasionally transparent crystals of developed rhombohedral planes. Occasionally it also occurs as crystal aggregate. Siderite is a common carbonate in these associations occurring as fine-grained pale yellowish crystal aggregates.

#### 3.3. The Bučim deposit

The mineral composition of this porphyry copper and gold deposit consists of the various parageneses including the *low temperature petrogenous paragenesis* (quartz, calcite, chalcedony) where the studied calcite sample was taken

from (BOEV et al. 1992, CIFLIGANEC 1993, TUGAROV & SERAFIMOVSKI 1995). Calcite occurs in association with quartz and chalcedony. It occurs in transparent crystals of variable size with clearly developed rhombohedral planes.

### 3.4. The Bešište deposit

A large travertine plate of some 20 km<sup>2</sup> in size has been found within the Pliocene sediments and volcanogene sediments between the villages of Bešište, Polčište and Manastirec in the Mariovo basin (JENKO 1958, PAVLOVSKI 1976). Large white calcite crystals of clearly pronounced rhombohedral planes can be found in this plate built up of carbonate groundmass.

### 3.5. The Sasa deposit

The Sasa lead-zinc deposit belongs to the hydrothermal deposits genetically associated with the Tertiary calc-alkaline intermediary magmatism. The mineral paragenesis of the deposit is rather complex containing various minerals (ALEKSANDROV 1992, ALEKSANDROV & SERAFIMOVSKI 1992, SERAFIMOVSKI & ALEKSANDROV 1995). The occurrence of carbonatite minerals present as calcite, dolomite, kutnahorite, rhodochrosite, siderite, ankerite, barite, octavite is of particular interest.

### 3.6. The 'Ržanovo deposit

The 'Ržanovo deposit is situated in the central part of Mount Kozuf. The open pit of this zone consists of ultrabasic rocks. The ore layer is about 750 meters long and 15 to 25 meters thick ending with faults in the NW and SE parts of the deposit. Veins filled with fibrous white minerals such as calcite, dolomite and aragonite can be observed within the serpentinized ultrabasic rocks (BOEV & STOJANOV 1982, JANKOVIC et al. 1997). The veins can be up to 80 cm thick.

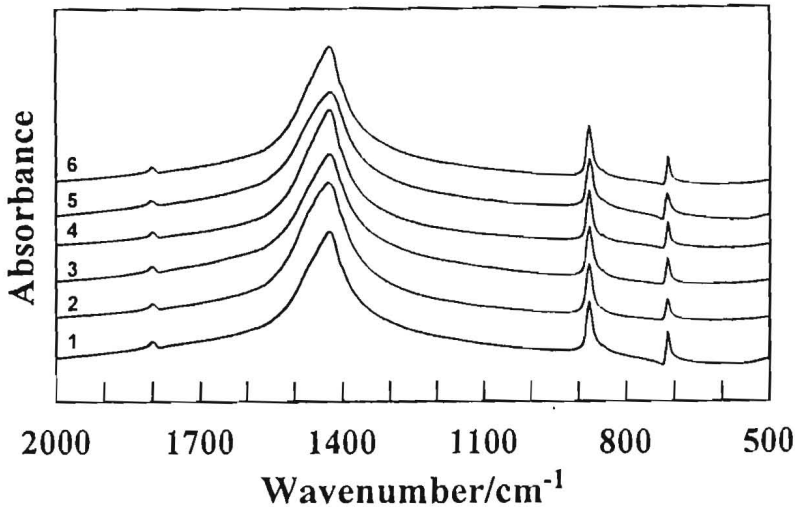
### 3.7 The Pčinja deposit

A magnesite occurrence in the form of veins and cherts wedging to depth has been found in close proximity to the flow of the River Pčinja into River Vardar (ARSOVSKI & DUMURGANOV 1995, ARSOVSKI & STOJANOV 1995). These are small bodies (about 1 m thick) occurring some 30 meters to depth. They are essentially joint in serpentinized dunites filled with magnesite, calcite and aragonite. Magnesite occurs as a large shell-like fracture and white to yellow mass.

## 4. Results and discussion

### 4.1. Identification and discrimination of minerals

Looking for genuine calcite specimens, we collected samples from the localities Sivec, Bešište, Bučim, Prilep, Sasa, Bela Pola – Nebregovo. The close



**Fig. 1.** The FTIR spectra of calcite mineral samples from Sivec (1), Bešište (2), Bučim (3), Prilep (4), Sasa (5) and Bela Pola (Nebregovo) (6).

similarity of the FT infrared spectra of all these specimens (Fig. 1) was taken as a strong indication that they belong to the same mineral species. The comparison of the wavenumber values of the IR-active internal  $\text{CO}_3^{2-}$  modes ( $\nu_2$  – out-of-plane bend;  $\nu_3$  – antisymmetric stretch and  $\nu_4$  – in-plane bend) with the corresponding values in the spectra of authentic calcite samples (WHITE 1974) showed that the collected mineral samples from various localities could indeed be characterized as being calcite specimens.

It should be pointed out that Fig. 1 demonstrates the reproducibility of the results of FTIR spectroscopy when various specimens of the same mineral species are studied: the wavenumber differences going from one spectrum to another do not exceed  $1 \text{ cm}^{-1}$  (a similar situation was encountered when Raman spectroscopy was used for analogous purposes (HERMAN et al. 1987). The comparison of the FTIR spectra of calcite and its synthetic analogue (Fig. 2) has shown that there is practically no frequency difference between the corresponding vibrational modes either.

On the other hand, when compared to the infrared spectrum of calcite from Sivec, the spectrum of the mineral from the Zletovo ore deposit (previously also believed to be calcite) exhibits observable differences (Table 1). Thus, the frequencies of the  $\nu_3$ ,  $\nu_2$  and  $\nu_4$  modes in the spectrum of the Zletovo mineral are  $1415$ ,  $866$  and  $732 \text{ cm}^{-1}$  whereas the corresponding values in the spectrum of the Sivec calcite are  $1424$ ,  $875$  and  $712 \text{ cm}^{-1}$  (the frequency difference is particularly pronounced for the  $\nu_4$  mode). Taken all together, it became clear

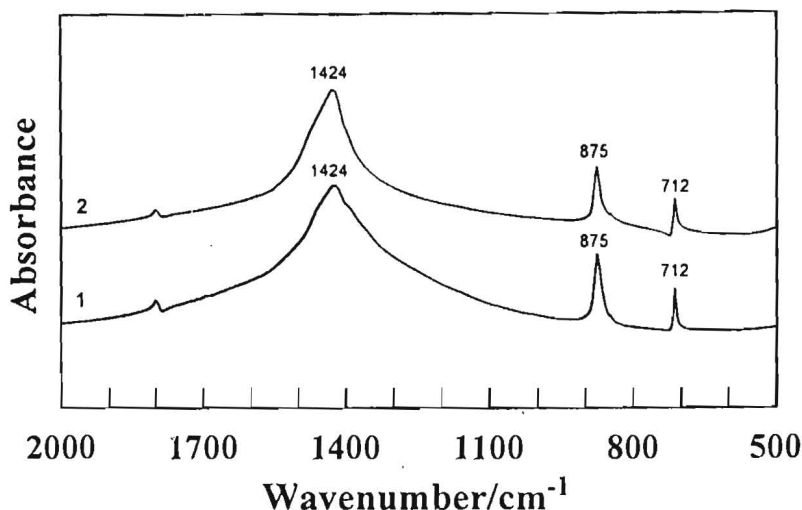


Fig. 2. The FTIR spectra of synthetic calcite (1) and mineral calcite (Sivec) (2).

that this specimen was not calcite, the outside appearance and the overall *similarity* of its IR spectrum with those of calcite (WHITE 1974) notwithstanding. It was shown that its FTIR spectrum is similar with the spectrum of the calcite type mineral siderite (WHITE 1974) (see Table 1).

Continuing the spectral study of the minerals of calcite type, significant differences between the spectra of the above discussed specimen considered as "siderite" and synthetic  $\text{FeCO}_3$  were registered in the region of  $\nu_3$  (1415 and  $1421\text{ cm}^{-1}$ , respectively) and  $\nu_4$  (732 and  $738\text{ cm}^{-1}$ , respectively) modes (Table 1). It was prescribed to the presence of significant amount (46.2%) of rhodochrosite ( $\text{MnCO}_3$ ) in the "siderite" mineral sample which was found by the elemental analysis (ZENDELOVSKA et al. 1999). Recently additional results concerning the elemental analysis of aragonite and siderite were published (ZENDELOVSKA et al. 2001, STAFILOV & ZENDELOVSKA 2001). They are in agreement with the results obtained by infrared spectroscopy.

As already pointed out, this made us more cautious and forced us to collect calcite samples from many locations and to include in our study other minerals (siderite, magnesite and dolomite) known (BRAGG & CLARINGBULL 1965) to be isomorphous with calcite. The IR-active carbonate bands are listed in Table 1. As can be seen, all these bands differ in their frequencies: the range for the  $\nu_3$  mode is  $1450\text{--}1415\text{ cm}^{-1}$ , that for the  $\nu_2$  mode is  $887\text{--}866\text{ cm}^{-1}$  and, finally, the highest frequency for the  $\nu_4$  mode is  $748\text{ cm}^{-1}$  and the lowest value for this mode is  $712\text{ cm}^{-1}$ . When the values for any particular band in the spectra of the four studied carbonates are compared, it is seen that the smallest frequency

**Table 1.** Some structural and spectroscopic characteristics of calcite type minerals (magnesite, dolomite, siderite, calcite) and aragonite.

Mineral	Characteristics of the cation			Average cation–oxygen distance/Å <sup>h</sup>	Covalent character of the cation–oxygen bond/% <sup>h</sup>	Vibrational frequencies/cm <sup>-1</sup>		
	Effective radius/Å <sup>a</sup>	A <sub>r</sub>	CN			v <sub>3</sub>	v <sub>2</sub>	v <sub>4</sub>
Magnesite MgCO <sub>3</sub>	0.72	24.31	6	2.14	29	1450	887	748
Dolomite CaMg(CO <sub>3</sub> ) <sub>2</sub>	(0.86) <sub>av</sub>	32.20	6	2.25	24	1438	881	729
Siderite <sup>d</sup> FeCO <sub>3</sub>	0.78	55.85	6	2.18	31	1422	866	737
“Siderite” FeCO <sub>3</sub> with 46.2% MnCO <sub>3</sub>						1415	866	732
Calcite CaCO <sub>3</sub>	1.00	40.08	6	2.37	19	1424	875	712
Aragonite <sup>c</sup> CaCO <sub>3</sub>	1.18	40.08	9	2.49	19	1474	858	699

<sup>a</sup> According to SHANNON (1976).

<sup>b</sup> Taken from BOLDREV & POVARENENYKH (1968).

<sup>c</sup> The v<sub>1</sub> mode in the FTIR spectrum of aragonite appears at 1083 cm<sup>-1</sup>.

<sup>d</sup> According to WHITE (1974).

difference is not less than 9 cm<sup>-1</sup> for the v<sub>3</sub> mode, 6 cm<sup>-1</sup> for the v<sub>2</sub> and 11 cm<sup>-1</sup> for the v<sub>4</sub> one – appreciable larger than the experimental error. It is thus evident that the frequencies of the three IR-active modes have a diagnostic value and can be used to distinguish the isomorphous calcite-type carbonates from one another.

#### 4.2. Influence of the cations

The series of the isomorphous minerals (calcite, siderite, magnesite and dolomite) is, in fact, an ideal test case for evaluating the influence of the *cations* (the building structural constituents which are different) upon the band frequencies of the carbonate v<sub>3</sub>, v<sub>2</sub> and v<sub>4</sub> modes in the studied compounds.

It should be recalled that the structure of calcite (BRAGG & CLARINGBULL 1965) (and those of the rest of calcite-type minerals) is built up of columns of alternating cations and anions so that the M<sup>2+</sup> ions are situated above and below the planes of the CO<sub>3</sub><sup>2-</sup> anions in which the *p* electrons are delocalized. Thus, no true covalent bonds could be formed and the cation-to-oxygen distances would serve more as an indication of how far the cations are from the anion planes than for an estimation of the degree of covalent character of the

M–O bonds. If the structures of all members of the series are known, the  $M^{2+}$ –O distances are a straightforward experimental fact. Alternatively, the values of these distances may be estimated knowing the effective ionic radii (SHANNON 1976) of the respective  $M^{2+}$  ions. This, then, is the reason why the values of the effective radii of the  $M^{2+}$  ions are included in Table 1. Also, the relative cation mass of the respective cations, the estimated degree of covalent character of the cation-oxygen bond together with the observed frequencies of the IR-active carbonate modes are listed in this table. Although the extent and the direction of their influence are not straightforward, the analysis of the data in Table 1 shows that the increase of the effective radius of the cation is generally accompanied by red shift of the vibrational modes. It is worth mentioning that the frequencies of the carbonate modes in dolomite [ $CaMg(CO_3)_2$ ] follow this trend and lie between the values of the corresponding modes in the spectra of magnesite and calcite.

#### 4.3. Detection of impurities

Like other methods, the detection of mineral impurities by IR spectroscopy is based on the presence of analytical bands in the regions where there are no signals from the other constituents of the studied system (in the case of IR spectroscopy – no absorption bands from the major constituent). The lower local symmetry of the  $CO_3^{2-}$  ions in aragonite ( $C_s$ ) than in calcite ( $D_3$ ) leads to the appearance (at  $1083\text{ cm}^{-1}$ ) of the  $\nu_1$  mode (symmetric  $CO_3^{2-}$  stretch) in its IR spectrum. Since the  $\nu_1$  mode is infrared inactive under  $D_3$  symmetry, there are no bands in the corresponding regions of the IR spectra of calcite and its isomorphous analogues (siderite, magnesite and dolomite (Fig. 3)). Thus, the  $1083\text{ cm}^{-1}$  band can be considered as a good analytical band which makes it possible to detect the presence of small amounts of aragonite in mixtures with calcite-type minerals and even to make semi quantitative estimation of the aragonite content and to determine the low detection limit of aragonite in mixtures with such minerals.

The results of the latter task are illustrated in Figure 4 in which the spectrum of pure calcite (Sivec) is compared with the spectra of mixtures of calcite with 1%, 2%, 5% and 10% of aragonite. It is obvious that without special manipulations of the spectra, the lower limit of detection of aragonite in calcite is rather low and amounts to about 1 wt %.

Similar or even better results were obtained by powder X-ray diffraction. It was previously shown (JOVANOVSki et al. 1999 b) that the low limit for detection of aragonite in calcite is around 1 wt %, whereas the presence of even lower than 0.5 wt % impurities of calcite in aragonite can be detected by powder X-ray diffraction. The comparison shows that, in the present case, the



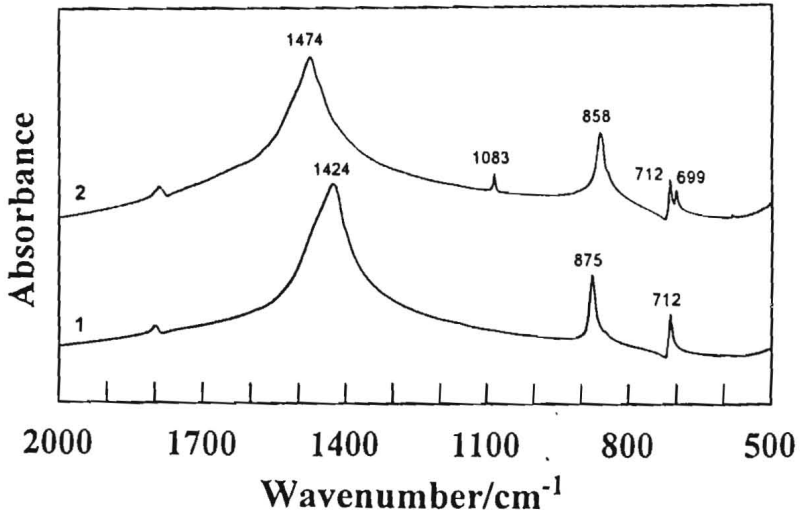


Fig. 3. The FTIR spectra of calcite (Sivec) (1) and aragonite (Ržanovo) (2).

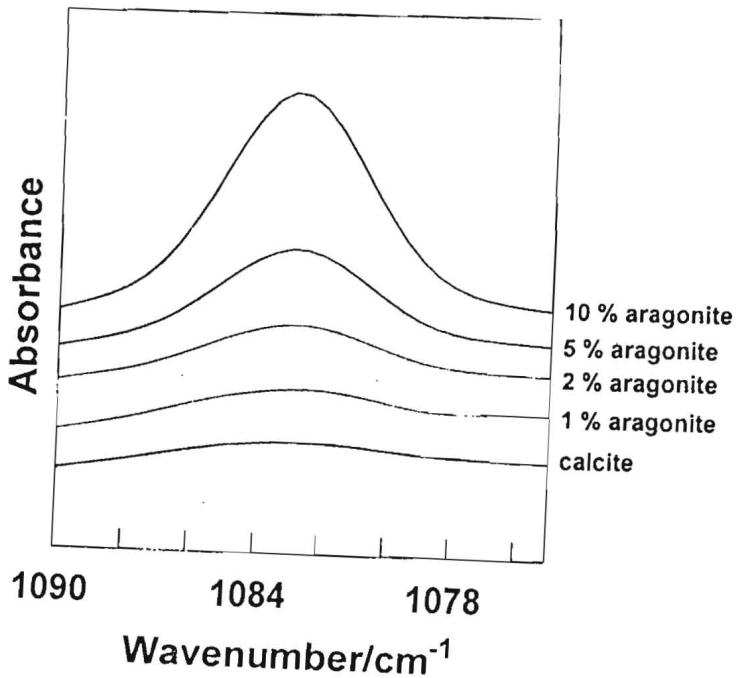


Fig. 4. The FTIR spectra of calcite (Sivec) and mixtures of calcite with aragonite (Ržanovo).

powder X-ray diffraction is a more sensitive method, compared to the FTIR spectroscopy. Since the sensitivity of a particular method depends on case to case, this should not, however, be used as a general conclusion.

## 5. Conclusions

It was shown that the series of the isomorphous calcite type minerals (calcite, siderite, magnesite and dolomite) is an ideal test case for the evaluating the influence of the corresponding cation upon the band frequencies of the carbonate  $\nu_3$ ,  $\nu_2$  and  $\nu_4$  modes in their infrared spectra. It means that the frequencies of the infrared vibrational modes are diagnostic and could be used to distinguish the isomorphous calcite type carbonates from one another.

In addition to other spectral differences, the appearance of the  $\nu_1$  mode (symmetric stretch) in the IR spectrum of aragonite (at  $1083\text{ cm}^{-1}$ ), which is absent in the spectra of the calcite type minerals, enables to distinguish between these two structurally different types of minerals as well as to detect the presence of small amounts of aragonite in the corresponding mixtures with the minerals of calcite type, the lower limit of detection of aragonite in calcite amounting about 1 wt %.

## Acknowledgements

This work was financially supported by the Ministry of Education and Science of the Republic of Macedonia. The authors are grateful to the authorities of the Zletovo, Sasa, Sivec, Bela Pola – Nebregovo, Bešište, Bučim and Ržanovo ore deposits for providing mineral samples for analysis.

## References

- ALEKSANDROV, M. (1992): Metalogenetic Characteristics of the Polimetallic Ore Deposit Sasa. – PhD Thesis, Štip, pp. 320.
- ALEKSANDROV, M. & SEĀAFIMOVSKI, T. (1992): Association of Elements in the Lead-Zink deposit Golema Reka-Sasa. – *Geol. Maced.* **6**: 3–14.
- ARSOVSKI, M. & DUMURGANOV, N. (1995): Alpine Tectonic Evolution of the Vardar Zone in Balkan Region. – *Internat. Workshop, Štip, Project 356 (IGCP-UNESKO)*, 1–5.
- ARSOVSKI, M. & STOJANOV, R. (1995): Geothermal Phenomenons Connected to Neotectonics and Magmatism in Macedonia, Skopje. – *Spec. Iss., MANU*, pp. 65.
- BARIC, LJ. (1967): Die Minerale im Dolomitmarmor von Sivec bei Prilep in Macedonien. – VI. Conf. of the Geol. Soc. of Yugoslavia, Ohrid, Book of Papers, 43–57.
- BISH, D. & POST, J. (1993): Quantitative Mineralogical Analysis using the Rietveld Full-pattern Fitting Method. – *Amer. Miner.* **78**: 932–940 (and references therein).
- BOEV, B. & STOJANOV, R. (1982): Metamorphism of Ni-Fe ores from Ržanovo-Studena Voda and the Zone Almopias. – *Geol. Maced.* **1**: 25–30.

- BOEV, B., SERAFIMOVSKI, T. & LEPITKOVA, S. (1992): The Isotopes of Strontium in the Tertiary Magmatic Rock from the Territory of Macedonia. – *Geol. Maced.* 5: 31–38.
- BOEV, B., CIFLIGANEC, V., STOJANOV, R. & LEPITKOVA, S. (1992): Oligocen-Neogenic Magmatism in the Locality of The Bučim. – *Geol. Maced.* 6: 23–32.
- BOLDYREV, A. I. & POVARENYYKH, A. S. (1968): Infrared Absorption Spectra of important Minerals from Carbonate and Nitrate Classes. – *Mineral. Sb.* 22: 11–21.
- BRAGG, W. L. & CLARINGBULL, G. F. (1965): *Crystal Structure of Minerals*. – Bell and Sons LTD, London, p. 134.
- CIFLIGANEC, V. (1993): Copper Mineralization in the Republic of Macedonia: Types and Distribution Patterns with Special Reference to the Porphyry Copper Deposit Bučim, Štip. – *Spec. Iss. No. 1.*, pp. 303.
- DENKOVSKI, G. (1974): Mineral Paragenesis of Dobrev-Zletovo Ore Deposit. – VIII. Congr. of Geol. of Yugoslavia, Bled, Book of Papers, 41–54.
- DUMURGANOV, N. & STEFKOV, N. (1994): The Geology and Technical Features of the Sivec Marble Deposit, Prilep, Republic of Macedonia. – *Geol. Maced.* 8: 29–33.
- FARMER, V. C. (1979): Infrared Spectroscopy in Mineral and Inorganic Chemistry. – Sixth Ceramic Chemists' Conference (on Silicate Analysis) *Spec. Publ. No. 98*, 101–122.
- GAFFEY, S. J. (1986): Spectra Reflectance of Carbonate Minerals in the Visible and Near Infrared (0.35–2.55 microns): Calcite, Aragonite and Dolomite. – *Amer. Miner.* 71: 151–162 (and references therein).
- GRAMS ANALYST for PE 2000 FTIR, Vers. 3.01 B, Galactic Industries Corporation, 1991–1993.
- GRAMS32 for Microsoft Windows, Vers. 4.10, Galactic Industries Corporation, 1991–1996.
- GRIFFITH, W. P. (1974): Infrared Spectra of Minerals. – In: FARMER, V. C. (ed.): *Miner. Soc.*, London, 119–135.
- HERMAN, R. G., BOGDAN, C. E., SOMMER, A. J. & SIMSON, D. R. (1987): Discrimination Among carbonate minerals by Raman Spectroscopy using the Laser Microprobe. – *Appl. Spectrosc.* 41: 437–440.
- JANKOVIC, S., BOEV, B. & SERAFIMOVSKI, T. (1997): Magmatism and Tertiary Mineralization of the Kozuf Metallogenetic District. – The Republic of Macedonia with Particular Reference to the Alšar Deposit, *Spec. Iss. No. 5*, Štip, pp. 262.
- JENKO, K. (1958): Geological Investigations of the Manastir-Bešište Region (Mariovo). – *Geoloski Zavod, Skopje, Macedonia, Spec. Iss. No. 6*, 32–40.
- JOVANOVSKI, G., ŠOPTRAJANOV, B., STEFOV, V., JOVANOVSKI, B. & KAITNER, B. (1999): Some Carbonate Minerals from Macedonia: Analytical Application of their FTIR Spectra and Powder XRD Patterns. – XVI Croatian Meeting of Chemists and Chemical Engineering, Split, Book of Abstracts, E6, 184.
- JOVANOVSKI, G., STEFOV, V., JOVANOVSKI, B., ŠOPTRAJANOV, B. & KAITNER, B. (1999): Minerals from Macedonia: I. Analytical Application of Powder X-Ray Diffraction Patterns of Calcite and Aragonite. – XVI Congress of Chemists and Technologists of Macedonia, Skopje, Book of Papers, 43–46.

- JOVANOVSKI, G., STEFOV, V., JOVANOVSKI, B., ŠOPTRAJANOV, B. & BOEV, B. (1999): Minerals from Macedonia. III. Determination of Calcite and Aragonite in Mineral Mixtures using FTIR Spectroscopy. – *Geol. Maced.* **13**: 69–74.
- MOLDOWSKI, E. A. & MORGAN, D. J. (1980): Identification and Estimation of Carbonate Minerals at low Levels by evolved CO<sub>2</sub> Analysis. – *Nature* **286**: 248–249 (and references therein).
- PAVLOVSKI, B. (1976): Geological Investigations of Mariovo Basen. – *Geoloski Zavod, Skopje, Macedonia, Spec. Iss.*, pp. 150.
- SERAFIMOVSKI, T. (1993): Structural-Metallogenic Features of the Lece-Halkidic Zone. – *Types of Mineral Deposits and Distribution, Spec. Iss. No. 2, Štip*, pp. 328.
- SERAFIMOVSKI, T. & ALEKSANDROV, M. (1995): Lead-Zink Deposits and Occurrences in the Republic of Macedonia. – *Štip, Spec. Iss. No. 4*, pp. 385.
- SHANNON, R. D. (1976): Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. – *Acta Crystallogr. Part A*, **32**: 751–767.
- STAFILOV, T. & ZENDELOVSKA, D. (2001): Determination of Trace Elements in Iron Minerals by Atomic Absorption Spectrometry. – *Turkish J. Chem.* **26**: in press.
- STEF OV, V., DIMITROVSKA, S., JOVANOVSKI, G. & ŠOPTRAJANOV, B. (1999): Minerals from Macedonia: II. Vibrational Spectra of some Sulfate Minerals. – *XVI Congress of Chemists and Technologists of Macedonia, Skopje, Book of Papers*, 47–50.
- STEF OV, V., JOVANOVSKI, G., ŠOPTRAJANOV, B., MINČEVA-ŠUKAROVA, B., DIMITROVSKA, S. & BOEV, B. (2000): Minerals from Macedonia, V. Characterization of Gypsum, Barite and their Synthetic Analogues by FTIR and Raman Spectroscopy. – *Geol. Maced.* **14**: 61–66.
- ŠOPTRAJANOV, B., TRAJKOVSKA, M., GRŽETIĆ, I., JOVANOVSKI, G. & STAFILOV, T. (1993) Infrared Spectra of M<sup>I</sup><sub>3</sub>M<sup>III</sup>S<sub>3</sub> Type Minerals (M<sup>I</sup> = Tl or Ag, M<sup>III</sup> = As or Sb). – *N. Jb. Miner. Abh.* **166**: 83–89.
- ŠOPTRAJANOV, B., TRAJKOVSKA, M., JOVANOVSKI, G. & STAFILOV, T. (1994): Infrared Spectra of Lorandite and Some other Minerals from Allchar. – *N. Jb. Miner. Abh.* **167**: 329–337.
- ŠOPTRAJANOV, B., TRAJKOVSKA, M., STAFILOV, T., JOVANOVSKI, G. & GRŽETIĆ, I. (1997): Infrared Spectra of Three M<sup>I</sup><sub>3</sub>M<sup>III</sup>S<sub>3</sub> Type Synthetic Minerals (M<sup>I</sup> = Ag or Tl, M<sup>III</sup> = Sb or As). – *Spectrosc. Lett.* **30**: 79–87.
- TRAJKOVSKA, M., ŠOPTRAJANOV, B., JOVANOVSKI, G. & STAFILOV, T. (1992): Vibrational Spectra of some Sulfide Minerals from Alšar. – *J. Mol. Struct.* **267**: 191–196.
- TRAJKOVSKA, M., ŠOPTRAJANOV, B., STAFILOV, T. & JOVANOVSKI, G. (1993): Determination of Lorandite and Realgar in Mineral Mixtures Using Infrared Spectroscopy. – *Geol. Maced.* **7**: 55–59.
- TUGAROV, N. & SERAFIMOVSKI, T. (1995): Geotectonic Setting and Metallogenic Features of the Borov Dol Porphyry Copper Deposit. – *Geol. Maced.* **9**: 89–96.
- WHITE, W. B. (1974): Infrared Spectra of Minerals. – In: FARMER, V. C. (ed.): *Miner. Soc., London*, 227–284.

- ZENDELOVSKA, D., STAFILOV, T. & BOEV, B. (1999): Determination of Zn, Mn and Fe in some Minerals by Flame Atomic Absorption Spectrometry. – *Geol. Maced.* **13**: 91–96.
- ZENDELOVSKA, D., PAVLOVSKA, G., ČUNDEVA, K. & STAFILOV, T. (2001): Electro-thermal Atomic Absorption Spectrometric Determination of Cobalt, Copper, Lead and Nickel Traces in Aragonite Following Flotation and Extraction Separation. – *Talanta* **54**: 139–146.

Received: August 7, 2001; accepted:

**Authors' addresses:**

G. JOVANOVSKI\*, V. STEFOV, B. ŠOPTRAJANOV, Institute of Chemistry, Faculty of Sciences, "Sv. Kiril i Metodij" University, P.O. Box 162, Skopje, Macedonia,  
e-mail: gligor@pmf.ukim.edu.mk

B. BOEV, Faculty of Mining and Geology, "Sv. Kiril i Metodij" University, Štip, Macedonia, e-mail: bboev@rgf.ukim.edu.mk

\* Corresponding author, e-mail: gligor@pmf.ukim.edu.mk