

## THE RAMAN STUDY OF CERTAIN CARBONATES

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### Abstract

Some of the most common carbonates have been investigated by non-contact Raman spectroscopy. The synthetic alkali carbonates  $K_2CO_3$  and  $Na_2CO_3$  have also been studied. The Raman spectrum of aurichalcite is different from that of malachite. This spectrum has a characteristic intense band at  $1069\text{ cm}^{-1}$  which is assigned to the  $\nu_1$  symmetric stretching mode of the carbonate unit. The two low intensity Raman lines of  $1485$  and  $1507\text{ cm}^{-1}$  may be ascribed to the  $\nu_3$  asymmetric stretching modes. To the  $\nu_4$  mode (doubly degenerate symmetric bending) are attributed the values of  $706\text{ cm}^{-1}$  ( $\nu_{4a}$ ) and  $733\text{ cm}^{-1}$  ( $\nu_{4b}$ ). A number of bands with different intensities are observed in the lowest spectral shift ( $285$ ,  $388$ ,  $430$ ,  $461$  and  $498\text{ cm}^{-1}$ ). These Raman lines are assigned to the CuO and ZnO stretching and bending vibrations. A single band of the OH-stretching modes is observed at  $3344\text{ cm}^{-1}$ .

**Key words:** nonpolarized Raman spectra, carbonates, alkali carbonates, aurichalcite

### Introduction

The Raman modes of carbonates, like those of sulfates, are classified into three types (Nakamoto, 1997): (i) vibrations of  $(CO_3)^{2-}$  groups (internal modes) (ii) vibrations of hydroxyl molecule (in the case of hydroxyl carbonates  $\approx 900\text{ cm}^{-1}$ ,  $1500$ - $1600\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ ), and (iii) vibration modes M-O from the interactions between the cation and O of either  $(CO_3)^{2-}$  or  $OH^-$  (external or lattice modes).

The carbonate ion  $(CO_3)^{2-}$  is a nonlinear four-atomic species and it must have  $3(4)-6=6$  normal modes of vibrations (Cotton, 1990). These six normal modes are illustrated in

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figures 1 and 2. The frequency of the fundamental vibration modes of the free carbonat ion are showed in table 1 (Scheetz and White, 1977). The  $\nu_2$  mode of  $(\text{CO}_3)^{2-}$ , which is Raman forbidden in the free ion, remains weak after coupling to the cations in the lattice.

Tab. 1 The frequency of the fundamental vibrational modes of the  $(\text{CO}_3)^{2-}$

Mode	Symmetry	Selection Rules	Frequencies ( $\text{cm}^{-1}$ )
			Scheetz and White (1977)
$\nu_1$ Nondegenerate symmetric stretch	$A'_1$	Raman	1064
$\nu_2$ Nondegenerate symmetric (out-of plane) bend	$A''_2$	IR	-
$\nu_3$ Doubly degenerate asymmetric stretch	$E'$	IR+Raman	1415
$\nu_4$ Doubly degenerate asymmetric (in-plane) bend	$E'$	IR+Raman	680

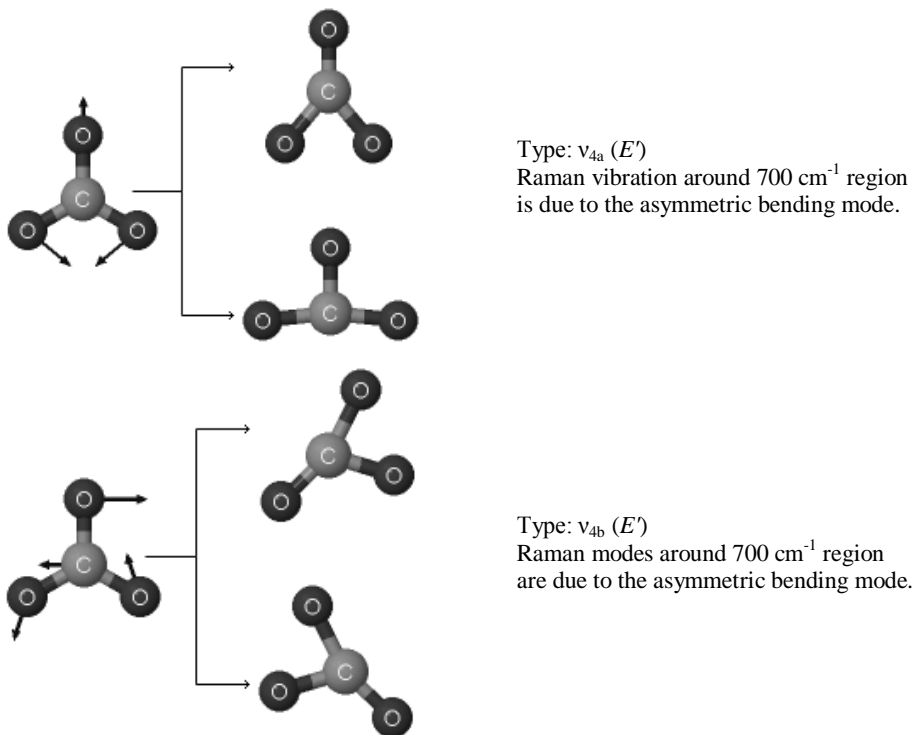


Fig. 1 Illustration for normal modes of vibration; displacement vectors are represented by arrows

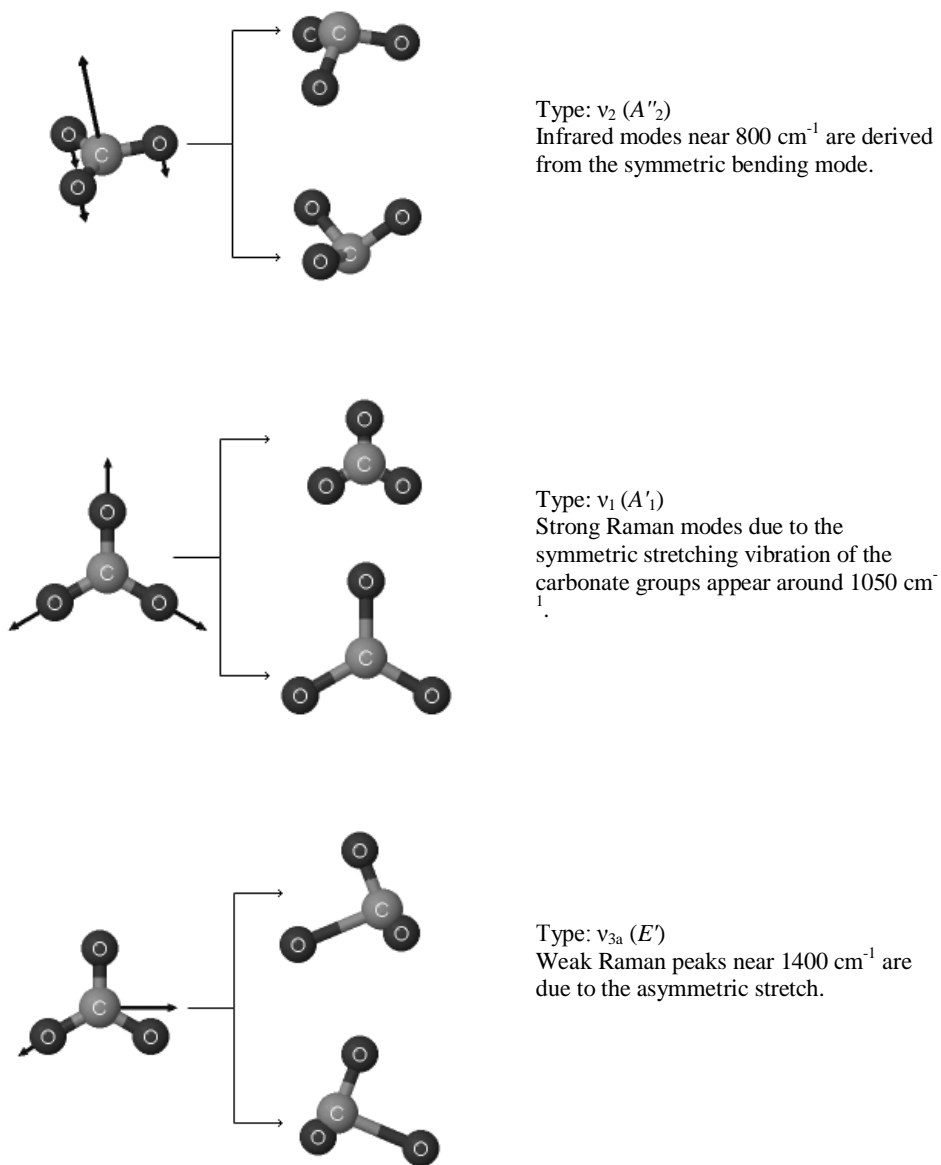


Fig. 2 Illustration for normal modes of vibration; displacement vectors are represented by arrows.

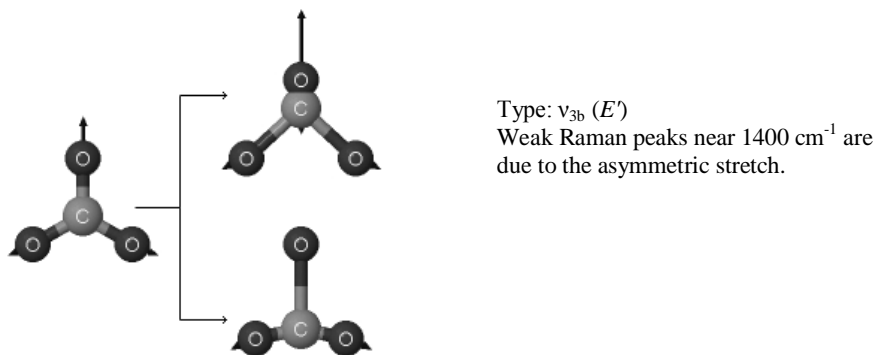


Fig. 2 (continued from the previous page)

## Analytical procedure

Raman spectra were obtained at room temperature with a Horiba Jobin-Yvon RPA-HE 532 Raman Spectrograph with multichannel air cooled ( $-70 \text{ }^\circ\text{C}$ ) CCD detector, using a doubled frequency NdYag laser,  $532 \text{ nm}/100 \text{ mW}$  nominal power. The spectral resolution is  $3 \text{ cm}^{-1}/\text{pixel}$ , and the spectral range between  $200$  and  $3400 \text{ cm}^{-1}$ . Raman system includes a “Superhead” fibre optic Raman probe for non contact measurements, with an 50X LWD Olympus visible objective,  $\text{NA} = 0.50$   $\text{WD} = 10.6 \text{ mm}$ .

Data acquisition was performed by 2-20 seconds exposure, 5-30 acquisitions, at laser magnification of 90-100%, to improve the signal-to-noise ratio. Spectra manipulations consists of a basic data treatment, such as baseline adjustment and peak fitting (Lorentz function).

## Samples

The samples used in the study are listed in table 2. The first nine samples with their sample number, belong to the collection of “*Grigore Cobălcescu*” Mineralogy and Petrography Museum of the “Alexandru Ioan Cuza” University of Iassy. The other two samples were synthetic alkaly carbonates.

## Results and discussions

### A. Anhydrous carbonates

#### 1. Calcite group

Three samples of minerals are used from the calcite group: calcite, siderite and rhodochrosite. The nonpolarized Raman spectra of the calcite, siderite and rhodochrosite are shown in figure 3.

Tab. 2 Samples used in the study

	Mineral	Sample no.	Location
1.	Calcite	5413	Guanajuato – Mexico
2.	Siderite	5455	Lobenstein – Germany
3.	Rhodochrosite	5438	Kohlenbach – Germany
4.	Aragonite	5421	Spania Dolina – Slovakia
5.	Witherite	5484	Alston – England
6.	Strontianite	5432	Drensteinfurt – Germany
7.	Azurite	5397	Namibia
8.	Malachite	5393	Eisenzeche – Germany
9.	Aurichalcite	5457	Lavrio - Greece
10.	KCO <sub>3</sub>	-	Synthetic
11.	Natrite	-	

The Raman spectra of these minerals are very similar. The intense band ( $\nu_1$ ) of the calcite spectrum corresponds to the symmetric stretching of CO<sub>3</sub> group at 1087 cm<sup>-1</sup>. The  $\nu_2$  (symmetric bending) vibration mode does not appear. The Raman lines attributed to  $\nu_3$  (asymmetric stretching) mode and  $\nu_4$  (asymmetric bending) mode have 1437 cm<sup>-1</sup>, respectively 714 cm<sup>-1</sup>. The Raman spectrum of siderite is characterized by the same Raman band corresponding to the symmetric stretching of CO<sub>3</sub> group as that of the calcite, at 1087 cm<sup>-1</sup>. The band at 1442 cm<sup>-1</sup> corresponds to the  $\nu_3$  normal mode and 736 cm<sup>-1</sup> to the  $\nu_4$  (O-C-O in-plane bending) mode. The Raman spectrum of rhodochrosite consists of a strongest intensity band at 1094 cm<sup>-1</sup> assigned to the  $\nu_1$  symmetric stretching mode of CO<sub>3</sub> group. The  $\nu_3$  normal mode appears at 1439 cm<sup>-1</sup> and the  $\nu_4$  normal mode at 725 cm<sup>-1</sup>.

The lower wavenumbers of calcite (285 cm<sup>-1</sup>), siderite (289 cm<sup>-1</sup>) and rhodochrosite (292 cm<sup>-1</sup>) observed in figure 3 arise from the external vibration of the CO<sub>3</sub> groups that involve translatory oscillations of those groups (relative translations between the cation and anionic group). There are no values below 200 cm<sup>-1</sup> because the Raman shift is 200-3400 cm<sup>-1</sup>.

A weak lines observed at 1749, 1729 and 1752 cm<sup>-1</sup> may be regarded as the combination bands of  $\nu_1 + \nu_4$  modes (Gunasekaran et al., 2006). The spectrum of siderite presents a band at 514 cm<sup>-1</sup>, which may be assigned to the vibration of a Fe-O bond.

The observed vibrational bands of calcite, siderite and rhodochrosite were compared with their documented values and are listed in table 3. The positions of the observed Raman bands are in agreement with those reported by Gunasekaran et al. (2006) for calcite and Beny (1991) for siderite and rhodochrosite. The minor shift in positions may be due to the effect of natural impurities present in the samples.

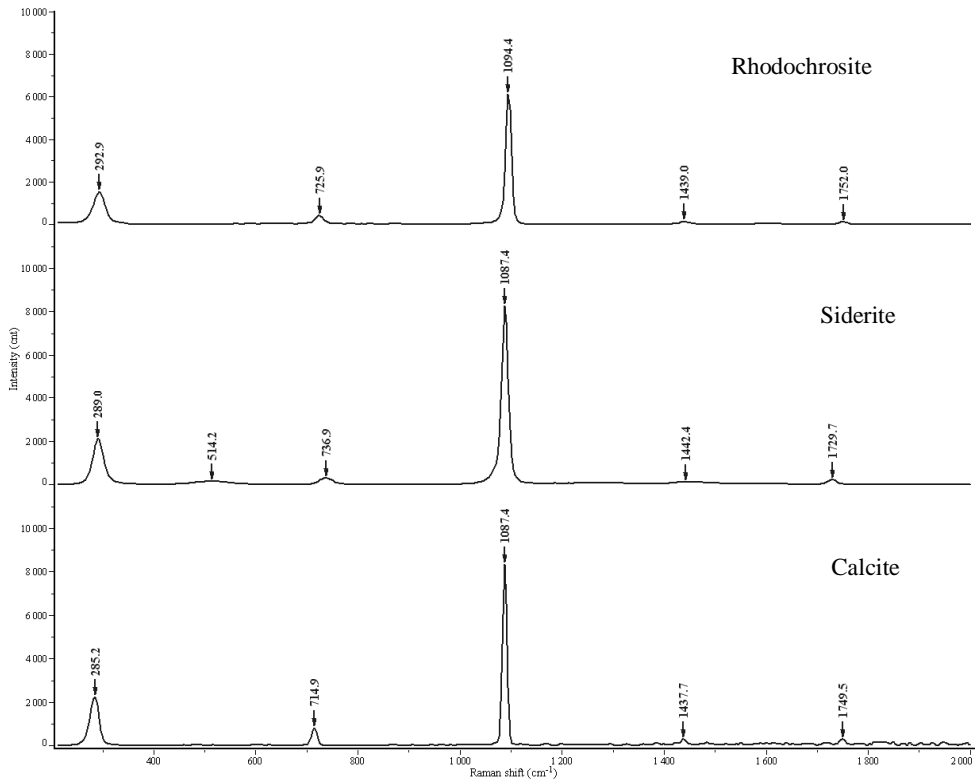


Fig. 3 Raman spectrum of calcite compared with those of siderite and rhodochrosite.

## 2. Aragonite group

The Raman spectra for the aragonite, witherite and strontianite are shown in figure 4. The spectra of these investigated samples show only five bands out of the 30 predicted Raman-active modes (Krishnamurti, 1960; Urmos et al., 1991). These spectra are governed by the very strong Raman line attributed to the  $\nu_1$  symmetric stretching mode of the carbonate group. The wavenumbers of this Raman band are 1083, 1069 and 1059  $\text{cm}^{-1}$  (tab. 4). They are similar to those reported by Urmos et al. (1991), Krishnamurti (1960) and Beny (1989).

Tab. 3 Raman bands in calcite, siderite and rhodochrosite (cm<sup>-1</sup>)

Calcite		Siderite		Rhodochrosite		Free CO <sub>3</sub> <sup>2-</sup>	Assignment
This study	Gunasekaran et al., 2006	This study	Beny (1991)	This study	Beny (1991)		
	89						R*(CO <sub>3</sub> )
	162		190		184		T(Ca, CO <sub>3</sub> )
285	288	289	294	293	289		T(Ca, CO <sub>3</sub> )
		514	506				T(Fe, CO <sub>3</sub> )
715	716	737	731 742	726	718	680	v <sub>4</sub> -Asymmetric bending mode
						879	v <sub>2</sub> -Symmetric bending mode
1087	1092	1087	1087	1094	1064 1085	1063	v <sub>1</sub> -Symmetric stretching mode
1437	1437	1442		1439	1414	1415	v <sub>3</sub> -Asymmetric stretching mode
1749	1754	1729	1726 1733	1752	1725		v <sub>1</sub> + v <sub>4</sub>

R\* - rotational

The Raman lines attributed to the v<sub>3</sub> asymmetric stretching mode can be observed at 1422 and 1511 cm<sup>-1</sup> for witherite, 1445 and 1543 cm<sup>-1</sup> for strontianite, respectively 1461 and 1573 cm<sup>-1</sup> for aragonite. The appearance of two lines corresponding to v<sub>3</sub> is in accordance with the splitting of v<sub>3</sub> predicted by theory. The Raman lines at 693, 700 and 701 cm<sup>-1</sup> were assigned to the v<sub>4</sub> normal mode. The v<sub>2</sub> vibration mode are not visible in our spectra. The Raman bands due to the external vibration mode for aragonite, strontianite and witherite have the frequencies 250, 242 and 227 cm<sup>-1</sup>. The frequencies of all Raman bands observed in this study can be correlated with the atomic masses of the cations.

### 3. Alkali carbonates

The Raman spectrum of K<sub>2</sub>CO<sub>3</sub> (fig. 5) shows a couple of bands at 1026 and 1063 cm<sup>-1</sup> that may be attributed to the v<sub>1</sub> symmetric stretching mode (tab. 5). The two bands may be explained by the presence of the molecules belonging to two structures, C<sub>2v</sub> bidentate form and D<sub>3h</sub>, in agreement with the theoretical values calculated by Koura et al. (1996). The v<sub>2</sub> vibration mode is not Raman active. The bands at 1374 cm<sup>-1</sup> and 1426 cm<sup>-1</sup>, can be assigned to v<sub>3a</sub> respectively v<sub>3b</sub>. To the v<sub>4</sub> mode (doubly degenerate asymmetric bending) are attributed the values of 677 cm<sup>-1</sup> (v<sub>4a</sub>) and 702 cm<sup>-1</sup> (v<sub>4b</sub>). The spectrum also presents three bands at 237 cm<sup>-1</sup>, 287 cm<sup>-1</sup> and 484 cm<sup>-1</sup>, which may be assigned to the external vibration modes between the cation and anionic group (T(K,CO<sub>3</sub>)).

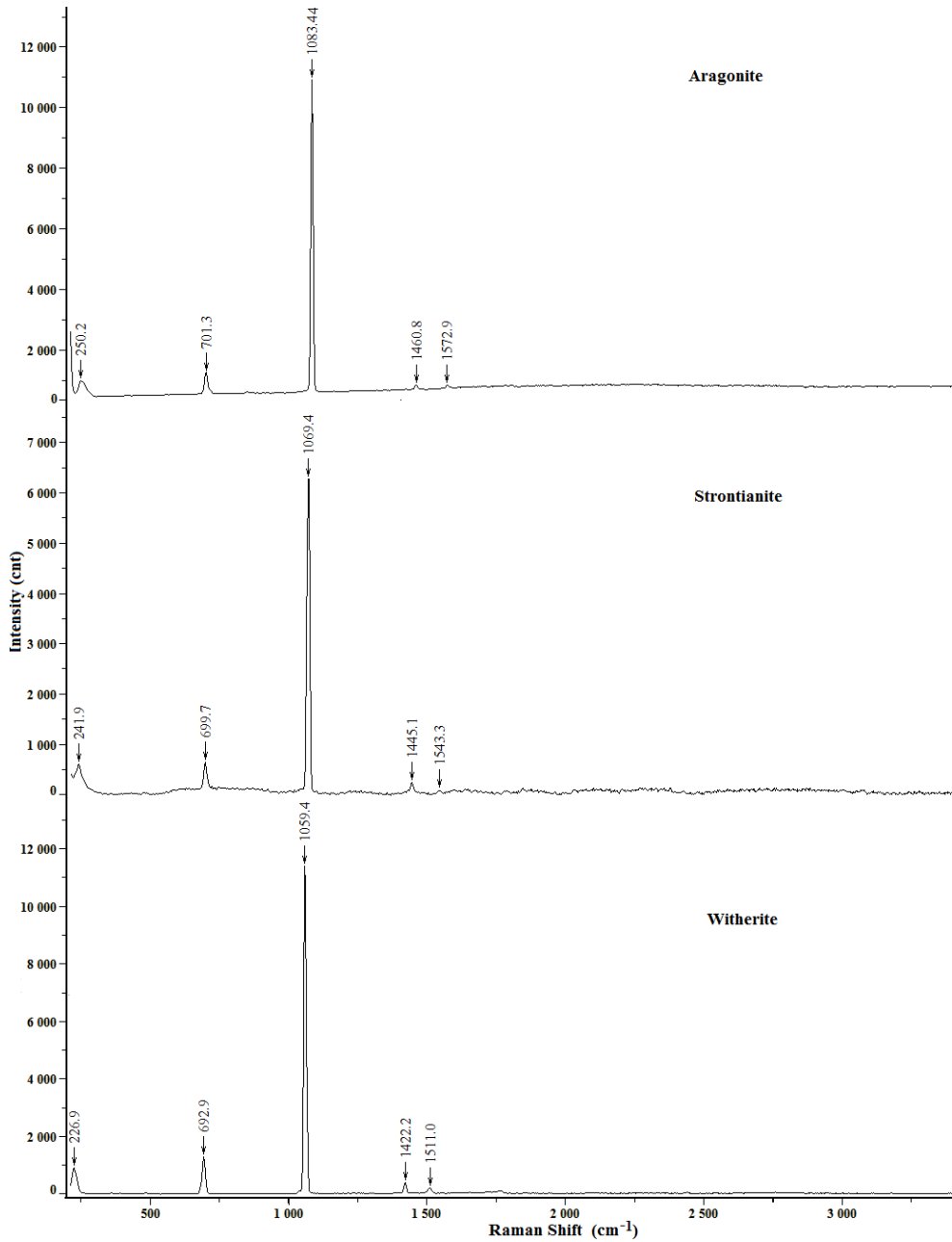


Fig. 4 Raman spectra of aragonite, strontianite and witherite.



Tab. 4 Raman bands in aragonite, strontianite and witherite (cm<sup>-1</sup>)

Aragonite			Strontianite		Witherite			Assignment
This study	Urmos (1991)	Krishnamurti (1960)	This study	Krishnamurti (1960)	This study	Krishnamurti (1960)	Beny (1989)	
250	284	285	242	246	227	227	224	T(M,CO <sub>3</sub> )
701	701 705 -	702 707 716	700 - -	701 711 -	693 - -	691 699 -	690 696 -	v <sub>4</sub>
NO	853	854	NO	855	NO	852	-	v <sub>2</sub>
1083	1085	1086	1069	1074	1059	1061	1035 1059	v <sub>1</sub>
- 1461 1573	- 1462 1547	- 1415 1463	- 1445 1543	1408 1438 1447	- 1422 1511	1394 1409 1421	- 1419 1505	v <sub>3</sub>
NO		2165			NO	2116*		2v <sub>1</sub>

NO = not observed; NA = not assigned

Tab. 5 Frequencies of the Raman lines of the alkali carbonates

K <sub>2</sub> CO <sub>3</sub>			Na <sub>2</sub> CO <sub>3</sub>			Assignment
This study	Koura et al. (1996)		This study	Beny (1988)	Burgio and Clark (2001)	
	Calculated	Measured				
237, 288, 484	76, 85, 122, 252, 278, 291	126, 141 192	290	111, 131 149, 171 189	NI*	T (K,CO <sub>3</sub> ) T (Na, CO <sub>3</sub> )
677	688	692	702	701	702	v <sub>4a</sub> (E') Asymmetric bending mode
702	706	697				v <sub>4b</sub> (E') Asymmetric bending mode
1026 1063	1025	1043 1064	1080	1069 1079	1071 1081	v <sub>1</sub> (A <sub>1</sub> ) Symmetric stretching mode
1374	1385	1405	1429	1421	NI*	v <sub>3a</sub> (E') Asymmetric stretching mode
1426	1557			1431		v <sub>3b</sub> (E') Asymmetric stretching mode

NI – Raman bands which appear in the figure 48 (Burgio and Clark, 2001) but without determined frequencies

For Na<sub>2</sub>CO<sub>3</sub>, the most intense Raman band, corresponding to the v<sub>1</sub> symmetric stretching vibration of the carbonate group, is at 1080 cm<sup>-1</sup>. The 1429 cm<sup>-1</sup> peak

corresponds to the  $\nu_3$  normal mode and line of  $702\text{ cm}^{-1}$  is attributed to the  $\nu_4$  asymmetric bending mode. The Raman spectrum of  $\text{Na}_2\text{CO}_3$  shows only one line of lattice mode, at  $290\text{ cm}^{-1}$ . The wavenumbers of Raman lines for two alkali carbonates are presented in table 5.

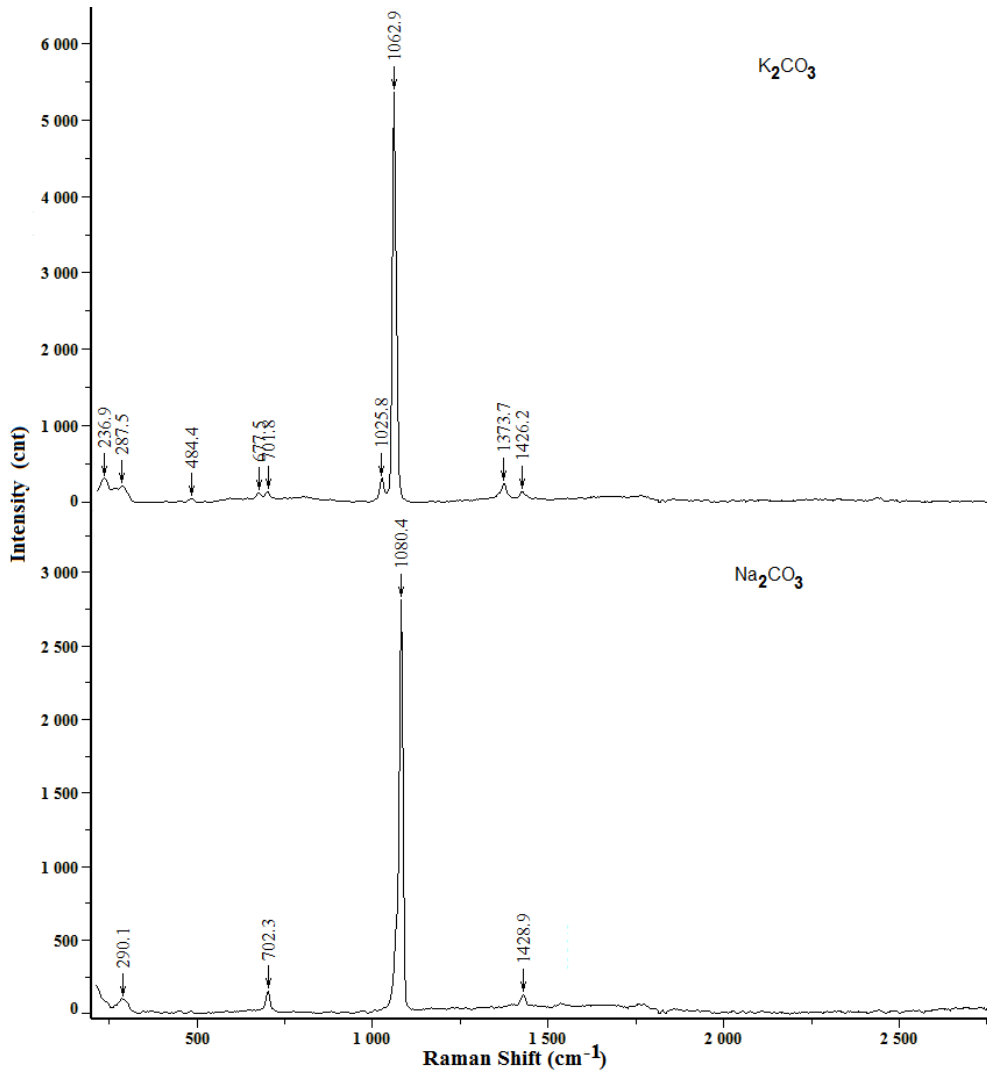


Fig. 5 Raman spectra of alkali carbonates (synth.)

## B. Carbonates with hydroxyl

### 1. Azurite

The spectrum of azurite is shown in figure 6. The wavenumbers of the detected bands are reported in table 6. This azurite spectrum is characterized by several lines that cover the spectral range of 200-1600  $\text{cm}^{-1}$ . The bands observed up to 600  $\text{cm}^{-1}$  are assigned to the translations of  $(\text{Cu}, \text{CO}_3)$  and those observed up to 1600  $\text{cm}^{-1}$  are assigned to  $\text{CO}_3$  complex (Frost et al., 2002). The Raman spectrum of our azurite does not show the O-H stretching band at about 3400  $\text{cm}^{-1}$ .

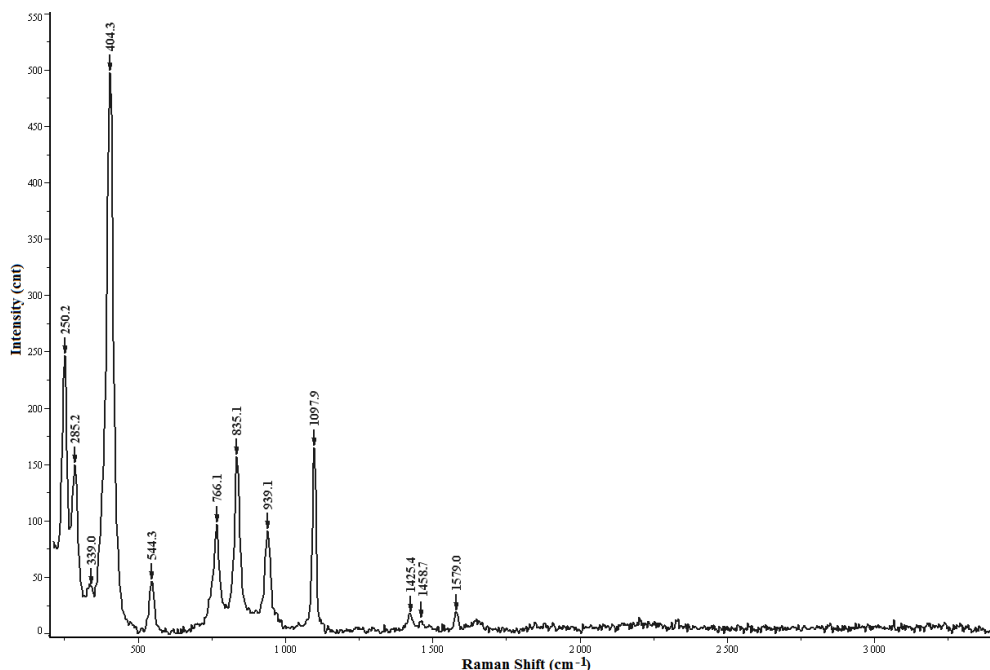


Fig. 6 Raman spectrum of azurite in the 200-3400  $\text{cm}^{-1}$  region

Azurite has a characteristic intense band at 404  $\text{cm}^{-1}$ . The  $\nu_1$  symmetric stretching band of the carbonate ion is observed at 1098  $\text{cm}^{-1}$ . The bands attributed to the carbonate ( $\nu_3$ ) asymmetric stretching vibration appear at 1425  $\text{cm}^{-1}$  and 1459  $\text{cm}^{-1}$ . One band is observed in the Raman spectrum of azurite at 766  $\text{cm}^{-1}$  and is assigned to the  $\nu_4$  mode. The band of 835  $\text{cm}^{-1}$  was assigned to the  $\nu_2$  symmetric bending vibration. A number of bands with different intensities are observed in the lowest spectral shift of the Raman spectrum of

azurite (250, 285, 339, 404 and 544  $\text{cm}^{-1}$ ). These Raman lines are assigned to the lattice modes. The O-H out-of-plane bending mode of azurite was reported at 939  $\text{cm}^{-1}$ . We have not found any information available for Raman line of 1579  $\text{cm}^{-1}$ . It is probably due to the O-H bending mode, in agreement with Nakamoto (1997).

Tab. 6 Raman bands of azurite ( $\text{cm}^{-1}$ )

This study	Azurite		Assignment
	Frost et al., 2002	Mattei et al., 2008	
250, 285, 339, 404, 544	112, 131, 139, 144, 154, 165, 171, 179, 194, 215, 237, 248, 265, 281, 332, 387, 400, 414, 540	157, 174, 182, 240, 250, 267, 282, 332, 387, 402, 542	T(Cu, CO <sub>3</sub> )
766	739 764	744 768	v <sub>4</sub> -Asymmetric CO <sub>3</sub> bending mode
835	815 835	840	v <sub>2</sub> -Symmetric CO <sub>3</sub> bending mode
939	952	937	O-H out-of-plane bending mode
1097	1095	1099	v <sub>1</sub> -Symmetric CO <sub>3</sub> stretching mode
1425 1459	1421 1431	1422 1433 1462	v <sub>3</sub> -Asymmetric CO <sub>3</sub> stretching mode
1579		1582	O-H bending mode
NO	3424 3446	3431	O-H stretching mode

NO = not observed

## 2. Malachite

The Raman spectrum of malachite is shown in figure 7. Malachite has two characteristic very strong bands at 435 and 1495  $\text{cm}^{-1}$ .

As in the case of azurite, the Raman bands at the lowest region of the spectrum of malachite (fig. 7) can be attributed to the lattice modes (tab. 7). In this region the spectrum shows an intense band at 435  $\text{cm}^{-1}$ , and the others at: 215, 270, 354, 537 and 597  $\text{cm}^{-1}$ .

The characteristic bands for the CO<sub>3</sub> group are observed at: 1059 and 1098  $\text{cm}^{-1}$  for the v<sub>1</sub> symmetric stretching modes (of two different CO<sub>3</sub> groups – doubly degenerate mode); 820  $\text{cm}^{-1}$  attributed to the v<sub>2</sub> symmetric bending mode (Frost et al., 2002); 1368, 1462 and 1495  $\text{cm}^{-1}$  assigned to the v<sub>3</sub> asymmetric stretching modes; 722 and 755  $\text{cm}^{-1}$  for v<sub>4</sub> asymmetric bending (doubly degenerate mode). For the hydroxyl-stretching region, the

spectrum shows bands at 3310 and 3382  $\text{cm}^{-1}$ . The vibration mode of the hydroxyl group (O-H bending mode) appears at 1639  $\text{cm}^{-1}$ .

Differences between the spectra of malachite and azurite may be explained by the molecular structure of azurite being based upon a distorted square planar arrangement compared with a distorted octahedral arrangement of the copper in malachite (Frost et al., 2002).

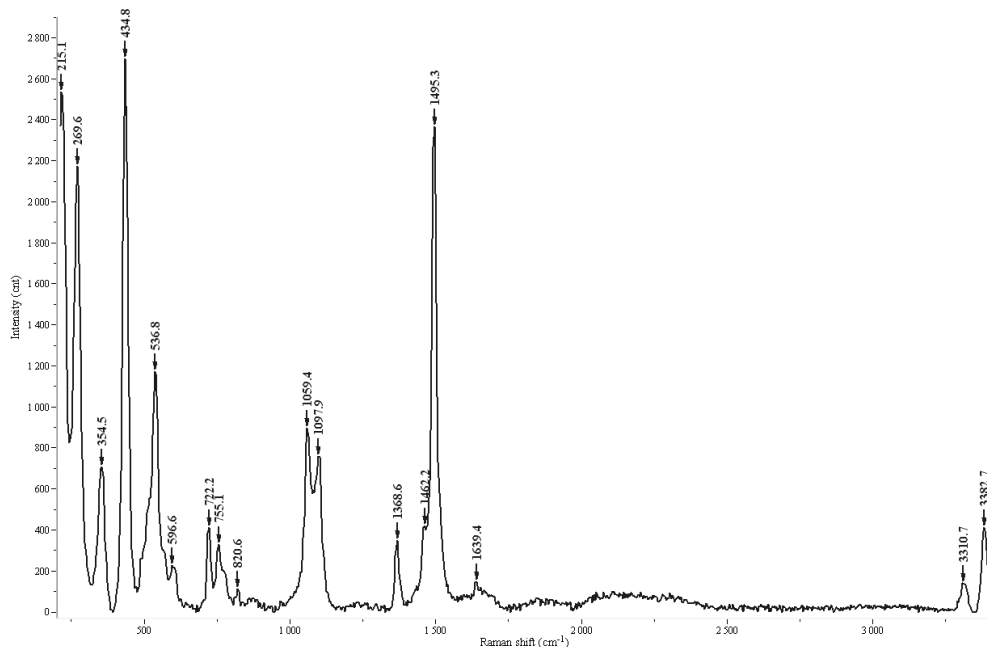


Fig. 7 Raman spectrum of malachite in the 200-3400  $\text{cm}^{-1}$  region.

### 3. Aurichalcite

The Raman spectrum of aurichalcite is different from those of malachite and azurite. This spectrum has a characteristic intense band at 1069  $\text{cm}^{-1}$  which is assigned to the  $\nu_1$  symmetric stretching mode of the carbonate unit (fig. 8, tab. 8).

The two low intensity Raman lines of 1485 and 1507  $\text{cm}^{-1}$  may be ascribed to the  $\nu_3$  asymmetric stretching modes. To the  $\nu_4$  mode (doubly degenerate asymmetric bending) are attributed the values of 706  $\text{cm}^{-1}$  ( $\nu_{4a}$ ) and 733  $\text{cm}^{-1}$  ( $\nu_{4b}$ ). A number of bands with different intensities are observed in the lowest spectral shift of the aurichalcite Raman spectrum (285, 388, 430, 461 and 498  $\text{cm}^{-1}$ ). These Raman lines are assigned to the CuO and ZnO

stretching and bending vibrations (Frost et al., 2007). A single band of the OH-stretching modes is observed at  $3344\text{ cm}^{-1}$ .

Tab. 7 Raman bands in malachite ( $\text{cm}^{-1}$ )

This study	Malachite		Assignment
	Frost et al. (2002)	Mattei et al. (2008)	
215, 269, 354, 434, 536, 596	130, 142, 151, 166, 176, 205, 217, 267, 294, 320, 249, 389, 429, 514, 531, 563, 596	157, 171, 182, 204, 224, 272, 352, 435, 513, 537, 601	T(Cu, CO <sub>3</sub> )
722	718	723	v <sub>4</sub> -Asymmetric CO <sub>3</sub> bending mode
755	750	753	
820	807 817		v <sub>2</sub> -Symmetric CO <sub>3</sub> bending mode
1059	1098	1058	v <sub>1</sub> -Symmetric CO <sub>3</sub> stretching mode
1097		1101	
1368	1365	1370	v <sub>3</sub> -Asymmetric CO <sub>3</sub> stretching mode
1462	1423	1463	
1495	1493	1497	
	1514		
1639			O-H bending mode
3310	3349		O-H stretching mode
3382	3380	3380	

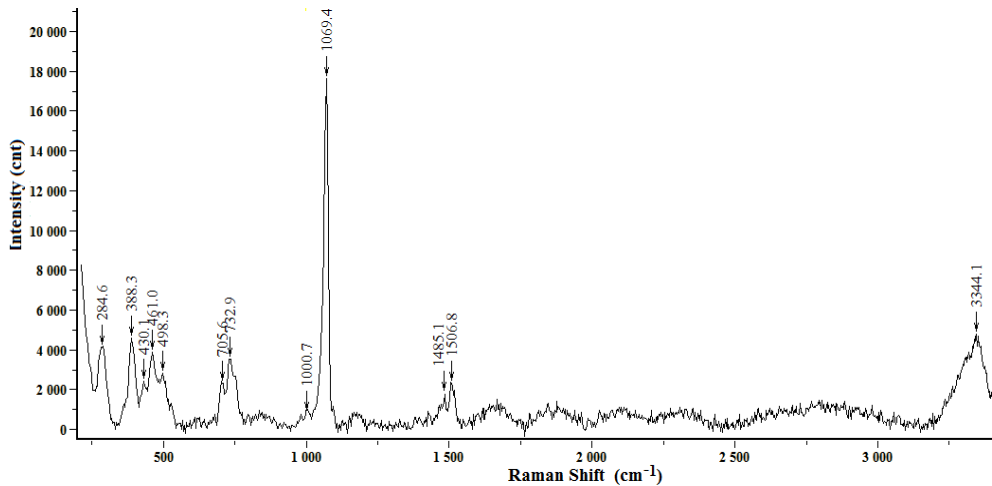


Fig. 8 Raman spectrum of aurichalcite

Tab. 8 Raman bands in aurichalcite (cm<sup>-1</sup>)

This study	Frost et al. (2007)	Assignment
285, 388, 430, 461, 498	278-283, 388-392, 428-432, 460-463, 498-499	T(Cu, CO <sub>3</sub> ) and T(Zn, CO <sub>3</sub> )
706 733 -	708-711 733-737 748-753	v <sub>4</sub> -Asymmetric CO <sub>3</sub> bending mode
-	849-860	v <sub>2</sub> -Symmetric CO <sub>3</sub> bending mode
1000 1069 -	1020 1060-1065 1071-1072	v <sub>1</sub> -Symmetric CO <sub>3</sub> stretching mode
1485 1507	1485 1506-1511	v <sub>3</sub> -Asymmetric CO <sub>3</sub> stretching mode
3344	3338-3355	O-H stretching mode

## Conclusions

In all spectra the three fundamental vibration modes of (CO<sub>3</sub>)<sup>2-</sup> were observed, with variations in band positions and splitting, caused by the influences of the different structures and cations.

The measured Raman bands of analyzed carbonates are similar to those reported in literature (v<sub>1</sub> between 1000-1100 cm<sup>-1</sup>, v<sub>2</sub> -800-900 cm<sup>-1</sup>, v<sub>3</sub> - 1400-1500 cm<sup>-1</sup>, v<sub>4</sub> - 690-790 cm<sup>-1</sup>). The slight differences between some Raman spectra were probably caused by either the instruments and techniques or the composition of the minerals.

Although the v<sub>2</sub> vibration mode is not normally active in Raman, it makes an exception in the case of the azurite and malachite samples.

The frequencies of all Raman bands of the orthorhombic carbonates (the aragonite group) can be correlated with the atomic masses of the cations. In the case of trigonal carbonates (the calcite group), the frequencies of the vibrational modes of (CO<sub>3</sub>)<sup>2-</sup> and the atomic masses of cations cannot be correlated.

The Raman spectrum of malachite and aurichalcite are different although the two minerals have similar structures.

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