Electrokinetic behaviour of calcite—the relationship with other calcite properties

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Abstract

Six carbonate samples of different origin were investigated for their properties: composition, grain size (Mz), specific surface area (SSA) and electrokinetic (ζ) potential. Four of the samples were of natural origin—one sample was sea sediment, one lake sediment and two limestone rocks. The remaining two samples were synthetic calcites.

The results of characterisation have shown that the samples consisted mostly of calcite. Traces of impurities (Si, Al, Fe, Mg) and organic matter were found in natural samples. The grain size of samples ranged between 2.0 and 10.3 μm, and SSA values were between 17.0 and 1.0 m^2 g^{-1} accordingly.

The electrokinetic mobility measurements were performed in the pH range from 6 to 10. The results have shown two different types of behaviour: synthetic calcites had positive ζ-potential at the point of equilibrium (pH$_{eq}$ = 8.4 $\pm$ 0.1), which decreased with either the increase or the decrease of the pH. Natural calcites, in contrast, had negative ζ-potential throughout the entire investigated pH range.

Electrokinetic behaviour of synthetic samples was the result of the exchange between the constituent ions in the solution and the available surface sites. The pH decrease caused the dissolution of the particles, and consequently the diminution of the grain size and surface area. Lower values of the ζ-potential were then the result of the specific adsorption of constituent anions on such reduced surface area. Going towards higher pH values, the decrease in the ζ-potential (and finally the charge reversal) was caused by the increasing concentration of the CO$_3^{2-}$. The isoelectric point (pH$_{IEP}$) was reached at about pH $\approx$ 9.5.

The electrokinetic behaviour of natural samples on the other hand was not the result of the exchange of constituent ions between the surface and the solution. Their ζ-potential was governed by the organic matter attached to the surface or incorporated in the structure of calcite. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Calcite; ζ-potential; Specific surface area; Organic matter

1. Introduction

The ability of mineral particles suspended in natural waters to react with dissolved substances depends on their properties—the specific surface area (SSA), cation exchange capacity (CEC), hydrophobicity/hydrophilicity of the surface, and surface charge (Horowitz and Elrick, 1987; Bišćan et al., 1991; Vdović et al., 1991; Mayer, 1994).

The formation of surface charge of mineral particles employs different mechanisms for different min-

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erals. Clay minerals carry a net negative surface charge deriving from the isomorphic substitutions in lattice (Schwartzen-Allen and Matijević, 1974). The surface charge of (hydr)oxides in water is characterised by a pH of zero surface charge, below which the surface is positively charged, and above which it is negatively charged (Stumm, 1992). The hydrolysis processes and complex formation reactions involving surface ions are responsible for the surface electrical properties of carbonate minerals. Van Capellen et al. (1993) postulated the formation of two types of surface sites $\equiv CaOH^0$ and $\equiv CO_3H^0$ (where $\equiv$ represents the surface) upon exposure of calcite surface to water. The evidence of the existence of these sites was provided by spectroscopic data (Stipp and Hochella, 1991; Stipp, 1999). The surface chemistry of carbonate minerals in contact with water is described in terms of the coordination reactions that mentioned surface sites undergo with solution species Ca^{2+}, CO_3^{2-}, HCO_3^-, $CaHCO_3^+$, H^+, OH^-. The surface charge, and consequently the electrokinetic potential, depend on the redistribution of Ca^{2+}, CO_3^{2-} and HCO_3^- (potential determining ions) between the surface and solution, while H^+ and OH^- (potential determining ions of the second order) regulate the concentration of particular anions (Foxall et al., 1979; Bell and Lindström, 1982; Siffert and Fimbel, 1984; Cicerone et al., 1992; Fuerstenau et al., 1992).

In the previous paper (Vdović and Bišćan, 1998) which dealt with ζ-potential of calcite, the major difference between electrokinetic behaviour of synthetic and natural calcite was observed. Suspended in simple electrolyte (10^{-3} mol dm^{-3} NaCl) synthetic calcite had positive ζ-potential, while natural calcite showed negative ζ-potential. Further experiments with organic substances introduced in the suspension of synthetic calcite revealed that organics adsorb to calcite surface rendering its surface potential less positive or even negative.

In this work, the studies of electrokinetic behaviour of calcite were expanded to several calcite samples of different origin. Two synthetic calcites and four natural samples (one sea sediment, one lake sediment and two calcareous rocks) were chosen for that purpose. The aim of the investigation was to discover if the trend of ζ-potential changes would follow the same pattern as described in the previous paper despite the different origin, and to find the relationship between the ζ-potential and some other characteristics of calcite. The results of these investigations could be of use to researchers whose main interest of work are the adsorption processes on calcite.

2. Materials and methods

2.1. Samples

Six calcite samples of different provenience were investigated in this work. They are referred to in the text by the name of their producer or by their sampling location.

"Socal" and "Aldrich" are synthetic calcites obtained from Solvay (UK) and Aldrich (USA) as reagents.

"Jadran" is a sea sediment sample, collected in the northern part of the Adriatic Sea, in the vicinity of the town of Rovinj (Istria, Croatia).

"Kozjak" is a lake sediment sample, collected from the lake Kozjak (the Plitvice Lakes, Croatia).

"Mirna" is Eocene limestone rock sample, collected in the upper part of the Mirna River drainage area (Istria, Croatia).

"Paravija" is Cretaceous limestone rock sample, collected in the coastal area near the town of Pola (Istria, Croatia).
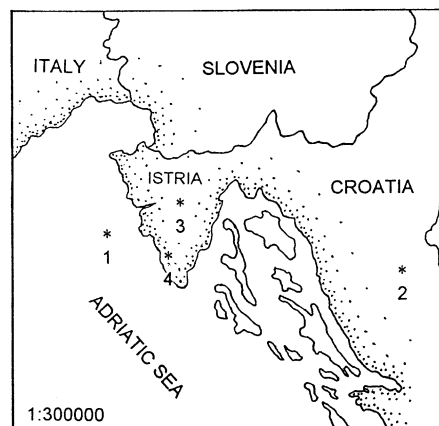

Fig. 1. Sampling locations: (1) sea sediment "Jadran", (2) lake sediment "Kozjak", (3) Eocene limestone "Mirna", (4) Cretaceous limestone "Paravija".
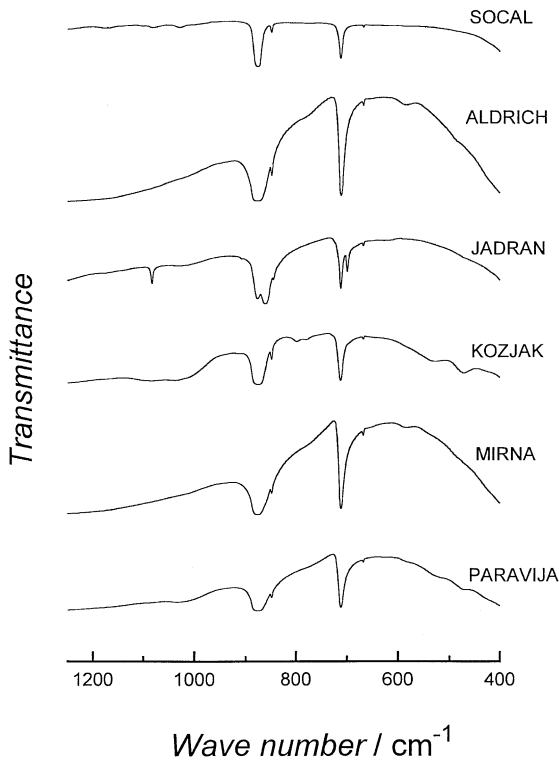
Fig. 2. FTIR spectra of samples.

Synthetic calcites were used as obtained, while natural samples "Jadran", "Mirna" and "Paravija" were ground in an agate mortar to powder. The sample "Jadran" was in addition sieved through a 500-μm sieve before grinding to remove clay particles. Sampling locations for natural samples are presented in Fig. 1.

2.2. Characterisation of samples

Composition of the samples was determined by FTIR spectroscopy (Mattson FTIR spectrophotometer, Genesis Ser), by X-ray diffraction (Philips PW 1050 diffractometer) and by atomic absorption spectroscopy (Perkin-Elmer AAS 3100).

Grain-size analysis was performed by using the Coulter Counter (TA II).

SSA was measured by nitrogen adsorption (Micromeritics Flowsorb II 2300 surface area analyser).

Organic matter content was estimated as the weight loss after treating the samples with NaOCl (Gaffey and Bronnimann, 1993).

2.3. Electrophoretic mobility measurements

Electrophoretic mobility of the samples was measured by means of an automated apparatus for microelectrophoresis (PenKem S3000). To this purpose a suspension of 40 mg of each sample in 100 cm^3 of an inert electrolyte (10^{-3} mol dm^{-3} NaCl) was prepared and left for a few hours to reach the equilibrium (until the pH reached the value of pH$_{eq}$ = 8.4 $\pm$ 0.1). Suspensions were then divided in two portions—one for acid titration (0.1 mol dm^{-3} HCl), and the other for base titration (0.1 mol dm^{-3} NaOH). Electrophoretic mobility was measured after each acid/base addition and ζ-potential was calculated from the obtained results by using Henry's equation (Hunter, 1981):

$$u_e = (2\varepsilon\zeta/3\eta)f_1(\kappa a)$$

where u_e is the electrophoretic mobility (m^2 s^{-1} V^{-1}); ϵ is the permitivity of the medium (F m^{-1}); ζ is the electrokinetic potential (mV); η is the viscosity (N m^{-2} s); $f_1(\kappa a)$ is a function dependent on particle size and shape; a is the particle radius (m); κ is the reciprocal double layer thickness (m^{-1}).

Assuming a high ratio between particle radius and the double layer thickness (giving $\kappa a \gg 1$) the relation between electrophoretic mobility and ζ-potential becomes:

$$\zeta = 12.8 \times 10^8 u_e.$$

3. Results

3.1. Composition of samples

Mineral composition of samples was obtained by FTIR spectroscopy (Fig. 2). In all the samples ab-

Table 1
Mineral composition of investigated samples obtained by X-ray and FTIR, and organic matter content

Sample	Mineral composition	% Organic matter
Socal (synthetic)	calcite	–
Aldrich (synthetic)	calcite	–
Kozjak (lake sediment)	calcite, quartz	5.6
Jadran (sea sediment)	calcite, aragonite	4.1
Mirna (limestone)	calcite	1.5
Paravija (limestone)	calcite	1.0

Table 2
Composition of natural samples

	%CaO	%SiO₂	%Al₂O₃	%K₂O	%NaO	%MgO	%Fe₂O₃	%MnO₂	%L.O.I.
Jadran	55.37	1.65	0.15	< 0.03	< 0.09	0.53	0.38	< 0.02	41.79
Kozjak	49.77	5.52	1.27	0.12	< 0.02	0.68	0.47	< 0.01	42.13
Paravija	56.41	1.42	0.36	< 0.07	< 0.02	0.24	0.28	< 0.01	41.19
Mirna	55.94	0.86	< 0.07	< 0.01	< 0.04	< 0.05	< 0.06	< 0.01	42.60

sorption bands at 713, 848 and 876 cm^{-1} were recorded, the values which correspond to the carbonate ion in calcite. The sample Jadran had also the bands at 700, 869 and 1083 cm^{-1}, which are characteristic for aragonite (Andersen and Brečević, 1991).

More information on the composition of the samples were obtained by the X-ray diffraction (Table 1), which also revealed the presence of quartz in sample "Kozjak".

The atomic absorption spectroscopy provided some more data on the composition of impurities in natural samples. The results compiled in Table 2 showed a significant amount of Si, Al, Mg and Fe.

The quantity of organic matter in natural samples was estimated from the weight loss after the treatment with NaOCl. The results are presented in Table 1, showing a higher amount of organic matter in the sediments than in limestones.

3.2. Grain size (Mz) and SSA

The results of grain size distribution and SSA are shown in Table 3. The highest value of the SSA (17.0 m^2 g^{-1}) was measured for the synthetic calcite Socal which had the mean grain size of Mz = 2.0 μm, and the lowest SSA value of 1.0 m^2 g^{-1} was found for the limestone sample Mirna of 10.3-μm sized particles. The other four samples had similar

Table 3
Mean grain size and specific surface area of samples

Sample	Mz (μm)	SSA (m^2 g^{-1})
Socal (synthetic)	2.0	17.0
Aldrich (synthetic)	5.9	2.2
Kozjak (lake sediment)	5.1	5.2
Jadran (sea sediment)	6.7	4.3
Mirna (limestone)	10.3	1.0
Paravija (limestone)	4.9	2.0

grain sizes (ranging between Mz = 4.9 and 6.7 μm) and the SSA between 2.0 and 5.2 m^2 g^{-1}.

3.3. ζ-Potential

The ζ-potential results obtained after measuring the electrophoretic mobility clearly distinguished two groups of samples. A group of synthetic calcites which were positively charged and showed positive ζ-potential in the major part of the investigated pH-range, and a group of natural calcites which had negative ζ-potential throughout the entire pH-range of 6 to 10 (Fig. 3).

However, some differences were observed even between the samples belonging to the same group. Synthetic calcites Socal and Aldrich had the same trend of ζ-potential changes although they differed in absolute values. The highest ζ-potential value was
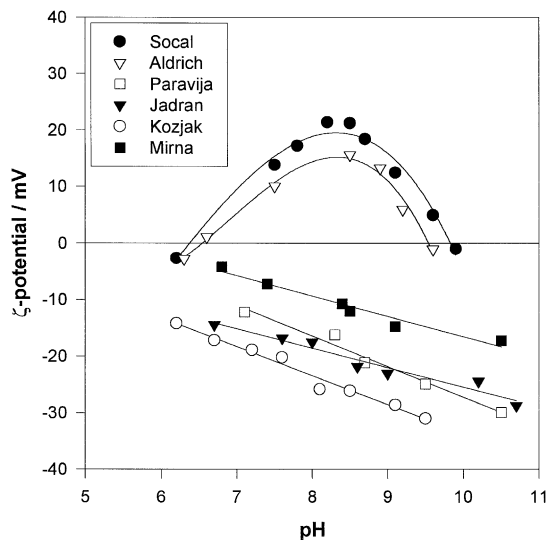

Fig. 3. ζ-potential dependence of samples on the pH. Supporting electrolyte is 10^{-3} mol dm^{-3} NaCl.

obtained at the point of equilibrium (pH = 8.4 ± 0.1) and it was ζ = 21.4 mV for Socal and ζ = 15.6 mV for Aldrich, respectively. The addition of acid caused the decrease in ζ-potential and finally a charge reversal (at pH ≈ 6.3 for Socal and pH ≈ 6.5 for Aldrich). The same effect was observed when introducing of a base in the suspension. ζ-potential decreased with each addition of the base, approaching the isoelectric point (pH$_{IEP}$) which was at approximately pH ≈ 9.5 for Aldrich and pH ≈ 9.8 for Socal.

Natural calcite samples, although all negatively charged, expressed also some particularities in their electrokinetic behaviour. The highest negative ζ-potential was measured for the sample Kozjak, (at the pH$_{eq}$ it was ζ = −26.1 mV). The addition of acid caused a ζ-potential decrease so that at the pH = 6.2 came down the value of ζ = −14.2 mV. Base titration, in contrast, increased the negative value of the ζ-potential to the value of ζ = −31.0 mV at the pH = 9.5.

The samples Paravija and Jadran had rather similar negative ζ-potentials at the point of equilibrium (ζ = −16.2 and −20.7 mV, respectively). The titration of their suspensions with acid also decreased ζ-potential to lower values while the addition of a base increased the negative value of ζ-potential to ζ = −29.9 mV (Paravija) and ζ = −28.7 mV (Jadran) at pH = 10.5.

The remaining natural sample, limestone Mirna, had somewhat lower initial ζ-potential (ζ = −10.7 mV), but its electrokinetic behaviour followed the same trend—a ζ-potential decrease with lower pH-values (ζ = −4.2 mV at pH = 6.8) and an increase with the pH raise (ζ = −17.2 mV at pH = 10.5).

4. Discussion and conclusion

4.1. Synthetic calcites

In the simple system calcite–water several ionic species are considered to be present: Ca^{2+}, CO_3^{2-} and HCO_3^-, the potential determining ions, and H^+ and OH^-, which control the carbonate ion speciation. According to the distribution diagram, in the pH-range up to pH ≈ 6.5 the prevailing carbonate species are dissolved molecular CO_2 and undissociated H_2CO_3. In the pH-range from pH ≈ 6.5 to 10, HCO_3^- is the most abundant anion, and above pH ≈ 10 the dominant anion is CO_3^{2-}.

The electrokinetic behaviour of synthetic calcite samples used in this work was governed by the constituent ions, and especially by the presence of a particular anion. At the pH$_{eq}$ = 8.4 ± 0.1 the ζ-potential had the highest positive value which resulted from the prevalence of the positively charged species over the HCO_3^-, which was at that point the most abundant anion.

By changing the pH to higher values, the ζ-potential decreased towards the pH$_{IEP}$ (Fig. 3). The increase of the pH had for a consequence the increase of CO_3^{2-} concentration. By the accumulation of those anions the surface is enriched with respect to CO_3H sites which rendered the surface potential less positive and finally, at pH > 9.5, negative.

Lowering of the pH below pH$_{eq}$ induced dissolution of calcite and a detachment of constituent ions from its surface. In this pH range (8.4–6.5), Van Capellen et al. (1993) predicted a model for surface charge redistribution which assumed the surface made up of nearly equal amounts of $\equiv CaOH_2^+$ and $\equiv CO_3^-$ sites and the increase of positive surface charge of calcite below pH = 8. However, the ζ-potential measurements of the synthetic calcite in this work showed that the surface was getting less positive (Fig. 3).

Similar results, the decrease of the ζ-potential of calcite at the pH values below the pH$_{eq}$, were obtained by Siffert and Fimbel (1984). To explain such a behaviour they assumed a formation of electric double layer in which hydrated carbonate ions adsorb closer to the surface of the mineral (inner Helmholz layer), while calcium ions remain in the outer layer.

Another possible explanation is in fact a reversed process of the one described by Siffert and Fimbel (1984)—not the adsorption, but detachment of ions from the surface. If dissolution is still in progress the less positive values of ζ-potential could be the consequence of non-simultaneous detachment of the constituent ions from the surface. Higher loss of CaOH than CO_3H during dissolution of calcite, directly observed by Stipp and Hochella (1991), could explain more negative surface when the system has not yet reached the equilibrium. However, the ζ-

potential decrease with the addition of acid was observed even if the measurements were made after a few days. If we assume that the equilibrium is reached after a few days, then the surface charge is formed by the specific adsorption of anions, as proposed by Siffert and Fimble (1984).

Nevertheless, there is another factor involved in the charge formation on the calcite surface revealed by the comparison of two synthetic calcite samples. Although the same trend of ζ-potential changes was observed for both synthetic calcite samples, there was a significant difference in absolute values probably originating from the difference between their SSAs and grain size. The sample Aldrich, having much lower surface area than the sample Socal ($SSA_{Aldrich} = 2.2$ m^2 g^{-1} vs. $SSA_{Socal} = 17.0$ m^2 g^{-1}), had somewhat lower ζ-potential at the beginning of the experiment ($\zeta = 15.6$ mV) compared to that of Socal ($\zeta = 21.4$ mV). Also, the isoelectric point of Aldrich calcite was reached at the lower pH value (9.5) than that of Socal (9.8) (Fig. 3). Siffert and Fimbel (1984) observed similar effect by changing the mass concentration. The smaller the quantity of sample the lower ζ-potential was measured.

In both cases, we can assume a similar process. Calcite grains in contact with water tend to reach the equilibrium by releasing a certain amount of their constituent ions in the solution. If a smaller quantity of sample is used or if the pH decreases, then the dissolution will cause a diminution of grains, and consequently the diminution of the available surface area, and the ζ-potential of calcite becomes more negative.

4.2. Natural calcites

The electrokinetic behaviour of natural calcites was more similar to that of clay minerals (Sondi et al., 1996) or organic matter (Sondi et al., 1996; Van der Waal et. al., 1997) rather than to that of pure calcite. Apparently, in these cases the surface charge was affected by some factors other than just the reactions between the constituent surface ions and those in the solution.

The negative ζ-potential of mineral particles in natural environments is usually result of the organic matter adsorption. Acting as a coating, organic matter renders the surface charge of particles uniformly negative regardless their composition and structure. Even though the literature data on the ζ-potential of organic substances are scarce (Sondi et al., 1996 reported on the negative ζ-potential of fulvic acid and Van der Waal et al., 1997 on the pH-dependent ζ-potential of bacterial cells), there are many data on the ζ-potential of particles influenced by organic matter that clearly show the negative ζ-potential formed after the organic matter adsorption (Neihof and Loeb, 1972; Hunter, 1980; Hunter and Liss, 1982; Loder and Liss, 1982; Beckett and Le, 1990). The experiments on the influence of organic matter on the surface charge of the pure calcite lead to the same conclusion—organic matter reduces the positive surface charge of calcite and reverses it to negative (Andersen et al., 1991; Cicerone et al., 1992; Vdović and Bišćan, 1998).

The negative ζ-potential of natural calcite samples investigated in this work was most probably influenced by the organic matter present as a coating and/or incorporated in the structure. The weight loss after NaOCl treatment pointed to a possible presence of organics. Knowing that processes of calcite dissolution and precipitation are inhibited by dissolved organics (Chave and Suess, 1970; Compton and Sanders, 1993; Thomas et al., 1993; Lebron and Suarez, 1996), it is possible that organic matter prevented the reactions between investigated calcite samples and the solution, reflecting its own properties.

Organic matter also hid another surface characteristic. Although it seemed that the value of the ζ-potential depended on the SSA as in the case of synthetic calcites (the sample with the highest SSA, Kozjak, had the highest value of ζ-potential, while the sample Mirna with the lowest SSA had also the lowest ζ-potential), in the case of natural calcites this relationship was not so clearly expressed. Also, it is difficult to discuss the SSA since some of the samples were ground to powder and some surface area might have been artificially created. The difference in ζ-potential value of natural calcites was probably the reflection of the surface charge of a certain type of organic matter and not of the SSA of the sample.

Other impurities detected in the samples were Si, Mg, Al and Fe. Si in the sample Kozjak derived from quartz detected by X-ray diffraction. Quartz might also be the origin of Si in other samples,

however because of the low amount was not detected by any method. Mg was probably incorporated in the calcite structure while Al and Fe were most likely present as amorphous oxides. Even though the amorphous (hydr)oxides are known to act as coatings on natural mineral particles and are partly responsible for their behaviour in natural waters, it is not probable that they are responsible for the negative ζ-potential of calcite samples. Namely, the isoelectric point of Al- and Fe-oxides is approximately around pH = 7–9 (Stumm, 1992), and it is not likely that their presence had significant effect on the electrokinetic behaviour of the calcites investigated in this work.

4.3. Concluding remark

The surface charge of calcite is not easy to deal with since it depends on so many factors. Some of them are discussed in this work: the origin of sample (synthetic or natural), the SSA, the amount of sample and the pH at which the experiments are performed. Each one of them could change the outcome of the experiment significantly. So, when dealing with surface processes and adsorption processes on calcite one should take in account all of these parameters before coming to the conclusion.

Acknowledgements

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