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# AUGER SPECTROSCOPY DETERMINATION OF THE SURFACE-MOST ADSORBED LAYER COMPOSITION ON ARAGONITE, CALCITE, DOLOMITE, AND MAGNESITE IN SYNTHETIC SEAWATER

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**ABSTRACT. The magnesium to calcium concentration ratio of the surface-most adsorbed layer (≈ 10 A) on aragonite, calcite, dolomite, and magnesite after their exposure to standard composition seawater at two different saturation states was determined by Auger spectroscopy. The results indicate that magnesium ions are adsorbed nearly 30 times less than calcium ions on the surface of aragonite, whereas both ions are adsorbed to a similar extent on the surface of calcite. The measured Mg to Ca ratio on the surface of magnesite is approximately equal to 120, whereas the Mg to Ca ratio on the surface of dolomite is close to 3. Variations from these values can be attributed to the adsorbed layer's response to cross-phase contamination resulting from heterogeneous precipitation on the bulk solid. A model based on specific site adsorption is used to illustrate the self-consistency of the data.**

## INTRODUCTION

Chemical interactions occurring at or near the solid-solution interface exert major influences on the behavior of carbonate minerals in the marine environment. Among the most significant of these influences are the control of calcite and aragonite solubility (for example, Chave and others, 1962; Jansen and Kitano, 1963; Weyl, 1965; Plummer and Mackenzie, 1974; Berner, 1975; Wollast, Garrels, and Mackenzie, 1980; Mucci and Morse, 1984); retention of the supersaturated state of near surface seawater with respect to calcite and aragonite (for example, Bischoff, 1968; Pytkowicz, 1965, 1973; Chave and Suess, 1970; Berner and others, 1978); the inhibition of calcite and aragonite dissolution and precipitation (for example, Suess, 1970; Meyers and Quinn, 1971; Mitterer, 1971; Berner and Morse, 1974; Morse, 1974); control of crystal morphology (for example, Kitano and Hood, 1962, 1965; Simkiss, 1964; Kitano and Kanamori, 1966; de Groot and Duyvis, 1966; Folk, 1974, 1978; Lahann, 1978); and the control of the rate and pathways of carbonate mineral diagenesis (Berner, 1966a,b, 1967; Bischoff and Fyfe, 1968; Jackson and Bischoff, 1971; Katz, 1973; Walter and Hanor, 1979; Mucci and Morse, 1984).

Although these influences have been clearly demonstrated, relatively little is known about the chemistry of the calcium carbonate-seawater interface that produces them. A combination of a large number of generally phenomenalistic observations and little quantitative data on interfacial chemistry has resulted in the proliferation of speculative articles on the

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mechanisms that may be responsible for the observed behavior of calcite and aragonite in the marine environment.

The seawater components that have been the subject of most surface or interfacial interaction studies with carbonate minerals are magnesium, strontium, orthophosphate, and various organic compounds or aggregates. The interaction of magnesium with the surface of calcite has received, by far, the most attention. However, fundamental quantitative data such as the adsorption of $Mg^{2+}$ on carbonate minerals from solutions similar in composition to seawater are scarce or practically nonexistent, with the exception of calcite, for which some studies have been carried out.

de Groot and Duyvis (1966) measured streaming potentials across compressed, wetted calcite and aragonite powder tablets in $CaCl_2$ and $MgCl_2$ solutions. They observed that the zeta potentials, which were calculated from the measured streaming potentials, increased with increasing $Ca^{2+}$ and $Mg^{2+}$ ion concentration. This increase was attributed to the specific adsorption of the divalent cations on the mineral surfaces. Their results indicated that $Ca^{2+}$ and $Mg^{2+}$ ions influence the $\zeta$ potential of calcite to the same extent whereas $Mg^{2+}$ ions influenced the $\zeta$ potential of aragonite considerably less than $Ca^{2+}$. de Groot and Duyvis (1966) concluded that $Mg^{2+}$ is adsorbed to a lesser extent than $Ca^{2+}$ on the aragonite, while both ions are adsorbed on the calcite surface to a similar extent.

At approximately the same time, Berner (1966a) conducted one of the first investigations of the concentration of exchangeable $Mg^{2+}$ on carbonate surfaces. His study was done with shallow water sediment from Florida Bay. The clay-sized fraction, which consisted of a mixture of $\sim$ 15 mol percent magnesian calcite and aragonite, was exposed to $CaCl_2$ and $MgCl_2$ solutions at various Mg to Ca ratios. By monitoring the changes that occurred in the composition of these solutions after reacting with the sediment, Berner established a strong relation between the $Mg^{2+}$ to $Ca^{2+}$ solution concentration ratio and the exchangeable $Mg^{2+}$ concentration. The relation indicated that at the seawater $Mg^{2+}$ to $Ca^{2+}$ solution concentration ratio, the surface Mg to Ca ratio should be approx 3. It was Berner's contention that this ratio was dominated by the biogenic Mg–calcite component of the sediment. However, Berner (1966a) found that the ion exchange was not totally reversible. It is suspected that magnesium ions may have been incorporated within the calcite crystal structure as an overgrowth or inclusion; therefore the estimated $Mg^{2+}$ to $Ca^{2+}$ ratio on the surface could be too large.

The chemical composition of the adsorbed outer layers on calcite in contact with solutions of varying amounts of $Mg^{2+}$ was determined by Möller and his associates (Möller and Werr, 1972; Brätter, Möller, and Rosick, 1972; Möller, 1973; Möller and Sastri, 1974; Sastri and Möller, 1974; Möller and Parekh, 1975) by a method of concurrent Ca-$^{45}$Ca isotope and $Ca^{2+}$-$Mg^{2+}$ ion exchange. Measurements were carried out on both calcite powders and single crystals. Möller and Sastri (1974) established that for a single calcite crystal not more than a monolayer participates in the Ca-$^{45}$Ca isotope exchange process. The group's various studies

indicated that at a solution $Mg^{2+}$ to $Ca^{2+}$ molar ratio of between 2 and 10, the Mg to Ca molar ratio on the surface of calcite reaches a value of about 1. Möller and Werr (1972) and Möller and Parekh (1975) demonstrated that $Na^+$, $Cl^-$, and $SO_4^{2-}$ up to concentration levels present in seawater did not interfere significantly in the exchange between $Mg^{2+}$ and $Ca^{2+}$. Brätter, Möller, and Rosick (1972) determined the Mg to Ca ratio on the surface of dolomite in solutions of varying amounts of $Mg^{2+}$ and obtained similar results to those for calcite, that is, a Mg to Ca surface ratio of 1 at a $Mg^{2+}$ to $Ca^{2+}$ solution ratio of 5.

Cooke (1977) determined the concentration of $Mg^{2+}$ on calcite surfaces equilibrated with seawater at various pressures by ESCA analysis. His results indicate a decrease in $Mg^{2+}$ surface concentration with increasing pressure and extrapolate to a Mg to Ca surface ratio of approx 1:3 at 1 atm.

Morse and others (1979) determined the Mg to Ca ratio in the surface-most adsorbed layer on Iceland spar calcite crystals after their exposure to natural near-surface seawater using scanning Auger spectroscopy. Their results indicated that the ratio was approx 1:4. However, this value was an estimate at best, since the analytical technique had not yet been shown to yield reproducible results, and elemental relative sensitivity factors for Ca and Mg in a carbonate matrix had not been determined.

More recently, Mucci and Kaminsky (1985) demonstrated the applicability of scanning Auger spectroscopy to the analysis of carbonate minerals and determined the relative elemental sensitivity factors of Ca and Mg in various carbonate minerals. These factors were later used by Mucci, Morse, and Kaminsky (1985) to determine the composition of solid magnesian calcite overgrowths precipitated from various synthetic seawater solutions at or very close to saturation.

In this paper we present the results of the scanning Auger spectroscopy analysis of the Mg to Ca ratio in the surface-most adsorbed layer (top $\approx$ 10 Å, see fig. 1) on various carbonate minerals after their exposure to

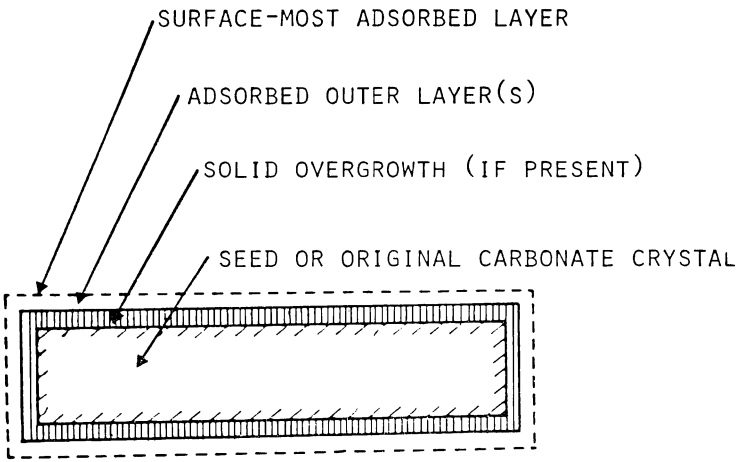


Fig. 1. A carbonate crystal after its exposure to a supersaturated seawater solution.

synthetic seawater ($[Mg^{2+}]/[Ca^{2+}] = 5.14$) at 25°C and 1 atm total pressure. The carbonate minerals studied were: Iceland spar calcite, aragonite, dolomite, and magnesite.

## MATERIALS AND METHODS

Synthetic seawater of salinity 35 per mil was prepared to include all major elements of natural seawater including $F^-$ according to the method of Kester and others (1967), modified slightly to fit the analysis of Millero (1974). Portions of the solution were adjusted at two different saturation states with respect to calcite by adding appropriate amounts of sodium bicarbonate to the preparations. Air pumped from outside the laboratory, saturated with water, was equilibrated with the solutions. The $P_{CO_2}$ of the solutions was monitored by measuring pH and total alkalinity. The solutions were equilibrated with air until the calculated $P_{CO_2}$ was 340 ± 10 ppm. The saturation state of the solutions was calculated from the $CaCO_3$ ion molal product and the stoichiometric solubility constant of calcite in seawater (Morse, Mucci, and Millero, 1980; Mucci, 1983). The saturation state of the solutions was adjusted at approx 1.2 and 8 with respect to the solubility controlling magnesian calcite phase (8 ± 1 mol percent Mg–calcite, see Mucci, Morse, and Kaminsky, 1984) in order to examine the effect of saturation on the adsorption of Mg on various carbonate minerals.

Large crystals of calcite, dolomite, and magnesite were either cleaved with a blade or cut with a diamond saw along their preferred cleavage plane. This cleavage plane corresponds to the $10\bar{1}4$ X-ray index with respect to the true hexagonal cell. Crystals of approx 0.5 $cm^2$ and 1 to 2 mm thick were chosen for the experiments. A long aragonite needle of approx 4 mm in diameter was mounted in an acrylic polymer resin and cut in 1 to 2 mm slices with a diamond saw perpendicular to its c axis. All carbonate crystal fragments, with the exception of the Iceland spar calcite were obtained from the Division of Mineralogy of the U.S. National Museum of Natural History. They are physically and chemically described in table 1. Other dolomite fragments of the same origin have been used by Busenberg and Plummer (1982) for dissolution kinetics experiments.

One side of the cleaved or cut crystals was polished by hand using progressively 600 grit silicon carbide grinding paper and a series of diamond polishing compounds (15, 6, 1, and 0.1$\mu$ m grit). The other side was numbered with a diamond point marker for identification purposes. Before being exposed to the synthetic seawater solutions the polished crystals were cleaned in an ultrasonic bath, successively, with three different solvents: trichloroethylene, methanol, and distilled water. The aragonite crystals were not cleaned in trichloroethylene, since it dissolved the acrylic resin mount. The cleaning procedure was necessary to remove the residual polishing compound material. SEM examination of the polished crystal surface at moderate magnification (≈ 5000 x) indicated that the surfaces were smooth except for a few scratches which were generally less than 0.3$\mu$m in diameter. Since the Auger primary electron beam diameter of our instrument is of the order of 3$\mu$m, the crystal surface was judged acceptably flat.

TABLE 1

Physical and chemical description of the four carbonate minerals used in this study

| Mineral | Description | Source |
|---|---|---|
| A. Aragonite | Hexagonal needle, clear | Czechoslovakia<br>U.S. National Museum #B9759 |
| B. Iceland spar calcite | Large rhombohedral crystal, clear | — |
| C. Dolomite | Rhombohedral cleavage fragment, clear | Austria<br>U.S. National Museum #R12596<br>Austria |
| D. Magnesite | Rhombohedral cleavage fragment, clear | U.S. National Museum #R10052 |

| | A* | B* | C** | D* |
|---|---|---|---|---|
| CaO | 54.58% | 54.23% | 30.46% | 0.84% |
| MgO | 0.07 | 0.17 | 21.59 | 46.56 |
| FeO | 1.85 | 0.96 | 0.09 | 0.26 |
| MnO | 0.00 | 0.00 | 0.015 | 0.00 |
| $CO_2$ | 43.35 | 43.53 | 47.54 | 51.65 |

* From analysis data sheet provided with sample.
** Busenberg and Plummer (1982).

The crystal was then immersed in one of the synthetic seawater solutions exposing its polished surface to the solution. This was achieved by laying the crystal down on a thinly rimmed dish held motionless in a vessel containing the synthetic seawater solution. The reaction vessel was described previously (Mucci, Morse, and Kaminsky, 1985). The solution was stirred once a day for a few minutes. After various periods of time, which ranged from a few days to several months, the crystal was removed from the solution. Excess residual solution on the surface of the crystal was shaken off. The crystal was dried for 24 hrs in a low vacuum dessicator prior to being introduced in the Auger spectrometer chamber, which was then pumped down to a pressure of $10^{-9}$ torr over a 2 to 3 day period.

The composition and saturation state of the solutions did not change significantly during the course of the exposure, since the solid to solution ratio was so small ($< 2$ cm$^2$ l$^{-1}$). This was verified by monitoring the pH of the solution over the duration of the experiments.

The analysis of the surface-most adsorbed layer on the various carbonate minerals exposed to synthetic seawater were performed by scanning Auger microanalysis (SAM). SAM is a surface sensitive analytical technique which can quantitatively analyze the surface-most layers of a solid with a depth resolution of approx 10 Å. The SAM analyses were conducted with a Physical Electronics Industries scanning Auger microscope model 545. The instrument is equipped with a single pass cylindrical mirror analyzer for electron energy determination. The Auger analysis was carried out at a pressure of $10^{-9}$ torr under an accelerating potential of 3 Kv at a 60° incidence angle to minimize charging problems on the surface of the nonconductive material.

The sputter etched crystals of calcite, dolomite, and magnesite described earlier were used to determine the sensitivity and to calibrate the spectrometer with respect to the Ca and Mg signals. Details of the working concept, analytical and calibration procedures for the Auger spectroscopy analysis of the carbonate mineral surfaces have been described previously (Mucci and Kaminsky, 1985; Mucci, Morse, and Kaminsky, 1985).

## RESULTS

An Auger spectra of the surface-most adsorbed layer on a calcite crystal after its exposure to synthetic seawater is shown in figure 2, with the elements being identified by their major peaks. The peak-to-peak amplitude of the Auger signal of an element is proportional to its atom density in the analyzed volume. However, we observed that the peak-to-peak amplitude of all the monitored elements varied with time under the influence of the analyzing electron beam, becoming constant after approx 20 to 30 min. A recording of the peak-to-peak amplitude of the Auger signal of several elements detected in the surface-most adsorbed layer on a seawater exposed calcite crystal as monitored by a multichannel analyzer as a function of time is shown in figure 3. This recording is typical of all the carbonate mineral surface-most adsorbed layers we have examined.

In all cases, the chlorine, sulfur, and sodium amplitudes decrease sharply in the first few minutes of analysis while the oxygen, calcium, and magnesium signals increase. The variation of the signal amplitudes with time is the result of electron sputtering. Electron sputtering, due to the impinging excitation beam, is a very slow etching process which is known to take place on the surface of ionic crystals (Szymonski, Overijnder, and DeVries, 1979). We have determined experimentally that under our work-

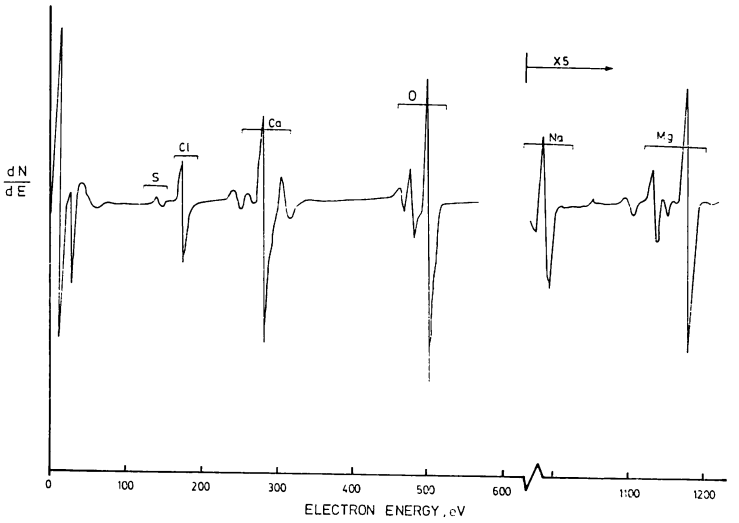


Fig. 2. Auger spectra of the surface-most adsorbed layer on a calcite crystal after its exposure to synthetic seawater.

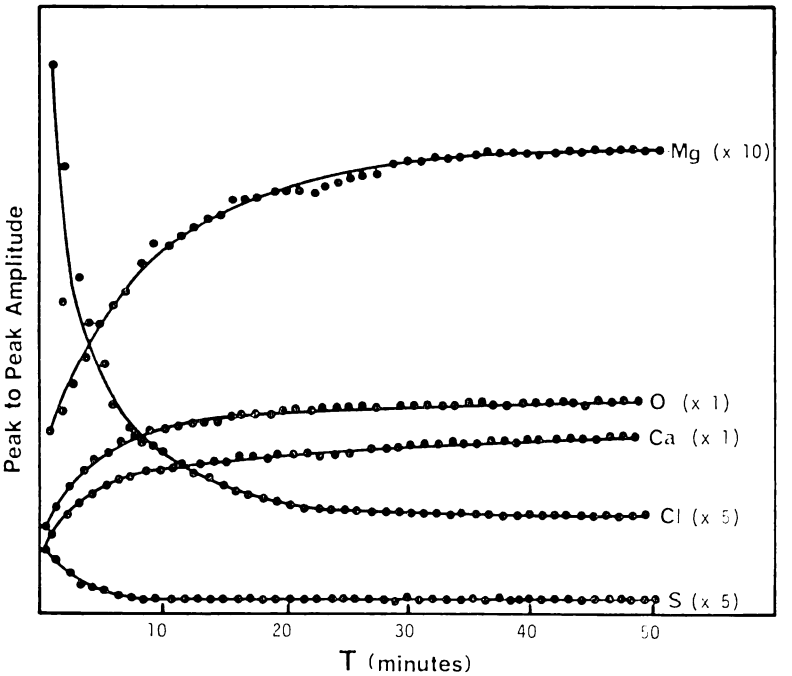


Fig. 3. Auger signal amplitude multichannel recording of the elemental surface composition of a calcite crystal exposed to synthetic seawater as a function of electron etching time.

ing conditions the etching rate is of the order of less than 3 Å per 100 min. The sharp decrease of the Cl, S, and Na signal amplitudes would therefore represent the removal of the very weakly bound residual solution salts from the surface. We believe that the composition given by the constant Auger peak-to-peak amplitudes is representative of the surface-most adsorbed layer. This adsorbed layer is most probably composed of highly hydrated ions.

The Mg to Ca concentration ratios on the surface of the various carbonate crystals exposed to synthetic seawater at two different saturation states are given in table 2. They were calculated from the Auger peak-to-peak amplitude ratio determined after 30 to 40 min of analysis and the normalized relative elemental sensitivity factors of Ca and Mg determined by Mucci and Kaminsky (1984) according to:

$$\left(\frac{[Mg]}{[Ca]}\right)_{surface} = \left(\frac{I_{Mg}}{I_{Ca}}\right)\left(\frac{S_{Ca}}{N_{Ca}}\right)\left(\frac{N_{Mg}}{S_{Mg}}\right) \qquad (1)$$

where $I_x$ is the peak-to-peak amplitude of the Auger signal of element x on the surface, $S_x$ is the relative elemental sensitivity factor of element x with respect to pure silver, $N_x$ is the atomic density of pure element x.

## DISCUSSION

Aragonite is the only one of the four carbonate minerals we have examined that does not have a calcite-type rhombohedral crystal structure. According to our results, aragonite is also the only carbonate mineral for which the surface-most adsorbed layer Mg to Ca concentration ratio is significantly affected by the saturation state of the solution. For all the minerals we examined, with the exception of aragonite, both solution saturation states represent a supersaturation situation. At a saturation state of 1.2 with respect to calcite, the seawater solution is undersaturated (0.8) with respect to aragonite, and, therefore, aragonite cannot precipitate on the seed material. On the other hand calcite can precipitate on the aragonite crystal, partially or completely covering the exposed surface. Hence, the composition of the surface-most adsorbed layer could approach a value equal to the adsorbed layer composition of calcite rather than that of aragonite. The results of the SAM analysis indicate that this may be what we observe. At the higher saturation state, the seawater solution is more than 5 times supersaturated with respect to aragonite so that aragonite would be expected to precipitate on the aragonite seed crystal. The surface composition of aragonite exposed to this seawater solution would therefore reflect the adsorption of Mg and Ca on aragonite. The results indicate that $Mg^{2+}$ is adsorbed significantly less on aragonite than on calcite. These results are qualitatively compatible with de Groot and Duyvis' (1966) zeta potential measurements.

The compositions of the surface-most adsorbed layers on calcite crystals after their exposure to either supersaturated seawater solutions are nearly identical. The lower Mg to Ca ratio of the adsorbed layer obtained from the less supersaturated solution may be the result of an incomplete coverage of the original Iceland spar calcite crystal by a magnesian calcite overgrowth. Mucci, Morse, and Kaminsky (1985) have demonstrated using ion-sputtering assisted SAM analysis that an 8 ± 1 mol percent magnesian calcite overgrowth is precipitated on a pure calcite seed crystal when ex-

TABLE 2

The Mg to Ca concentration ratios on the surface of four carbonate mineral crystals after an extended exposure to synthetic seawater at two different saturation states

| Mineral | $([Mg^{2+}]/[Ca^{2+}])_{surf}$ | |
|---|---|---|
| | $\Omega_c^* \cong 1.2$ | $\Omega_c \cong 8$ |
| Aragonite | 0.63 ± 0.10** ( 8)*** | 0.0346 ± 0.0031 ( 4) |
| Calcite | 0.83 ± 0.16 ( 3) | 1.34 ± 0.32 (10) |
| Dolomite | 3.05 ± 0.09 ( 5) | 2.67 ± 0.55 ( 7) |
| Magnesite | 120 ± 10 (12) | 68 ± 15 ( 7) |

* $\Omega_c$ = saturation state with respect to calcite = $([Ca^{2+}]\ [CO_3^{2-}])_{soln}/K_c^*$, where $K_c^*$ is the stoichiometric solubility of calcite in seawater.

** Errors represent standard deviations from the mean.

*** Values in parentheses are the number of independent measurements from which the average was calculated.

posed to a slightly supersaturated seawater solution. The overgrowth can be easily distinguished from the surface-most adsorbed layer as it is found after ion-sputtering the crystal for more than 20 min, to a depth of approx 60 Å below the surface-most adsorbed layer. In the case of calcite, during the initial ion-sputtering procedure the amplitude of the magnesium Auger signal decreases nearly tenfold, while the calcium almost doubles. The presence of an overgrowth is reflected by the constancy of the magnesium and calcium signal upon further sputtering, until the pure calcite seed crystal is reached. The depth profiling SAM analysis of the magnesian calcite overgrowth indicated that its thickness was not always proportional to the exposure period of the crystal to a seawater solution at a saturation state of 1.2. This observation could be attributed to an irregular growth process or patchiness which in turn would affect the composition of the surface-most adsorbed layer. Nevertheless, the Mg to Ca ratio in the surface-most adsorbed layer on calcite exposed to both saturation state solutions is in close agreement with the value of 1 obtained by Möller and his associates (Möller, 1973; Sastri and Möller, 1974; Möller and Parekh, 1975) in a solution with a $[Mg^{2+}]$ to $[Ca^{2+}]$ ratio of 5.

The Mg to Ca concentration ratios in the surface-most adsorbed layer on magnesite after its exposure to both saturation state seawater solutions are close to a factor of two apart. However, the depth profiling SAM analysis of the magnesite crystal after its exposure to the most supersaturated seawater solution indicates that an overgrowth precipitated on the original pure magnesite crystal. This overgrowth has a composition corresponding to a 1.5 mol percent calcian magnesite with a thickness of as much as 500 Å after a 40-day exposure period. Unfortunately, we could not verify the mineralogy of this overgrowth. This overgrowth is more likely to be composed of a mixture of minerals, possibly of a hydrated magnesium carbonate and calcite formed through heterogeneous precipitation. The depth profiling SAM analysis could not detect the presence of an overgrowth under the surface-most adsorbed layer on the magnesite crystal exposed to the less supersaturated solution. Considering the facts described above, the contamination of the magnesite crystal by an uncharacterized overgrowth, it is our opinion that a Mg to Ca concentration ratio of 120 in the surface-most adsorbed layer on magnesite is the more accurate estimate.

The Mg to Ca concentration ratios in the surface-most adsorbed layer on dolomite after its exposure to both seawater solutions are statistically identical. However, as for the case of magnesite, a slightly lower Mg to Ca adsorbed layer concentration ratio measured after exposure of the dolomite crystal to the more supersaturated solution may be indicative of cross-phase contamination. The Mg to Ca concentration ratio of 3 is three times larger than the value reported by Brätter, Möller, and Rosick (1972). This value may depend strongly on which crystal plane the adsorption measurements are carried out. We believe that a Mg to Ca adsorbed layer concentration ratio of 3 at a $([Mg^{2+}]/[Ca^{2+}])_{soln}$ of 5.24 may be more accurate, since it can be predicted from the adsorption behavior of Mg

and Ca on calcite and magnesite, if we assume that a simple specific site adsorption model can be applied. According to its stoichiometry, dolomite should offer an equal amount of $Ca^{2+}$ and $Mg^{2+}$ adsorption sites. The preferred cleavage rhombohedral plane used in this study of Mg and Ca adsorption on dolomite, $(10\bar{1}4)_{hex}$ X-ray index, exhibits an equal number of Ca and Mg adsorption sites (Lippmann, 1973). From the magnesite adsorption data we can suppose that almost all magnesium sites will be covered by $Mg^{2+}$ ions. From the calcite data we can suppose that approximately an equal number of $Ca^{2+}$ and $Mg^{2+}$ ions cover the $Ca^{2+}$ adsorption sites. The expected Mg to Ca surface ratio on dolomite would therefore be equal to a value of approx 3 which is the result of our measurements.

The same line of thought can be applied to calcite, if we assume that the surface composition we measured corresponded to the adsorption on an 8 mol percent magnesian calcite rather than pure calcite. The predicted value of the Mg to Ca surface ratio would be 1.2 compared to our measured value of 1.3 ($\pm$ 0.3). The small difference between our results and the previously published value of 1 can probably be associated with the fact that we measured the surface layer composition on an 8 mol percent magnesium calcite overgrowth rather than pure calcite. The presence of magnesium in the crystal structure will favor the adsorption of magnesium ions in the surface layers.

## CONCLUSIONS

The determination, by Auger spectroscopy, of the chemical composition of surface layers on four carbonate minerals exposed to standard composition seawater at different saturation states with respect to calcite has allowed us to reach the following conclusions based on quantitative evidence:

1. Magnesium ions are adsorbed much less than calcium ions on the surface of aragonite.
2. Calcium and magnesium ions are adsorbed to a similar extent on the surface of calcite.
3. Magnesium ions are adsorbed almost exclusively on magnesite.
4. The ratio of adsorbed magnesium to calcium ions on the surface of dolomite is close to 3.
5. Solution calcium carbonate ion activity products (saturation state) can influence the phase that precipitates on a surface (for example, calcite on aragonite).

These results were used to formulate a specific site adsorption model. This model seems to predict accurately the Mg to Ca surface ratio of an isostructural magnesium and/or calcium carbonate mineral of given stoichiometry and thus lends support to the validity of the data presented in this study.

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