


Effect of ionic strength on the dissolution and precipitation of carbonate minerals and the nature of ionic species from some calcareous soil

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A laboratory study was conducted to demonstrate the effect of ionic strength on the dissolution and precipitation of carbonate minerals and ionic species using well water with ionic strengths of (0.013, 0.065, 0.130) mol l⁻¹ by the method of wetting and drying of natural, unexcited soil columns taken from five different sites in their content of calcium carbonate within Nineveh Governorate / northern Iraq, classified within the Calciothirds soil group, and for five wetting and drying cycles, the duration of one cycle being ten days. After the fifth cycle of wetting and drying, water is added in the amount of two pore sizes to obtain a displacement solution of one pore size, which is collected in plastic bottles to conduct analysis of the main dissolved ions and entered into the VisualMinteq A₂ geochemical equilibrium program to obtain saturation index values for carbonate minerals. The outputs of the program showed the superiority of well water with an ionic strength of (0.130) mol l⁻¹ in the quantity and number of precipitated carbonate minerals represented by minerals (Calcite, Argonite, Vitrite, Regular Dolomite, Irregular Dolomite, Honet and Magnesite). The results of the theoretical correlation showed that the dominant ionic species were arranged as follows: CaSO₄.2H₂O > MgCl₂ > CaCl₂ > Ca(HCO₃)₂ > MgSO₄ > Mg(HCO₃)₂. The results show an increase in the percentages of all ionic species for all sites with an increase in the ionic strength of the water.

Keywords: Ionic strength, dissolution, precipitation, carbon minerals, ionic species, saturation index, Ionic composition.

INTRODUCTION

The processes of dissolution and precipitation of carbonate minerals that bearing calcium and magnesium in the soil, including (Calcite, Argonite, Vitrite, Dolomite, Magnesite, and others) are affected by several factors, including ionic strength, concentration or activity of calcium and magnesium ions for the soil solution, the soil pH, partial pressure of CO₂ gas, and temperature (Abdullah, 2006). carbonate minerals differ in their stability, as the less soluble the mineral is, the more stable it is, depending on the K_{SP} constant, as calcite is characterized by being more stable and stable compared to arconite, while vitrite is considered the least stable form of carbonate and turns into calcite (Abdulkarrem *et al.*, 2013), and accordingly, the stability of carbonate minerals is related to solubility and has phases that range in solubility, resulting in the emergence of different forms and shapes of carbonates, which are calcite, dolomite, arconite, siderite, and magnesite, and the most common of these forms in the soil are calcite and dolomite minerals, and the solubility of calcite is affected as between them (Rezaei *et al.*, 2004) with the quality of the water used for dissolving. When using a water mixture (fresh

water - salt water), a transfer of hydrogen ions and CO₂ gas occurs to the fresh water side, and this is controlled by several factors, the most important of which is the ionic strength. Alhadede *et al.* (2017) indicated that the presence of calcium carbonate with magnesium carbonate in an aqueous solution leads to an increase in the solubility of calcium carbonate and decreases the solubility of magnesium carbonate, and the dissolution products of calcium carbonate differ in the presence of magnesium carbonate, especially that the presence of magnesium is in balance with calcium in a solution Soil can affect the solubility of calcium carbonate, because increasing the ionic strength of water leads to precipitation of calcium and carbonate ions in the form of calcium carbonate, and the water used led to a decrease in the saturation index values, and this decrease is due to the presence of the common ion (Ca⁺²) in the water used, which increases the concentration of calcium, more precisely, the ionic activity of calcium resulting from the addition of water, which caused the precipitation of part of the carbonate in the form of calcium carbonate. The intensity of weathering, which in turn increases the ionic strength as a result of an increase in the concentration of dissolved salts in the soil

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solution, while the ionic strength has an effect on the speed of dissolving calcium carbonate accompanied by a change in concentration and ionic composition with its dissolution and transformation into calcium and carbonate ions. (Saksono *et al.*, 2009) stated that There is a direct relationship between the solubility of calcite and the ionic strength under the influence of sodium chloride, as the common ion plays a role in its effect on the dissolution and precipitation of calcium carbonate, such as adding calcium to the soil solution from sources other than CaCO₃. This case occurs when CaCO₃ precipitates in the presence of calcium ions resulting from the dissolution of this CaSO₄. Precipitation continues until calcium and carbonate ions decrease and reach equilibrium.

Al-Sultani (2015) used three types of water (river water, derange water and wiles water) to study the effect of the ionic strength of this water in dissolution and leaching calcium carbonate. The river has a low ionic strength, and the efficiency of fresh water for the leaching process is attributed to the fact that when this water enters the interfacial pores of the soil, it is free of any ionic pairs, so its energy is high for displacement, especially the calcium ion, which is considered one of the ions that are difficult to liberate when treated with water with high ionic strength, since these salts are It has the ability to form ion pairs, which impedes the dissolution process and reduces its solubility yield. The outputs of the (V. MinteqA₂) program applied by (Al-Taee, 2022) showed the effect of using three types of water (distilled water, river water and well water). in dissolving and precipitating carbonate minerals when leaching unexcited natural soil columns, so I got a sedimentation system (arconite, regular dolomite calcite, and irregular dolomite) when using distilled water, and when treating the soil with river water and well water with higher ionic strength, I got a sedimentation system similar to the distilled water treatment With an increase in the amount of precipitation of the aforementioned minerals, as well as the appearance of the mineral vitrite, which requires a high concentration of calcium ion to be deposited. Therefore, the study aims to predict the ability of water of different ionic strength to dissolve and precipitate carbonate minerals in the soil treated with this water using the V. MinteqA₂ program, as well as the ionic species and their concentrations in the solutions of these soils.

MATERIALS AND METHODS

Location: Several sites were selected in Nineveh Governorate / northern Iraq on the basis of the discrepancy in their content of calcium carbonate, which are (Abbasiya, Masayed, Shora, Qayyarah and Batnayah). Soil samples were brought to each site for the purpose of laboratory analysis, while natural undistributed soil columns were taken to a depth of (20 cm). And treated with well water with electrical conductivity (1 ,5, 10) dSm⁻¹ and five cycles of wetting and drying.

Table 1. The geographical location of the study sites.

Location	Geographical location	Land use
Abbasiya	36° 2552.44 "N 43° 1139.97 "E	field crops
Masayed	36° 1628.63 "N 42° 5355.61 "E	field crops
Shora	35° 5941.03 "N 43° 1324.30 "E	field crops
Qayyarah	36° 4755.54 "N 43° 1730.41 "E	field crops
Batnayah	36° 3220.81 "N 42° 0723.13 "E	field crops

Laboratory analysis: Chemical and physical analysis were carried out on soil samples and well water in the laboratories of the Department of Soil Sciences and Water Resources / College of Agriculture and Forestry / University of Mosul according to the methods presented in Salem and Ali (2017). A soil extract was made at a ratio of (1:1) distilled water: soil. Soil pH was measured using the pH-meter and the electrical conductivity using the EC-meter, and the positive ions were estimated as follows: calcium and magnesium by the titration method with (0.01) M and sodium. And potassium using the Flame Photometer device, and the chloride ion was estimated by the method of titration with silver nitrate (0.01) M and carbonate and bicarbonate by aliquot with dilute sulfuric acid (0.01) M. As for the sulfate, it was estimated through the difference between the number of mill equivalents of the dissolved positive and negative ions. The ionic strength of well water samples and a solution was calculated. Soil according to the equation of Griffin and Jurinak (1974).

Table 2. The concentration of dissolved ions in the soil samples of the study.

Location	meq l ⁻¹						
	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ⁻²
Abbasiya	5.0	1.5	0.6	0.3	2.0	1.0	4.4
Masayed	5.5	1.0	0.7	0.2	1.0	1.0	5.4
Shora	25.0	2.5	1.1	1.1	3.5	1.0	25.2
Qayyarah	30.5	15.0	8.1	1.5	6.0	1.0	48.1
Batnayah	5.0	1.5	0.7	0.2	1.5	1.0	4.7

The organic matter was estimated by the wet oxidation method using potassium dichromate (1.0N) according to Walkley and Blak reported in (Black, 1965). Calcium carbonate was estimated by adding an excess amount of hydrochloric acid (1.0N). The remaining acid was estimated by leaching with sodium hydroxide (1.0M) in the presence of The ph.ph index is according to (Page *et al.*, 1982), and the capacity exchange cation of the positive ions was estimated by sodium acetate (1.0M) with (pH = 8.2) and sodium was measured in the extract, and from it the CEC was calculated according to (Page *et al.*, 1982) and the hydrometer method was used In estimating soil texture according to (Gee and Bauder, 1986).

Preparation of soil columns: Undistributed natural soil columns were taken from the selected study sites. Plastic columns were used with an inner diameter of (7.0 cm) and a



Table 3. Some physical and chemical properties of the study soil samples.

Location	EC dS m ⁻¹	pH	O.M	CaCO ₃	CEC gm kg ⁻¹	Clay	Silt	Sand	Texture
Abbasiya	0.6	7.6	20.0	32.0	17.0	375	450	175	C-L
Masayed	0.8	7.7	11.4	30.0	16.0	300	475	225	C-L
Shora	2.5	7.4	8.6	27.5	16.1	450	350	200	C
Qayyarah	3.4	7.1	12.2	21.0	15.6	225	325	450	L
Batnayah	0.8	7.9	14.0	36.0	20.0	415	410	175	S-C

Table 4. Some chemical properties of well water samples used in the study.

Well No.	EC dS m ⁻¹	I Mol l ⁻¹	pH	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ⁻²
							meq l ⁻¹			
1	1.0	0.013	7.4	03.5	01.5	05.2	0.05	05.5	0.5	04.3
2	5.0	0.065	7.8	13.5	18.5	17.4	0.30	10.0	2.0	19.8
3	10.0	0.130	7.9	28.5	35.5	34.3	0.60	64.0	6.5	28.4

length of (20 cm). The inner wall of each column was coated with silicone oil to reduce the effect of the walls on water flow. A base of diameter slightly larger than the outer diameter was placed at the bottom of the column. The column has a screen wire with a hole diameter of (0.1 mm) installed inside it to prevent the passage of large soil particles, and glass wool and gravel washed with 1M (HCl) and a thickness of (0.3 cm) are used as a filter, after which the columns are placed on a wooden stand and then the columns are treated with well water depending on The porous volume and five cycles of wetting and drying. The duration of one cycle is ten days. After the end of the fifth cycle, a batch of water equivalent to two pore volumes is added to obtain a displacement solution equivalent to one pore volume. It is received in plastic bottles, not to conduct chemical analysis on it. The porous volume of each column was calculated according to (Selassie *et al.*, 1992) by wetting the soil inside the column by capillary action. (Column + soil + water = W1) was weighed, then the column was left to dry to reach a weight equal to its weight before wetting, then (column + soil = W2) was weighed, after which the volume was calculated. porosity according to the following relationship:

$$Pv=W1-W2..... (1)$$

RESULTS AND DISCUSSION

The ability of water to dissolve and precipitate carbonate minerals: After obtaining an offset solution in the amount of one pore size after the fifth cycle of wetting and drying, a chemical analysis of these solutions is carried out to obtain the values of ionic strength, the degree of interaction, and dissolved ions of calcium, magnesium, sodium, potassium, bicarbonates, and sulfate chlorides, Table 5, in order to include them in the geochemical balance program V. MinteqA2 to get the output of the program so that we can know the ability of the water used to dissolve and precipitate carbonate minerals depending on the saturation index values,

and the results of Table 6 show the saturation index values that were obtained from dividing the ion activity product by the solubility product constant for each mineral, The positive values represent the ability of the water used to precipitate minerals, while the negative values represent the solubility state of the minerals. It is noted that the use of water with an ionic strength of (0.013) mol l⁻¹ led to the precipitation of calcite, aconites, vitrite, regular dolomite, and irregular dolomite at all study sites, except for vitrite, which was not deposited in the Al-Masaid and Al-Qayarah sites, and the irregular dolomite mineral at Al-Qayarah site. The degree of stability of carbonate minerals and their stability has a relationship with solubility. Therefore, vitrite is more soluble because of its low stability compared to calcite, as it reaches. The solubility product of calcite is (3.36 x 10⁻⁹) and vitrite (1.22 x (10⁻⁸). Therefore, the sedimentation of vitrite requires high concentrations of calcium and bicarbonate, as indicated by (Abdulkarrem *et al.*, 2013) Table 5. As for the reason for the non-precipitation of irregular dolomite In this Qayyarah site, this is due to the low concentration of magnesium as well as bicarbonate, as indicated by (Sakeer, 2007). The results indicate in Table 6 that the use of water with an ionic strength of mol l⁻¹ (0.065) mol l⁻¹ led to the precipitation of calcite, arconite, vitrite, and regular dolomite. And irregular dolomite for all study sites, and the increase in ionic strength led to an increase in the liberation of ions present at the exchange sites during the flow of water through the soil columns after the fifth cycle of wetting and drying, and this led to an increase in the concentrations of ions in the leaching solutions, and thus an increase in the amount of precipitated minerals as well as the appearance of a mineral Vitrite in the sites of Masayad and Qayarah and the irregular mineral dolomite, which requires their deposition of high concentrations of calcium and magnesium in addition to bicarbonate, as mentioned in Table 5. When using water with an ionic strength of (0.130) mol l⁻¹, it led to the precipitation of the minerals Calcite, Argonite, Vitrite, and regular Dolomite. And irregular



Table 5. Input data in the V. MinteqA2 program.

Location	I	pH	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Cl ⁻	HCO ₃ ⁻	SO ₄ ⁻
	Mol l ⁻¹								
Abbasiya	0.021	7.9	12.0	5.0	2.5	0.5	4.5	2.0	11.3
	0.058	7.7	32.5	14.5	2.5	0.7	30.0	2.5	16.6
	0.113	7.7	62.5	25.0	2.7	1.0	77.5	3.0	13.5
Masayed	0.023	7.9	10.0	7.5	2.8	0.2	7.0	1.0	11.4
	0.073	7.7	42.0	15.0	12.2	0.4	35.0	2.0	32.4
	0.127	8.0	80.0	21.0	25.6	0.6	85.0	2.5	39.7
Shora	0.043	8.0	32.5	11.5	7.4	0.2	17.5	1.0	33.0
	0.075	7.7	40.0	12.0	17.4	0.9	41.0	2.0	27.1
	0.126	8.1	45.0	31.5	30.4	1.3	52.0	3.0	53.0
Qayyarah	0.028	7.9	10.5	4.0	6.1	0.8	5.5	1.0	17.8
	0.069	8.2	20.0	18.0	20.4	0.8	30.0	2.0	27.2
	0.125	8.1	42.5	23.0	31.7	1.4	67.5	3.0	27.1
Batnayah	0.021	8.1	15.0	5.0	1.5	0.1	7.5	2.0	11.6
	0.060	7.8	50.0	10.0	10.0	0.2	39.5	2.0	29.3
	0.121	7.7	95.0	25.0	24.4	0.4	102.5	2.0	40.7

Table 6. The effect of the ionic strength of water on the saturation index values according to the outputs of the V. MinteqA2 program.

Location	I	Calciet	Argoniet	Viteriet	Dolomiet oder	Dolomiet disorder	Huniet	Magnsiet
	Mol l ⁻¹							
Abbasiya	0.013	0.675	0.531	0.109	0.892	0.342	-3.017	-0.933
	0.065	0.858	0.751	0.291	1.497	0.947	-1.568	-0.511
	0.130	1.110	0.966	0.543	1.938	1.388	-0.748	-0.322
Masayed	0.013	0.288	0.145	-0.278	0.593	0.034	-3.140	-0.864
	0.065	0.786	0.643	0.220	1.265	0.715	-2.120	-0.672
	0.130	1.331	1.187	0.764	2.209	1.659	-0.378	-0.272
Shora	0.013	0.710	0.566	0.144	1.118	0.568	-2.408	0.742
	0.065	0.779	0.635	0.212	1.170	0.620	-2.389	-0.759
	0.130	1.262	1.118	0.696	2.511	1.961	0.668	0.099
Qayyarah	0.013	0.322	0.178	-0.244	0.394	-0.156	-3.803	-1.078
	0.065	0.962	0.818	0.395	2.019	1.469	-0.209	-0.093
	0.130	1.286	1.142	0.720	2.428	1.878	0.371	-0.008
Batnayah	0.013	0.830	0.686	0.264	1.227	0.677	-2.320	-0.753
	0.065	0.859	0.715	0.292	1.115	0.605	-2.594	-0.854
	0.130	0.908	0.764	0.341	0.946	0.414	-3.267	-1.094

Dolomite for all study sites with an increase in the amount of sedimented minerals, through the high values of the saturation index compared to the value of water with ionic strength mol l⁻¹ (0.013) and (0.065) Table 6, as well as the deposition of Hunet mineral in the sites of Shora and Qayyarah and the mineral magnasite at the Shora site, which required high concentrations of magnesium and bicarbonate to be deposited. As for the reason for the failure of these two minerals to be deposited in the Abbasiya, Al-Masaid and underground sites, despite the convergence of magnesium and bicarbonate concentrations in them with the Shora and Qayyarah sites, in which deposits of the minerals Hunet and Magnasite occurred, is the high concentration of calcium, which was prevented by the Table 5 In this regard, (Alhadede

et al., 2017) mentioned that when calcium carbonate is present with magnesium carbonate in the soil solution, this leads to an increase in the solubility of calcium carbonate and decreases the solubility of magnesium carbonate. The solubility product of calcium carbonate also differs in the presence of magnesium carbonate, especially since the presence of magnesium is in balance. With calcium in the soil solution, it can affect the solubility of calcium carbonate. We conclude from the foregoing that there is a relationship between the ionic strength of the used water and the intensity of weathering of the solid phase when they touch, as the ionic strength has a strong effect on dissolving salts and minerals, and this affects the change of concentration and ionic composition, and thus more free calcium and magnesium ions



Table 7. Odd and even ionic species of calcium and magnesium for the soils of the study sites.

Location	I Mol l ⁻¹	Ca ⁺²	Mg ⁺²	CaHCO ₃	CaSO ₄	CaCl ₂	MgHCO ₃	MgSO ₄	MgCl ₂
		meq l ⁻¹							
Abbasiya	0.013	7.3	1.8	2.0	10.0	0.9	0.2	0.8	2.2
	0.065	13.6	6.1	2.5	16.0	1.4	0.2	0.4	14.5
	0.130	29.8	11.9	3.0	13.4	2.6	0.2	0.2	25.0
Masayed	0.013	5.5	4.1	1.0	9.0	1.4	0.2	2.2	7.0
	0.065	16.3	5.8	2.0	32.4	12.2	0.3	1.0	15.0
	0.130	25.5	6.7	2.5	39.7	25.6	0.2	0.8	21.0
Shora	0.013	15.0	4.6	1.0	31.5	1.6	0.5	0.6	11.5
	0.065	15.5	5.5	2.0	27.1	10.7	0.5	0.7	12.0
	0.130	14.5	10.0	3.0	42.0	1.2	0.9	0.8	31.0
Qayyarah	0.013	11.4	4.5	1.0	11.5	1.2	0.4	0.2	5.0
	0.065	16.3	14.6	2.0	18.0	2.0	0.3	0.2	18.0
	0.130	30.0	16.2	3.0	27.1	11.4	0.2	0.1	23.0
Batnayah	0.013	9.5	6.3	1.5	11.6	1.9	0.4	0.2	4.0
	0.065	41.5	8.3	1.5	29.3	19.2	0.2	0.2	10.0
	0.130	30.8	8.1	1.5	40.7	52.8	0.2	0.1	25.0

are liberated with the bicarbonate root and when the concentration reaches above saturation The carbonate minerals are deposited forming a number of solid phases. The solid phase formed first will be of the type that can be connected when the activity ratio of these ions is closer to their initial values in the soil solution. When the ionic strength of the water passing through the study soil columns increases, more of these ions will be released. The ions, and thus the decrease in their effectiveness rates, are followed by the appearance of the remaining solid phases that can be reached, which are formed in an increasing order according to the change in the concentration and ionic composition of the soil solution (Sposito, 2008).

The nature of ionic species: As shown in Figure 1 shows that the hypothetical combination of cations and anions in the site of the Shora that the types of salts formed are the most important of which is calcium sulfate salt CaSO₄ with a percentage of (37, 40, 48)% at ionic strength (0.013, 0.065, 0.130) respectively, the second salt is magnesium chloride MgCl₂ with percentages of (17, 16, 30)% at ionic strength (0.013, 0.065, 0.130) respectively, while the rest of the salts had percentages of about 1% at all ionic strengths except calcium chloride salt CaCl₂, whose percentage was 15% at ionic strength 0.065, while the percentage of calcium ranged between (14-23)% and magnesium between (6-10)%, Table 7 shows the concentration of ionic species of calcium and magnesium, odd and even, prevailing in the equilibrium solutions of soil samples treated with water of (0.013,0.065,0.130) mol l⁻¹ ionic strength. These concentrations were obtained depending on the hypothetical combination correlation between positive and negative ions in Equilibrium solutions and the results of the theoretical correlation indicate that the dominant ionic species are arranged as follows:

Mg(HCO₃)₂ >MgSO₄ > Ca(HCO₃)₂>

CaCl₂ >MgCl₂> CaSO₄.2H₂O

The results show an increase in the percentages of all ionic species for all sites with an increase in the ionic strength of the water used in the process of leaching and displacing the ions present on the exchange sites in a direct manner, and thus the equilibrium solution is rich in positive and negative ions and with a concentration that allows the formation of ionic pairs depending on the solubility product. The least soluble ionic species precipitate and the most soluble ionic species remain to precipitate at the end (Kopittke *et al.*, 2006). Accordingly, the prevailing percentages of the total ionic species were calculated by the hypothetical combination n of positive and negative ions. Other ionic species were excluded and special ionic species were included. The two ions of calcium and magnesium are the subject of research and study, according to what was reported by (Zakarina, 1963).

As shown in Figure 1 positive and negative ions unite with each other, forming ionic types whose proportions are according to the values of the solubility yield. Therefore, we notice that the percentages of CaHCO₃ and MgCO₃ are few compared to the rest of the ionic species (Table 7). The appearance of magnesium chloride in proportions that exceed calcium chloride is due to the process Ionic exchange between calcium and sodium on the exchange complex, which led to an increase in the percentage of magnesium ion with an increase in ionic strength and its appearance in the soil solution at high levels of salinity (Al-Hadidi, 2021), as well as Table 7 showing that the equilibrium solution is saturated with calcium sulfate This led to the dominance of this species over all the paired ionic species of calcium and magnesium, and this is consistent with what (Saksono *et al.*, 2009) concluded, that the soil solution is saturated with calcium sulfate when the ratio of soil: water is (1:1), which is the



product of chemical precipitation at depths. Different fresh and terrestrial waters from the surface with calcium and sulfate ions.

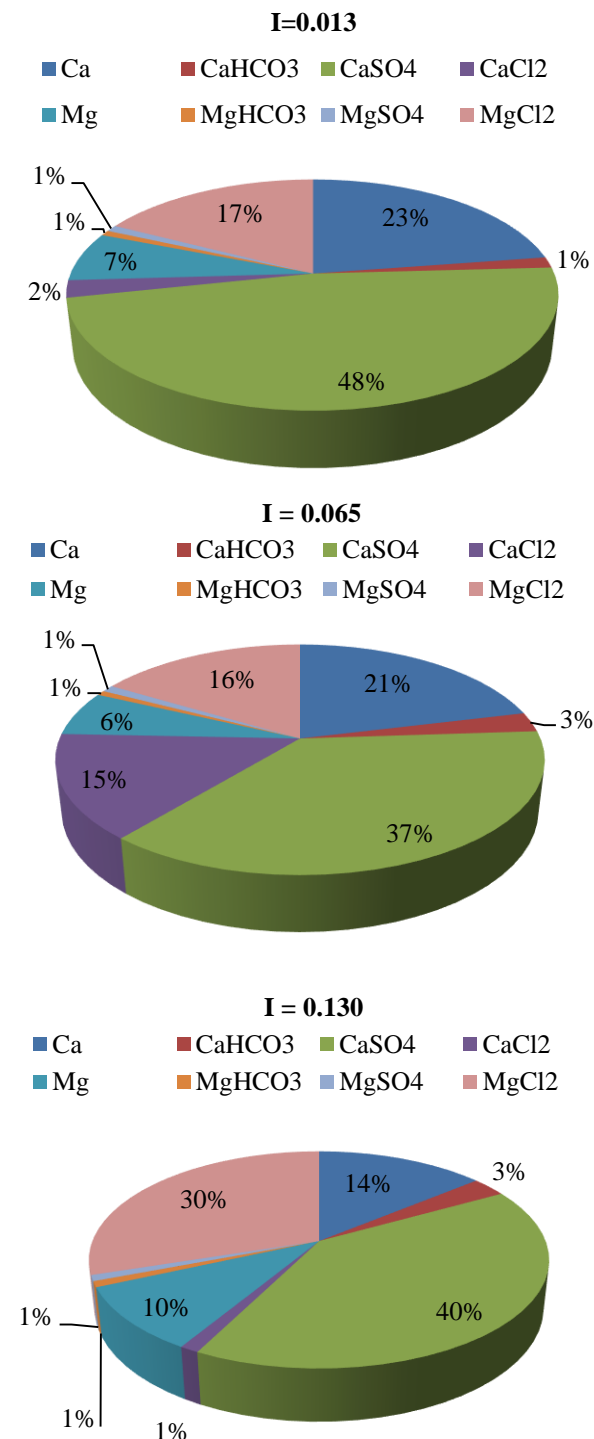


Figure 1. The effect of ionic strength on the odd and even ion forms of calcium and magnesium at the Shora site.

Conclusion: There is a relationship between the ionic strength of water and the intensity of weathering of the solid phase, thus releasing calcium, magnesium and bicarbonate ions, and when the concentration reaches above saturation, carbonate minerals precipitate. The percentages of all ionic species increase with the increase in the ionic strength of the water used, thus the equilibrium solution is rich in positive and negative ions and at a concentration that allows the formation of ionic pairs depending on the solubility product.

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SDGs addressed: Clean Water and Sanitation, Climate Action, Life on Land.

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