Journal of University of Zakho, Vol. 2(A), No.1, Pp 166-175, 2014

# DIAGNOSIS OF MINERALS CONTROLLED THE CARBONATE SOLUBILITY IN SOME CALCAREOUS SOILS FROM NORTH IRAQ

**H**.**M**. **A**hmed, **M**.**A**. **Al**-**O**baidi and **A**.**W**. **A**bdel-Kareem
Soil and Water Dept., College of Agricultural and Forestry, Mosul University, Iraq.

***(Accepted for publication: February 24, 2014)***

## Abstract

**Four locations were chosen from North Iraq having different soil orders namely: (Zawaita-Mollisols), (Batail-Vertisols), (Ninevah forest-Inceptisols), (Tel-Afer-Aridisols) in order to study the role of solubility diagram and x-ray diffraction analysis in determining the type of mineral which effect the carbonate solubility.**

**Results showed that the calcite mineral effected the carbonate solubility depending on solubility diagram indicating by the points that falls under calcite mineral line represented the state under saturation with respect to this mineral. Also the results of x-ray diffraction stated the presence of calcite at d-spacing (0.304nm) and dolomite at (0.289nm), therefore the peak intensity of calcite (d-spacing) was sharpened and most height than the peak of dolomite, this conclusion was in agreement with the results of solubility diagram that were obtained above.**

***Keywords:*** *Minerals, Carbonate Solubility, Calcareous, X-Ray Diffraction.*

## Introduction

Carbonate extent a major influence on the chemical properties of soils, for example adsorption and pH-related phenomena affect the availability of plant nutrients such as Zn and Fe, Mn (Bui *et al*., 1990). Calcium carbonate characterized by interaction with soil system, also their chemical and geochemical reactions interacted with other phases in soils which caused a large different in their properties especially the dissolution (Rezaei *et al*., 2004). This solubility is affected mainly by $HCO_3^-$ and $CO_3^{-2}$ concentration with effect on the chemistry of carbonate (Manahan 2005). Carbonate having different phases in soils named calcite, dolomite, aragonite, siderite, vaterite, magnesite depending on their solubility, but calcite and dolomite minerals formed a major carbonate phases in soils (Holtzclaw *et al*., 1986) and (Karl and Vodvic, 2000). The differentiation between these phases has important implication in soil genesis, chemistry and fertility (Holtzcalw *et al*., 1986). Langmuir, 1997 considered dolomite as one of the carbonate minerals common in sedimentary rocks, its solubility controlled by tow reactions:

1. Congruent reaction: happen in one step.

$$CaMg(CO_3)_2 \rightleftharpoons Ca^{+2} + Mg^{+2} + 2CO_3^{-2}$$

2. Incongruent reactions: happen in two steps.

$$CaMg(CO_3)_2 \rightleftharpoons CaCO_3 + Mg^{+2} + CO_3^{-2}$$
$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$$

Karbery *et al*., 2005 stated that the weathering and solubility of carbonate minerals is controlled by partial pressure of $CO_2$ according to Hennry's law which stated that the increase in carbonic acid is followed by increasing the rate of minerals weathering in soils. The chemical weathering of carbonate based on physo-chemical conditions of water and solid phase, with some parameters play an important role in the solubility of carbonate such as pH, $PCO_2$, ionic strength, $Ca^{+2}$ ions, foreign ions (Abril *et al*., 2003).

The objective of this study was to differentiate the mineral which control the carbonate dissolution using solubility diagram and x-ray diffractometer (XRD).

## Materials and Methods

This study was conducted on four locations from north Iraq having different soils orders namely: Zawaita-Molliosls, Batail-Vertisols, Ninevah forest-Inceptisols and Tel-Afer-Aridisols. These soils were classified at soil series (table 1) depending on (Soil Survey Staff, 1994) and (Al-Agaid, 1989).

**Table (1):** Soils classification at soil series

| Location | Order | suborder | great group | series |
|---|---|---|---|---|
| Zawaita | Mollisols | Xerolls | Calcixerolls | 653 CCE |
| Batail | Vertisols | Xererts | Chromoxererts | 452 CCW |

| | | | | |
|---|---|---|---|---|
| Ninevah forest | Inceptisols | Ochrepts | Xerochrepts | 432 CCF |
| *Tel-Afer* | Aridisols | Orthids | Calciorthids | 453 CCW |

Therefore the soils samples were collected from horizons of each pedon and prepared for chemical analysis presented in (table 2) as described by Rowell , 1996.

**Table (2)** Some chemical characteristics of studied soils

| **depth (cm)** | **Horizon** | **pH** | **EC** | **Organic matter** | **Calcium carbonate** | **Active carbonate** | **CEC** |
|---|---|---|---|---|---|---|---|
| Measurement unit | | | $dS.m^{-1}$ | | $gm.kg^{-1}soil$ | | $C.mol.kg^{-1}$ |
| | | | | Zawaita-653 CCE | | | |
| 0-17 | Ah | 7.53 | 0.21 | 23.40 | 116.20 | 61.30 | 36.41 |
| 17-50 | $B_t$ | 7.61 | 0.12 | 9.50 | 323.40 | 108.10 | 25.87 |
| 50-87 | $C_{1k}$ | 7.70 | 0.11 | 8.10 | 369.60 | 87.21 | 19.65 |
| | | | | Batail-452 CCW | | | |
| 0-18 | Ap | 7.48 | 0.17 | 15.80 | 123.20 | 102.60 | 32.75 |
| 18-44 | $B_{2t}$ | 7.73 | 0.13 | 12.00 | 177.10 | 98,30 | 30.97 |
| 44-81 | $C_{1Ca}$ | 7.52 | 0.19 | 11.00 | 231.00 | 112.40 | 25.86 |
| | | | | Ninevah forest-432 CCF | | | |
| 0-22 | Ah | 7.40 | 0.17 | 19.40 | 111.00 | 27.80 | 18.54 |
| 22-48 | (B) | 7.64 | 0.13 | 12.00 | 127.60 | 38.90 | 14.32 |
| 48-80 | BC | 7.48 | 0.18 | 8.50 | 134.40 | 24.30 | 15.21 |
| | | | | Tel-Afer-453 CCW | | | |
| 0-20 | Ap | 7.65 | 0.13 | 11.60 | 323.40 | 81.20 | 24.87 |
| 20-52 | $B_t$ | 7.75 | 0.15 | 8.50 | 327.20 | 93.50 | 21.09 |
| *52-85* | $C_{1Ca}$ | 7.81 | 0.31 | 8.20 | 351.60 | 108.60 | 20.98 |

## Diagnosis of carbonate minerals:

### I. Using Solubility diagram:

Dynamic equilibrium were made by preparing a soil suspension 1:20 (soil:water) at 298° Kelvin for 48hr. (Lindsay, 1979), after that the equilibrium extracts were collected to determine the electrical conductivity, pH, $Ca^{+2}$ ion, as well as thermodynamic parameters were calculated as follows:

1- Ionic strength (I) using Griffin and Jurinak, 1973 equation.

$$I = 0.013 \times EC$$

2- Activity coefficient of calcium calculated by Davis equation.

$$-\log f_i - \frac{AZ_i^2\sqrt{I}}{1+\sqrt{I}} - 0.3\,I$$

3- Ionic activity

$$a_i = C_i \times f_i$$

4- Potential of calcium ion.

$$P_{Ca} = -\ Loga_{Ca}$$

### II. Using X-ray diffraction analysis:

Mineralogical analysis were made to differentiate carbonate minerals (calcite and dolomite) in soil samples firstly before dissolution and secondly after dissolution.

**Firstly:** Air dry soil samples represent the soil before carbonate dissolution.

**Secondly:** Soil samples represent the soil after dissolution, through an columns experiment (10 cm depth, 3 cm diameter) as follows. 40 gm of soil were added to each column and compacted to their bulk density, distilled-water was added everyday equal to porous volume of water. At the end of experiment (21 days) the soil samples were dried, grinded and sieved which formed the soil after dissolution. The two samples were put in a special pellets of x-ray diffractometer and exposured to the x-ray at ϴ angle between (26-34°).

## Results and Discussion

To distinguish the minerals which control the carbonate solubility, thermodynamic parameters as shown in table (2) were used. Soils under study are non saline characterized by low levels of ionic strength ranged from 1.0-2.1mol.L$^{-1}$, the activity of coefficient ranged from 0.85 to 0.89, ion activity of calcium raised from 1.07 to 1.88mol.L$^{-1}$, the ionic potential of calcium are between (-logCa$^{+2}$) (-2.74) and (-2.97). all points of calcium ions potential were located under the line of calcite (Fig.1), reflecting an undersaturation of this minerals associated with calcite dissolution. The solubility and precipitation of carbonate minerals especially calcite is associated with downward movement of percolating water and upward by capillary as well as vertically and horizontally movement (Dunling and Anderson, 2000).

**Table (3):** Thermodynamic parameters using in solubility diagram

| depth (cm) | Horizon | Ionic strength($10^{-3}$) mol.L$^{-1}$ | Activity coefficient of Ca$^{++}$ | Activity of Ca$^{++}$ ($10^{-3}$) Mol.L$^{-1}$ | -logCa$^{++}$ | pH |
|---|---|---|---|---|---|---|
| | | | Zawaita-653 CCE | | | |
| 0-17 | Ah | 1.5 | 0.86 | 1.31 | - 2.88 | 7.6 |
| 17-50 | $B_t$ | 1.7 | 0.85 | 1.88 | - 2.74 | 7.5 |
| 50-87 | $C_{1k}$ | 1.2 | 0.87 | 1.32 | - 2.87 | 7.7 |
| | | | Batail-452 CCW | | | |
| 0-18 | Ap | 1.8 | 0.85 | 1.28 | - 2.89 | 7.7 |
| 18-44 | $B_{2t}$ | 1.6 | 0.85 | 1.21 | - 2.91 | 7.2 |
| 44-81 | $C_{1Ca}$ | 2.1 | 0.84 | 1.28 | - 2.89 | 7.7 |
| | | | Ninevah forest-432 CCF | | | |
| 0-22 | Ah | 1.0 | 0.89 | 1.35 | - 2.86 | 7.5 |
| 22-48 | (B) | 1.3 | 0.88 | 1.10 | - 2.95 | 7.1 |
| 48-80 | BC | 1.1 | 0.86 | 1.34 | - 2.87 | 7.3 |
| | | | Tel-Afer-453 CCW | | | |
| 0-20 | Ap | 1.9 | 0.83 | 1.29 | - 2.88 | 7.9 |
| 20-52 | $B_t$ | 1.8 | 0.86 | 1.64 | - 2.78 | 7.9 |
| *52-85* | $C_{1Ca}$ | 1.7 | 0.85 | 1.07 | - 2.97 | 7.4 |

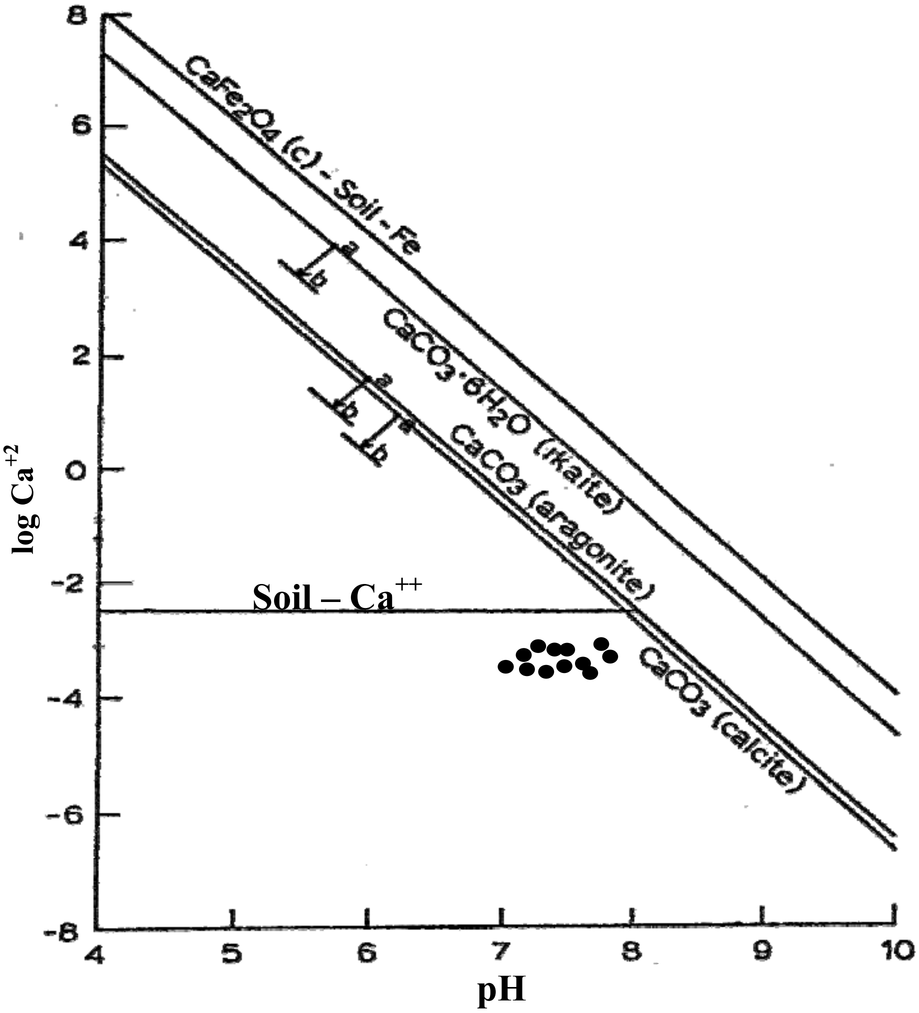

**Fig. 1:** Solubility diagram of carbonate minerals according to (Lindsay, 1979)

**Clay minerals diffraction:**

Carbonate minerals are numerous, some of them are common, others are unknown depending on their stability, some are unstable and transformed to other minerals, accordingly, they behave differently when analyzed with x-ray diffraction, calcite, the most common, show a d-spacing on 0.304nm, secondly Dolomite on 0.289nm. the main mineralongical feature of the studied soils are:

**Zawaita region:**

Figure (2) showed a sharp peaks at (0.304 nm) for calcite with heights (4.5, 8.8 cm) at subsequent horizons after dissolution, dolomite peaks dosppeared in the surface horizon before and after dissolution giving peaks of subsequent depths at (4.5, 5 cm) height. This indicated that dolomite was the dominant mineral at deeper horizons especially $C_k$ horizon (Reeder, 1983).

**Batail soil:**

Figure (3) indicated that peaks of dolomite didn’t appear in recognized horizons before and after dissolution, but calcite gives a clear peaks at (4, 4.8, 5.5 cm) heights after dissolution. The differences in peaks intensity after and before dissolution is because these soils are characterized by height content of swelling-type clays, which in dry seasons cause the soils to develop deep, wide cracks, associated with a phenomena called pedoturbation. (Dunling and Anderson, 2000) stated that peaks intensity of calcite increase with decreasing dolomite presence in soil.

**Ninevah forest soil:**

As shown in (Fig. 4) the peaks of calcite appeared at (0.304 nm) before dissolution with lower intensity in the studied profiles reflected by peaks height of (2, 2.6 cm). after dissolution the Calcite appearance increased at the surface layer and 48-80 cm depth, reaching a 5.0cm height. This increment is due to the removal of precipitated non-crystalline particles on the surface of calcite mineral causing an increase in intensity of crystalline mineral. In addition this increase resulted from precipitation of secondary carbonate on the surface of coarse particles as coatings or as individual districts due to pedogenic processes (Miller *et al.*, 2000) and (Al-Kaysi, 2000).

**Tel-Alfer soil:**

The height of calcite peaks were (5.5, 5.5, 6 cm) at the surface, (20-52 cm) respectively before dissolution (Fig. 5). So the dissolution increased the heights to (8.5, 8.5, 9 cm). The results indicated that calcite was dominant correlated with clay content, therefore the expectation of calcite dominany is to take into consideration since carbonate in clay particles is pedogenic as shown by (Dunling and Anderson, 2000) that 72-100% of carbonate in clay separates has a pedogenic origin. The disappearance of dolomite indicated that it is inherited from parent material (Gile, 1995).

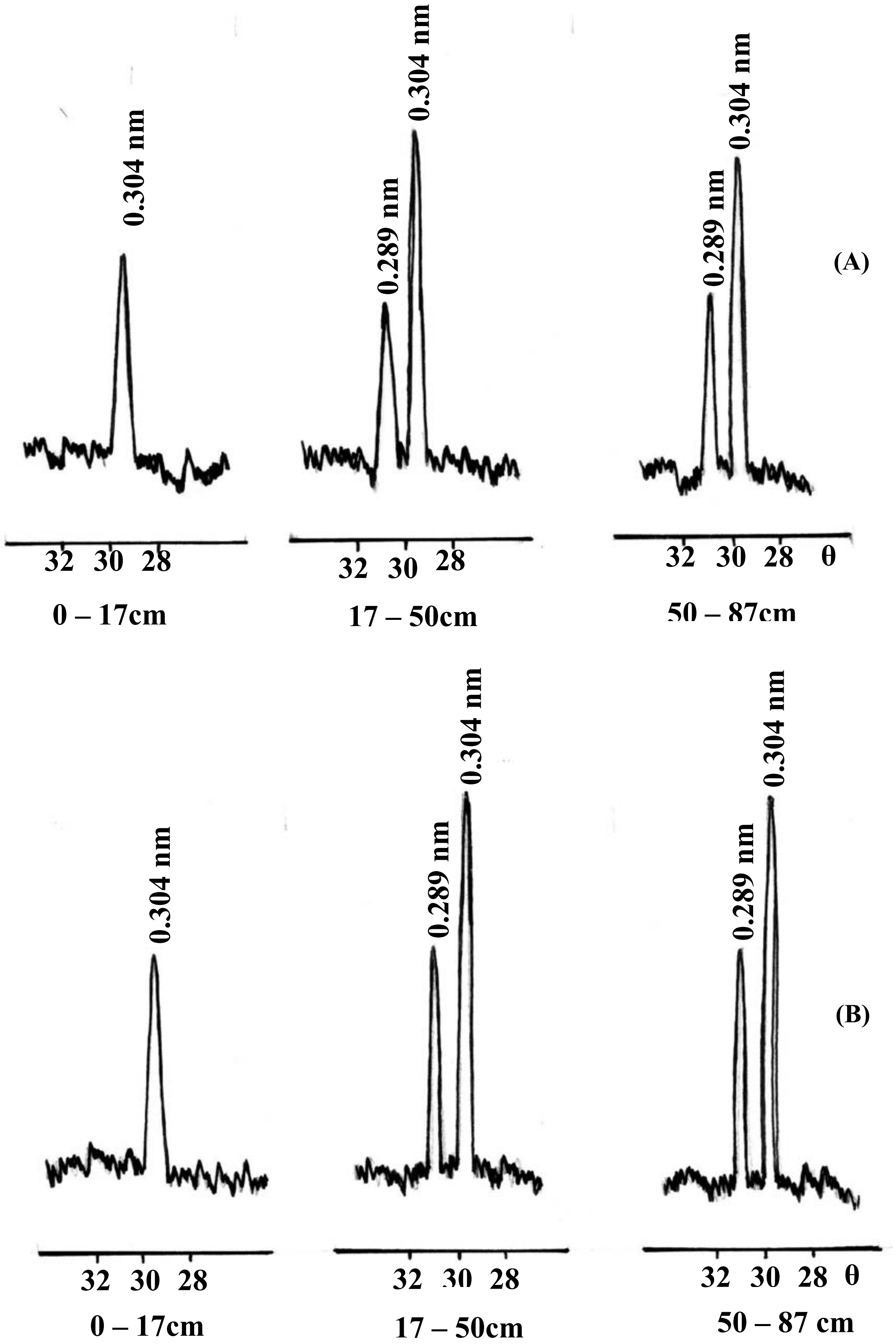

Fig. 2: x-ray diffraction of carbonate minerals – Zawaita soil

A- before dissolution.

B- after dissolution.

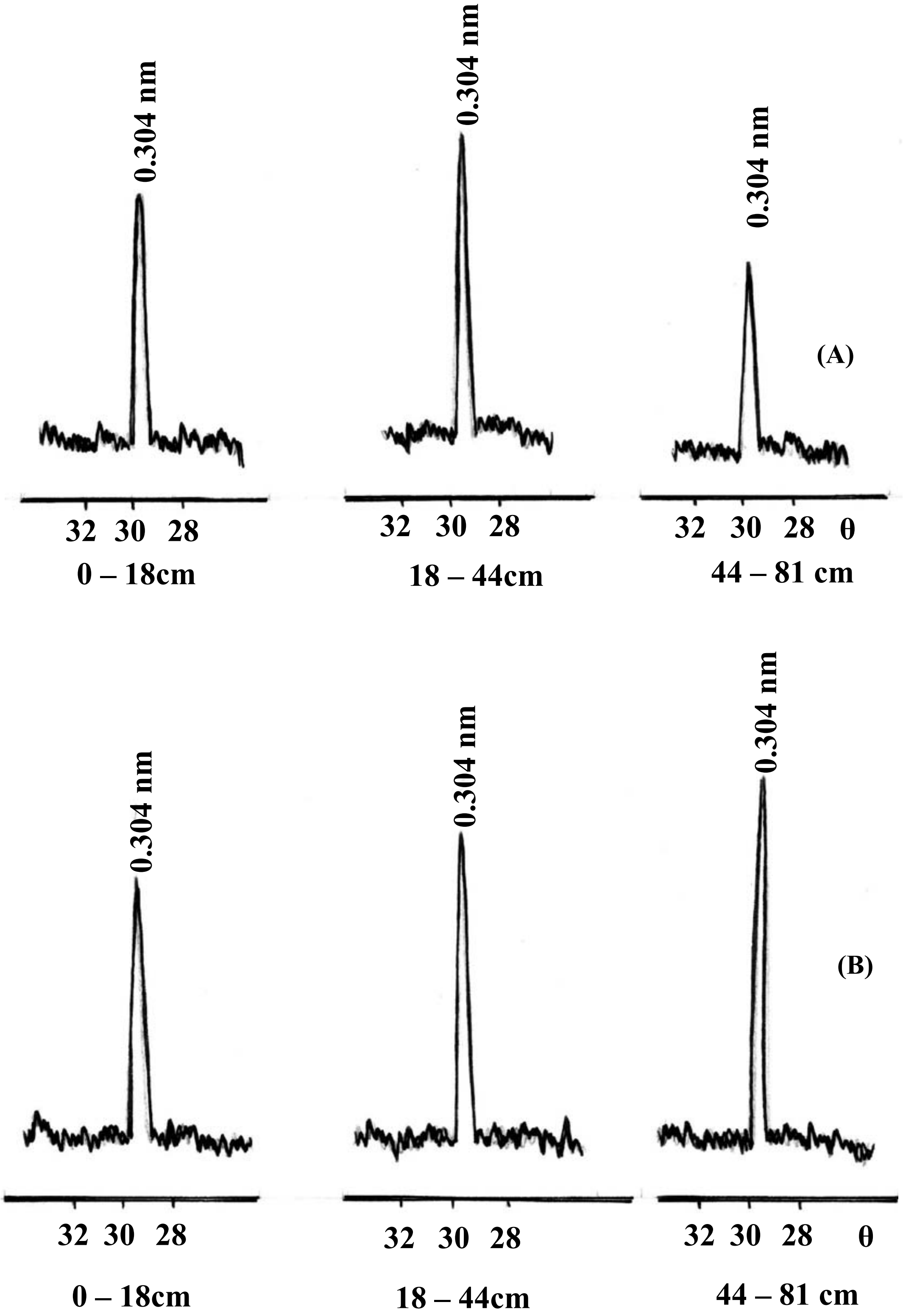

Fig. 3: x-ray diffraction of carbonate minerals – Batail soil

A- before dissolution.

B- after dissolution.

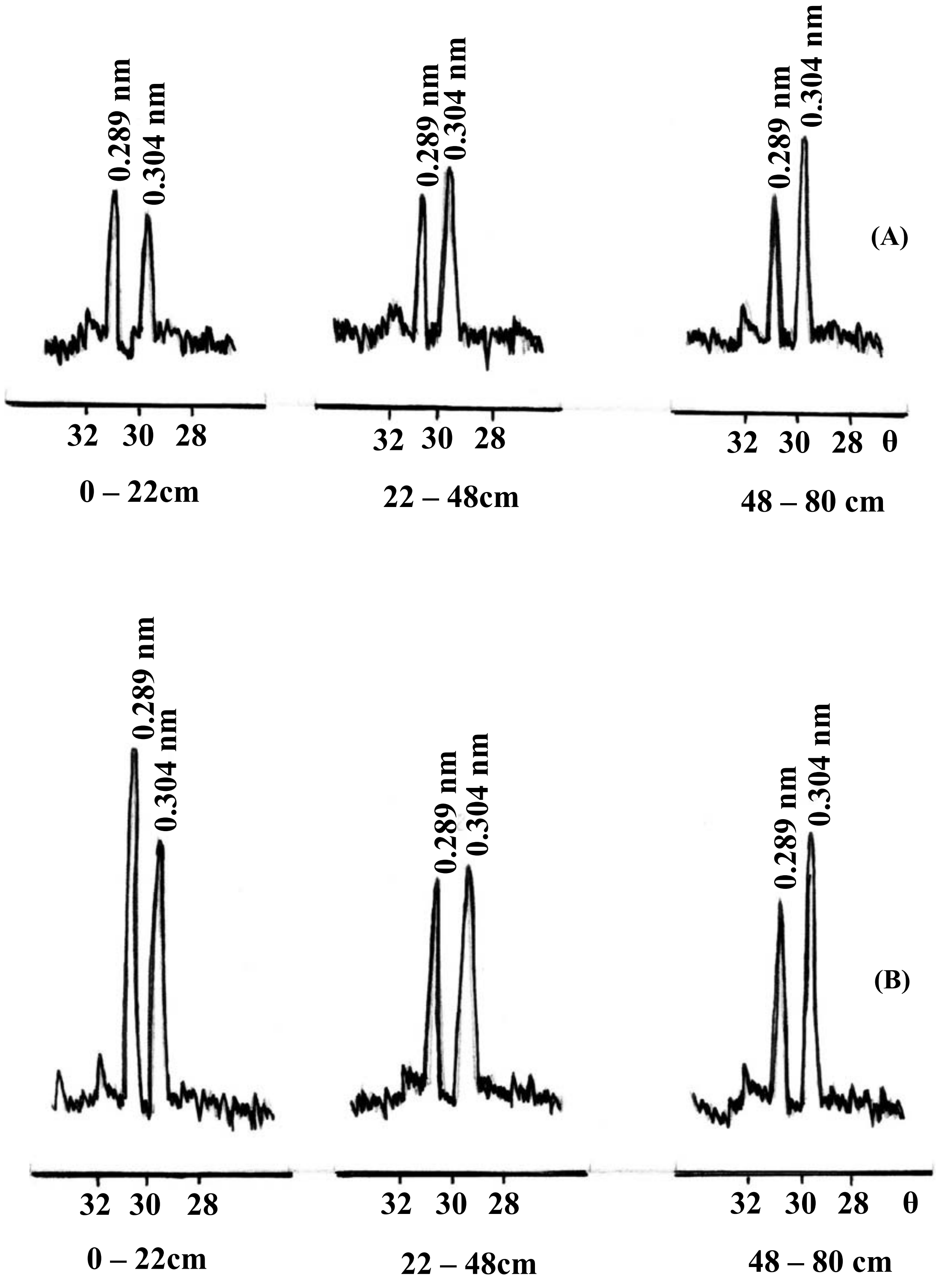

Fig. 4: x-ray diffraction of carbonate minerals – Ninevah forest soil

A- before dissolution.

B- after dissolution.

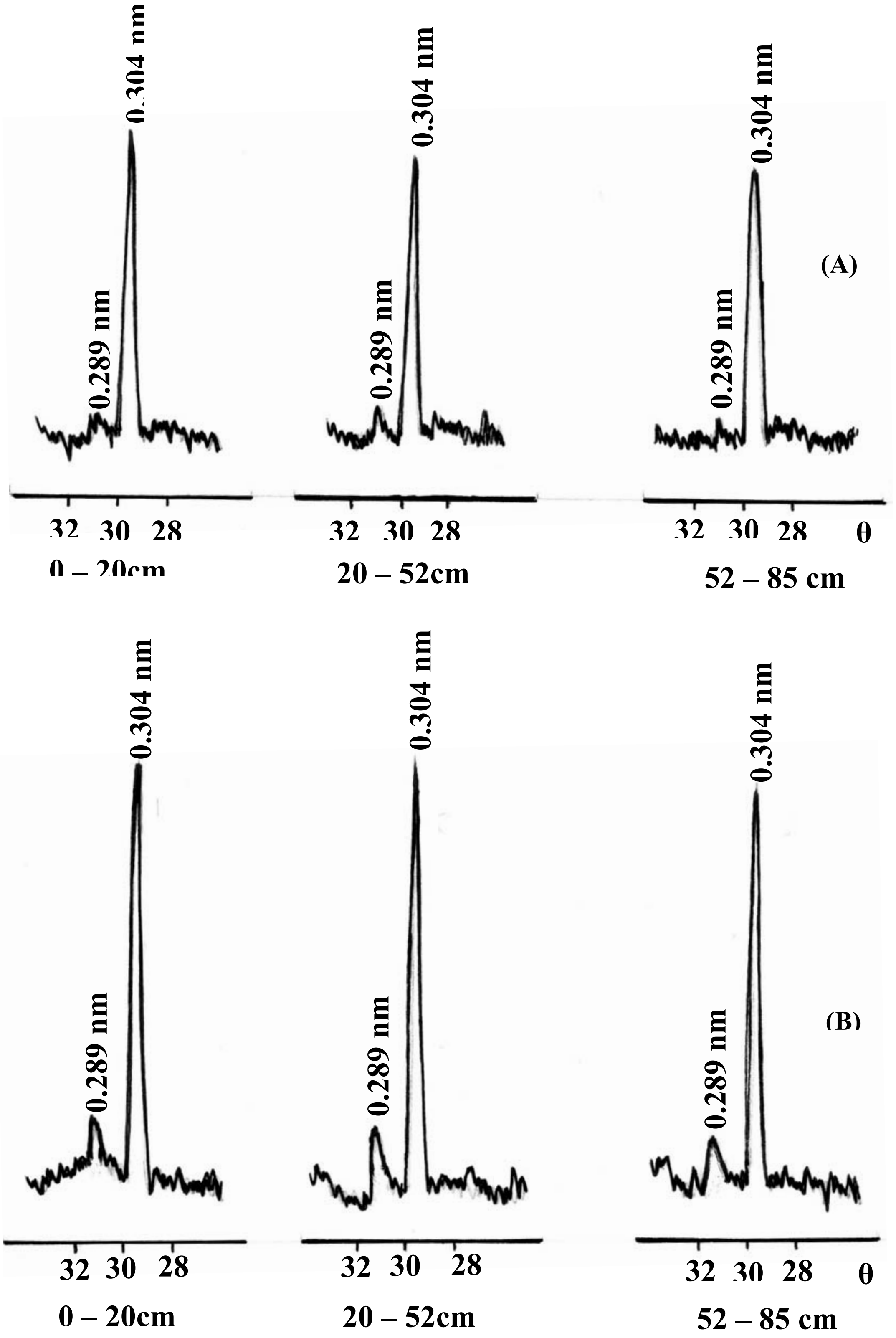

Fig. 5: x-ray diffraction of carbonate minerals – Tel-Afer soil

A- before dissolution.

B- after dissolution.

## References

**Abril, G., H. Etcheber and B. Dellile. 2003.** Carbonate dissolution in the turbid and eutrophic Loire estuary. Marine Ecology Progress Series. 259: 129-138.

**Al-Agaidi, W.K. 1989.** Proposed soil classification at the series level for Iraq soil. Vertisols, Lithosols and Regosols. Soil Science Dept. Univ. of Baghdad, Iraq.

**Al-Kaysi, S.C. 2000.** The influence of the forms of the carbonate minerals on particle size distribution of soil before and after carbonate removal. Iraqi J. of Agric. Sci. 31(2): 585-586.

**Bui, E.N., R.H. Loeppert and L.P. Wilding. 1990.** Carbonate phases in calcareous soils of the western united state. Soil Sci. Soc. Am. J. 54: 39-45.

**Dunling, W. and D.W. Anderson. 2000.** Pedogenic carbonate in chernozemic soils and landscapes of southeastern Saskatchewan. Can. J. Soil Sci. 80: 251-261.

**Gile, L.H. 1995.** Pedogenic carbonate in soils of the isaack's ranch surface, Southern New Mexico. Soil Sci. Soc. Am. J. 59: 501-508.

**Griffin, R.A. and J. Jurinak. 1973.** The interaction of phosphate with calcite. Soil Sci. Soc. Am. Proc. 37: 847-850.

**Holtzclaw, K.M., G. Sposito and J.D. Rhoades. 1986.** improved selective dissolution method for determining calcite and dolomite in soil. Soil Sci. 142: 63-68.

**Karberg, N.J., K.S. Pregitzer and J.S. King. 2005.** Soil carbon dioxide partial pressure and dissolved inorganic carbonate chemistry under elevated carbon dioxide and ozone. Oecologia, 142: 296-306.

**Kralj, D. and N. Vdovic. 2000.** The influence of some naturally occurring minerals on the precipitation of calcium carbonate polymorphs. Water Res. 34: 179-184.

**Langmuir, D. 1997.** Aqueous environmental geochemistry. Printic Hall, Upper Saddle River, N.J.PP (193-229).

**Lindsay, W.L. 1979.** Chemical equilibria in soils. John Wiley and Sons, New York.

**Manahan, S.E. 2005.** Environmental Chemistry, International Standard Book, CRC Press, New York.PP (200-223).

**Miller, J.J., M.J. Dudas and F.J. Longstaffe. 1987.** Identification of pedogenic carbonate minerals using stable carbon and oxygen isotopes, X – ray diffraction and SEM analysis. Can. J. Soil Sci. 67: 953-958.

**Reeder, R.J. 1983.** Carbonates: mineralogy and chemistry. Reviews in mineralogy, vol. 11, Mineralogical Society of America, Washington, p. 394.

**Rezaei, M., E. Sanz and E. Rezaei. 2004.** Simulation of dissolution in the salt water mixing zone of carbonate Aquifers. European Union Project (SALTRANS), Barcelona, Spain.

**Rowell , D.**L. 1996. Soil science methods and application . Welsy , Longman , London.

**Soil Survey Staff. 1994.** Key of soils taxonomy. A basic system of soil classification or making and interpreting soil survey Agric. Handbook. No. 136. USA

# تشخيص المعادن المحددة لذوبانية معادن الكاربونات في بعض الترب الكلسية في شمالي العراق

**الملخص**

اختيرت اربعة مواقع من شمالي العراق مصنفة بمستوى السلسلة تمثل ترب (زاويتا – **Mollisols** وباتيل **Vertisols** وغابة نينوى **Inceptisols** وتلعفر **Aridisols** ، لغرض دراسة دور مخططات الاذابة وحيود الاشعة السينية في تحديد نوع المعادن المتحكمة بذوبانية معادن الكاربونات.

اظهرت النتائج بان معدن الكلسايت هو المتحكم بعملية ذوبان الكاربونات . وان مخططات الاذابة بينت بان جميع مواقع الدراسة كانت تحت خط ذوبان معدن الكلسايت ، كما اشارت نتائج التحليل المعدني باستخدام **XRD** الى تشخيص معدن الكلسايت عند **d- Spacing** ٠,٣٠٤**nm** ومعدن الدولومايت عند ٠٢٨٩ **nm** واتصفت منحنيات الحيود لمعدن الكلسايت بكونها حادة وكانت اكثر طولاً من منحنيات الحيود لمعدن الدولومايت.