

Chemical Model for Origin and Distribution of Elements in Salts and Brines during Evaporation of Waters. Application to some Saline Lakes of Tibesti, Chad

J. Y. GAC,[†] A. AL-DROUBI,[‡] H. PAQUET,[‡] B. FRITZ,[‡] and Y. TARDY[‡]

[†]O.R.S.T.O.M. 24, rue Bayard, 75008 Paris, France

[‡]Institut de Géologie, 1, rue Blessig, 67000 Strasbourg, France

Abstract

During evaporation of natural waters, many possibilities of successive salt parageneses and of variations in chemical facies of residual solutions are offered. Chemical model based on equilibrium reactions can be very useful for explaining the complexity of natural geochemical paths and distribution of elements in salts and brines. This model calculates the distribution of complex aqueous species, ionic strength, activity coefficients, saturation of solutions with respect to salts and amounts of minerals precipitated along progressive evaporation of water.

The model was applied to saline lakes of Ounianga Kebir in Tibesti (northern Chad), which occupy several depressions within the Nubian sandstone formation. In the initial diluted waters springing from sandstone all the major elements are present in the same order of magnitude. After concentration by evaporation, brines become strongly depleted in calcium and magnesium, initially enriched in sodium and bicarbonate and finally in potassium and chloride. Salt parageneses control chemical composition of waters, the calculated chemical model being in excellent accordance with natural observations. Silica and magnesium concentrations are controlled by an early precipitation of Mg-montmorillonite; magnesium molality is then regulated by the formation of huntite and dolomite; calcium is controlled by calcite, huntite, dolomite, pirssonite and gaylussite; sodium is first trapped in trona or natron, then by thenardite; potassium is finally picked up by sylvite; pH rises until reaching a maximum at about 10.

Behavior and distribution of elements in salts and brines can be discussed considering the relative proportions of these elements in the initial solutions and the order in which salts precipitate.

Introduction

In natural cases, when waters evaporate, many possibilities of successive salt parageneses and variations in chemical facies of residual solutions are offered. Distribution and behavior of the elements are chiefly determined by the relative amount of these elements in the initial solutions and by the nature and the order of salts precipitating (Van'Thooff *et al.*, 1912; d'Ans, 1933; Lotze, 1957; Borchert and Muir, 1964; Jones, 1965, 1966; Jones *et al.*, 1966, 1969; Hardie, 1968; Bradley and Eugster, 1969; Truesdell and Jones, 1969; Hardie and Eugster, 1970; Lerman, 1967, 1970; Eugster, 1970; Braitsh, 1971; Lerman and Jones, 1973; Phillips and Van Denburgh, 1971; Jones *et al.*, 1976).

Predictions of such behaviors can be approached using equilibrium reactions as proposed by Garrels and Mackenzie (1967), Hardie and Eugster (1970), Wood (1975), Fritz (1975), Al-Droubi (1976), Al-Droubi *et al.* (1976a, b, 1977), Gac *et al.* (1977) have shown that chemical models can be very useful to understand natural processes and to explain observed salt parageneses and chemical compositions of brines.

As an example of application, the geochemistry of Ounianga lakes was studied because of the large variety of salts encountered and of the presence in the initial solution of all the major anions, cations and silica in almost similar proportions.

Saline Lakes of Tibesti

1. Localization

In the northern part of Chad Republic, near the Lybian frontier and between Tibesti and Ennedi massives, saline lakes of Ounianga Kebir and Serir occupy several depressions within the Nubian sandstone formation. The most extended one, Lake Yoa, is surrounded by sandstone cliffs from which diluted waters spring in many points. Under very arid conditions, waters are evaporated and concentrated in the lake and salts are deposited on the edges (Fig. 1).

2. Salt Paragenesis

Forty samples collected on beaches were analyzed by means of X-ray diffraction. The different minerals found in the saline paragenesis are the following:

chlorides: halite (NaCl) and sylvite (KCl);

sulfates: thenardite (Na_2SO_4);

sulfates-carbonates: burkeite ($\text{Na}_6\text{CO}_3(\text{SO}_4)_2$);

carbonates: calcite (CaCO_3), aragonite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), huntite ($\text{CaMg}_3(\text{CO}_3)_4$), pirssonite ($\text{Na}_2\text{CO}_3, \text{CaCO}_3, 2\text{H}_2\text{O}$), trona ($\text{Na}_2\text{CO}_3, \text{NaHCO}_3, 2\text{H}_2\text{O}$), thermonatrite ($\text{Na}_2\text{CO}_3, \text{H}_2\text{O}$), nahcolite (NaHCO_3) and small amounts of gaylussite ($\text{Na}_2\text{CO}_3, \text{CaCO}_3, 5\text{H}_2\text{O}$), magnesite (MgCO_3) and siderite (FeCO_3);

silicates: montmorillonite ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ supposed)

On the surface, from the lake to the cliff, the following mineral sequence is observed:

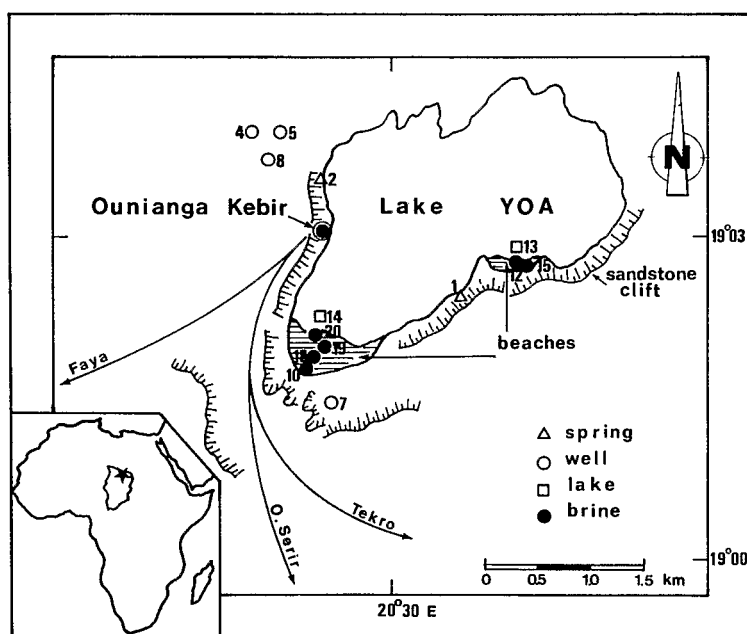


FIG. 1. Localization of the studied area and collected waters.

montmorillonite, calcium carbonates, calcium–magnesium carbonates, sodium carbonates, sodium sulfates, sodium and potassium chlorides.

In depth (60 cm) from the lake to the cliff, an inverse sequence is found: sodium chlorides and sulfates, sodium carbonates, sodium–calcium carbonates, magnesium–calcium carbonates, calcium carbonates and montmorillonite.

The sequences of salts as well as chemical compositions of waters indicate that in depth, near the water table, the gradient of concentration increases from the cliff to the lake. In contrast, at the surface of the beaches, the gradient of concentration increases from the lake to the cliff (Table 1).

TABLE 1. DISTRIBUTION OF SALTS IN BEACHES OF LAKE YOA

	Lake		Cliff
Surface	{	Aragonite–calcite Mg–Montmorillonite	huntite natron burkeite nahcolite
			trona thenardite sylvite halite
Depth	{	Dolomite Pirssonite	dolomite pirssonite gaylussite thenardite halite
			dolomite pirssonite trona thenardite halite
Depth	{	Pirssonite Gaylussite Thenardite Halite Sylvite	pirssonite halite calcite
			aragonite–calcite Mg–Montmorillonite

3. Behavior of Silica and Magnesium

Chemical analyses were performed on the soluble fraction of salts samples. Magnesium appears as expected, in samples in which dolomite and huntite are present, in the median part of the sequence. Moreover, magnesium is still abundant in calcium carbonate facies associated with montmorillonite and located in surface, near the lake and in depth near the cliff. These samples do not contain magnesium carbonates but yield the highest amount of soluble silica. It must be emphasized that magnesium and silica may be associated in a Mg-bearing montmorillonite, as already shown in the Lake Chad area (Tardy *et al.*, 1974; Al-Droubi, 1976; Gac *et al.*, 1977). This magnesium–silica association is confirmed by the chemical evolution of waters.

4. Chemical Evolution of Natural Solutions

Twenty samples were collected in the springs, wells, lake and brines. Chemical analyses are given in Table 2 and are plotted on Fig. 2, molality of sodium being chosen as a linear function of the concentration factor. It is shown that potassium, chloride and sulfate molalities increase almost like the sodium one until a concentration factor of about 3500. Magnesium and calcium molalities increase and then decrease, after having reached a concentration factor of about 10, while silica and alkalinity go on to increase but more

TABLE 2. CHEMICAL COMPOSITION OF WATERS (mmoles/kg H₂O)

Location of water samples	No.	Conc. factor	pH	Alkalinity (meq.)	Cl	SO ₄	Na	K	Ca	Mg	SiO ₂	log <i>f</i> _{CO₂}	Ionic strength
Springs													
KS ₁	1	1.0	7.0	1.50	0.16	0.29	1.19	0.18	0.18	0.26	0.31	—2.04	0.0029
KS ₂	2	1.6	6.8	1.45	1.10	0.63	1.98	0.22	0.42	0.27	0.27	—1.86	0.0046
KS ₃	9	25.7	9.7	12.80	1.00	10.82	30.72	2.42	0.20	0.25	0.39	—4.20	0.0445
KS ₄	3	1.7	7.1	1.90	0.46	0.98	2.03	0.59	0.60	0.18	0.62	—2.05	0.0058
KS ₅	6	5.4	7.9	3.60	1.56	1.51	6.45	0.61	0.35	0.19	0.73	—2.59	0.0098
Wells													
KP ₆	7	5.7	7.1	5.00	1.38	3.58	6.75	0.88	0.70	2.25	1.08	—1.66	0.0177
KP ₇	5	3.9	7.1	2.80	1.88	2.43	4.62	0.26	0.80	1.45	0.40	—1.90	0.0127
KP ₈	8	6.9	7.1	3.90	4.93	3.44	8.25	0.66	1.65	1.25	0.32	—1.77	0.0197
KP ₉	4	2.0	6.9	2.64	0.93	1.15	2.42	0.31	0.90	0.68	0.45	—1.72	0.0080
Lakes													
KL ₁₀	14	945.6	9.9	440.00	292.10	241.75	1130.00	81.29	0.12	0.12	5.58	—3.69	1.0838
KL ₁₁	13	596.0	9.7	300.00	204.90	134.75	712.00	58.80	0.12	0.12	2.99	—3.37	0.7257
K ₁₈	11	96.3	9.3	45.00	23.33	27.22	115.00	7.43	0.50	0.11	1.06	—3.20	0.1362
K ₁₉	17	2711.0	9.7	1460.00	1115.70	436.00	3240.00	191.50	—	—	9.15	—3.08	2.7267
K ₂₀	16	2502.0	9.7	1360.00	1065.00	378.30	2990.00	176.04	—	—	9.52	—3.10	2.5445
Brines													
KPL ₁₂	20	5023.0	9.8	2035.50	2048.90	1203.36	6002.61	555.55	0.18	0.06	17.48	—3.29	4.8730
KPL ₁₃	19	3715.0	9.7	1225.50	639.00	914.50	4440.00	198.50	0.30	0.10	19.56	—2.97	3.3286
KPL ₁₄	18	3263.0	10.0	2130.00	618.71	691.50	3900.00	222.40	0.15	0.08	21.64	—3.53	3.0092
KPL ₁₅	10	60.7	10.3	65.00	12.17	1.25	72.50	6.98	0.17	0.52	2.04	—4.63	0.0903
KPL ₁₆	15	2276.0	9.8	1860.00	1002.10	206.50	2720.00	127.60	0.07	0.06	5.49	—3.16	2.5324
KPL ₁₇	12	102.5	7.9	75.00	62.74	13.02	122.50	13.40	0.52	0.16	3.18	—1.37	0.1633

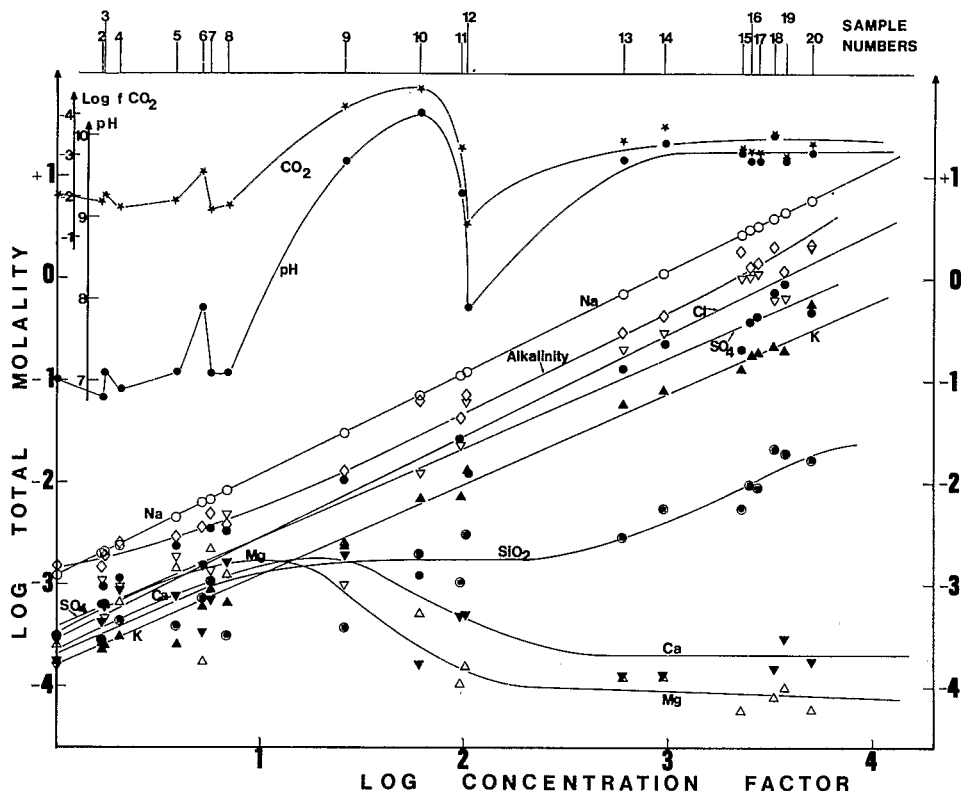


FIG. 2. Evolution of the concentration of elements as a function of concentration factor.

weakly. It must be noted that magnesium and silica together are affected before calcium depletion, which is interpreted as a formation of Mg-bearing silicate preceding calcite precipitation. The equivalent partial pressure of CO₂ is equal to $10^{-1.8}$ atm in the spring and well waters and tends progressively to a value of $10^{-3.5}$ atm, when waters evaporate at the contact with atmosphere. In a general way, pH increases and then stabilizes for a concentration factor of about 3500. At this stage (pH = 9.6), total molality of silica increases, which corresponds to the formation of H_3SiO_4^- in solution. Calcium and magnesium molalities are very low in waters, according to saturation with respect to Mg- or Ca-carbonates (Fig. 3).

Simulation Model of Evaporation

A computer program called EVAPOR (Fritz, 1975; Al-Droubi, 1976) derived from the PATH CALC of Helgeson *et al.* (1970) was used to calculate the evolution of chemical composition of solutions which concentrate by evaporation. Starting from an initial composition (in this case, the spring water no. 1), the program computes, for incremented concentration factors, the ionic strength of the solution, the distribution of the aqueous complex species, the activities of the ions and the amount of minerals precipitated when saturation points are reached.

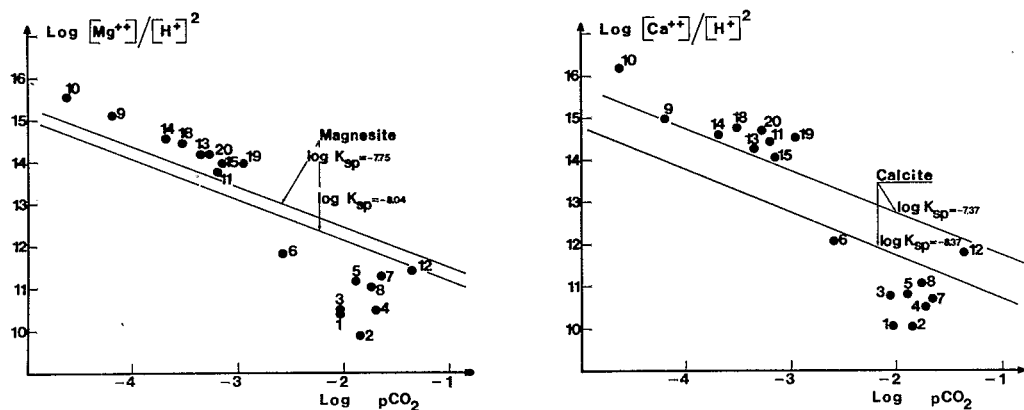


FIG. 3. Saturation with respect to magnesite and calcite.

The evolution of chemical composition of the Ounianga Kebir solutions as a function of concentration factor is reported on Fig. 4. A good agreement is obtained with natural data until a concentration factor of 1000, after which the evolution is only expected. Data used for the calculation and the corresponding reactions are listed in Table 3.

The sequence of salts precipitated is the following: Mg-montmorillonite, highly soluble magnesite, calcite, nahcolite, thenardite and finally sylvite for a concentration factor of about 20,000. This calculated paragenesis is confirmed by the distribution of salts in the field.

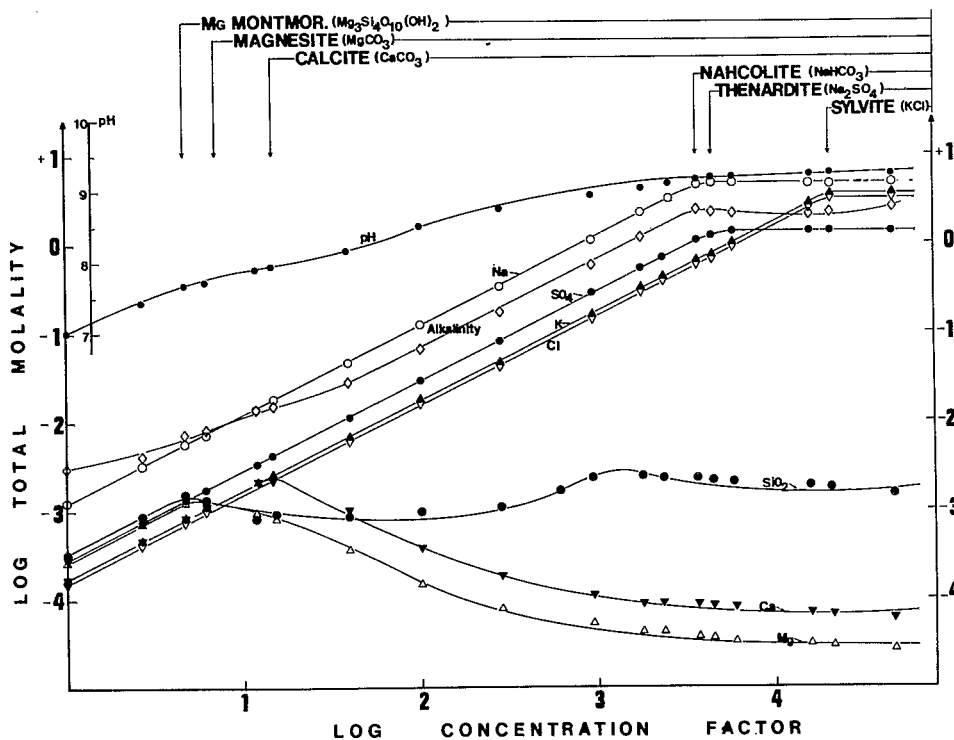


FIG. 4. Chemical evolution during simulated evaporation of the spring water no. 1.

TABLE 3. EQUILIBRIUM CONSTANTS FOR MINERALS AT 25°C

Mg-montmorillonite:	$3 \log [\text{Mg}^{2+}]/[\text{H}^+]^2 + 4 \log [\text{H}_4\text{SiO}_4]$	= +25.0
Amorphous silica	: $\log [\text{H}_4\text{SiO}_4]$	= -2.70
Calcite	: $\log [\text{Ca}^{2+}]/[\text{H}^+]^2 + \log f_{\text{CO}_2}$	= +10.76
Magnesite	: $\log [\text{Mg}^{2+}]/[\text{H}^+]^2 + \log f_{\text{CO}_2}$	= +10.38
Gypsum	: $\log [\text{Ca}^{2+}] + \log [\text{SO}_4^{2-}] + 2 \log [\text{H}_2\text{O}]$	= -4.85
Thenardite	: $2 \log [\text{Na}^+] + \log [\text{SO}_4^{2-}]$	= -0.87
Trona	: $3 \log [\text{Na}^+]/[\text{H}^+] + 2 \log f_{\text{CO}_2} + 4 \log [\text{H}_2\text{O}]$	= +24.89
Sylvite	: $\log [\text{K}^+] + \log [\text{Cl}^-]$	= +0.78
Halite	: $\log [\text{Na}^+] + \log [\text{Cl}^-]$	= +1.58
Hydrophyllite	: $\log [\text{Ca}^{2+}] + 2 \log [\text{Cl}^-]$	= +11.49

The problem of an early precipitation of Mg-montmorillonite (in the form of a highly soluble talc $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) may be discussed. In fact, in the initial solution the magnesium molality is higher than the calcium one, but after evaporation it becomes lower. Furthermore, magnesium depletion occurs before the calcium one, but together with the beginning of silica consumption. This is interpreted as a precipitation of Mg-bearing silicate, as already shown (Gac *et al.*, 1977), and calculated as a highly soluble talc. The different possibilities offered are presented on Fig. 5 and it seems obvious that only the hypothesis no. 4 fits with natural observations: Mg-montmorillonite is the first mineral precipitated, followed by calcite and afterwards by magnesite (or Mg-rich carbonates).

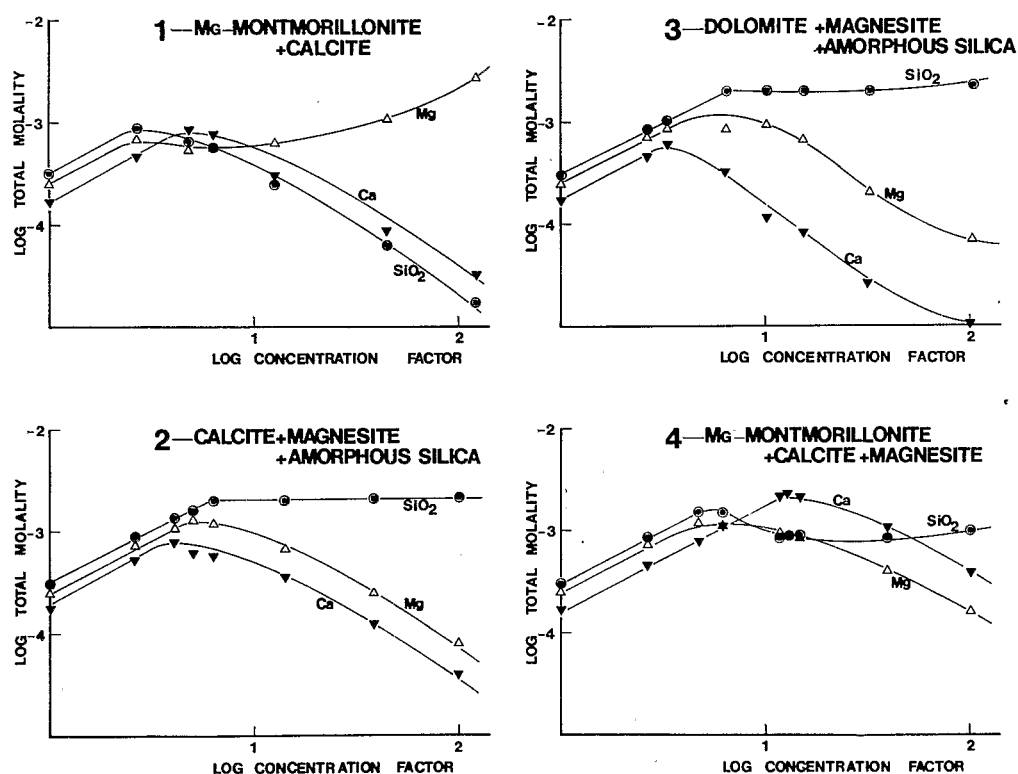


FIG. 5. Four different cases of simulated evaporation (first steps: water no. 1).

Discussion and Concluding Remarks

Along evaporation steps of natural waters, concentration of soluble species can fluctuate: generally all the molalities begin to increase during the initial stages, but afterwards, some of them may go on to increase, some others may decrease and later on increase again. Each case yields a different pattern depending on the nature, on the order of salt precipitating and on the relative amount of these species in the initial solutions. Attempts at predicting such behaviors were proposed for many years such as those of Eaton (1950), Garrels and Mackenzie (1967), Hardie and Eugster (1970), Van Beek and Van Breemen (1973). In the situations in which many elements are involved, we think that computer program calculations are needed for solving correctly the problem (Al-Droubi *et al.*, 1977).

The good agreement with natural observations such as these described here or these already presented for the Lake Chad system (Al-Droubi, 1976; Al-Droubi *et al.*, 1976b; Gac *et al.*, 1977) and for the Euphrate River (Al-Droubi *et al.*, 1977) permits the extrapolation of the calculations to a great number of natural environments.

In nature, salts precipitated are generally complex ones: magnesian calcite, dolomite, huntite, pirssonite, gaylussite, glauberite, burkeite, lecontite and above all montmorillonites, etc. The example presented shows that a fairly good pattern is obtained by using simple salts for which solubility products are empirically corrected (with respect to pure minerals), taking into account oversaturations commonly found in nature (Table 3).

In many cases, geochemical evolution of solutions and brines may be interpreted as the result of near equilibrium water-rock interactions and could be used quite accurately as a witness of mineral precipitations. The computer model, based on equilibrium reactions is then useful to understand or predict the origin and distribution of elements.

Acknowledgements

Authors are deeply indebted to Captain Yves Merliet and General Negue-Djogo for having organized the expedition to Tibesti and to Gérard Krempp and Daniel Million, for their analytical help.

References

- AL-DROUBI, A. (1976) Géochimie des sels et des solutions concentrées par évaporation. Modèle thermodynamique de simulation. Application aux sols salés du Tchad. Thèse Université Louis Pasteur, Strasbourg et *Sci. Géol.*, Mém. no. 46, 177 pp.
- AL-DROUBI, A., FRITZ, B. and TARDY, Y. (1976a) Equilibres entre minéraux et solutions. Programmes de calcul appliqués à la prédiction de la salure des sols et des doses optimales d'irrigation. *Cah. ORSTOM, sér. Pédol.* XIV, 13-38.
- AL-DROUBI, A., CHEVERRY, C., FRITZ, B. and TARDY, Y. (1976b) Géochimie des eaux et des sels dans les sols des polders du lac Tchad: Application d'un modèle thermo-dynamique de simulation de l'évaporation. *Chem. Geol.* 17, 165-177.
- AL-DROUBI, A., FRITZ, B., GAC, J. Y. and TARDY, Y. (1977) Prediction of the chemical evolution of natural waters during evaporation. *2nd Int. Symp. on Water-Rock Inter.*, Strasbourg, section II: Salts and brines, 13-22.
- BEEK, C. G. E. M. VAN and BREMMEN, N. VAN (1973) The alkalinity of alkali soils. *J. Soil Sci.* 24, 129-136.
- BORCHERT, H. and MUIR, R. O. (1964) *Salt Deposits. The Origin, Metamorphism and Deformation of Evaporites*, Van Norstrand Co. Ed., London, 338 pp.
- BRADLEY, W. H. and EUGSTER, H. P. (1969) Geochemistry and paleolimnology of the trona deposits and associated authigenic minerals of the green river formation of Wyoming. *U.S. Geol. Surv., Prof. Paper*, 496 B, 71 pp.
- BRATSCH, O. (1971) *Salt Deposits, their Origin and Composition*, Springer-Verlag Ed., New York, 297 pp.

- D'ANS, J. (1933) *Die Lösungsgleichgewichte des Systems der ozeanischen Salzablagerungen*, Berlin: Kaliforschungsanstalt, Text 254 pp., Atlas 88 pp.
- EATON, F. M. (1950) Significance of carbonates in irrigation waters. *Soil Sci.* **69**, 123–133.
- EUGSTER, H. P. (1970) Chemistry and origin of the brines of Lake Magadi, Kenya. *Mineral. Soc. Amer.*, Spec. paper, **3**, 213–235.
- FRITZ, B. (1975) Etude thermodynamique et simulation des réactions entre minéraux et solutions. Application à la géochimie des altérations et des eaux continentales. *Sci. Géol.*, Mém. no. 41, 152 pp.
- GAC, J. Y., AL-DROUBI, A., FRITZ, B. and TARDY, Y. (1977) Geochemical behaviour of silica and magnesium during the evaporation of waters in Chad. *Chem. Geol.* **19**, 215–228.
- GARRELS, R. M. and MACKENZIE, F. T. (1967) Origin of the chemical compositions of some springs and lakes. In *Equilibrium Concept in Natural Water Systems*, GOULD, ed., Amer. Chem. Soc., Ser. 67, 222–242.
- HARDIE, L. A. (1968) The origin of the recent non-marine evaporite deposit of saline water, Inyo County, California. *Geochim. Cosmochim. Acta* **32**, 1279–1301.
- HARDIE, L. A. and EUGSTER, H. P. (1970) The evolution of closed-basin brines. *Mineral. Soc. Amer.* Spec. Paper **3**, 273–290.
- HELGESON, H. C., BROWN, T. H., NIGRINI, A. and JONES, T. A. (1970) Calculation of mass transfer in geochemical processes involving aqueous solutions. *Geochim. Cosmochim. Acta* **34**, 569–592.
- JONES, B. F. (1965) The hydrology and mineralogy of deep springs lake, Inyo County, California. *U.S. Geol. Surv., Prof. Paper*, 502 A, 56 pp.
- JONES, B. F. (1966) Geochemical evolution of closed basin water in the western great basin. *2nd Symp. on Salt; Northern Ohio, Geol. Soc. Rau*, Ed. 1, 181–200.
- JONES, B. F. and VAN DENBURGH, A. S. (1966) Geochemical influences on the chemical character of closed lakes. *Int. Ass. Sci. Hydrol., Symp. of Garda* **70**, 435–446.
- JONES, B. F., VAN DENBURGH, A. S., TRUESDELL, A. H. and RETTIG, S. L. (1969) Interstitial brines in playa sediments. *Chem. Geol.* **4**, 253–262.
- JONES, B. F., EUGSTER, H. P. and RETTIG, S. L. (1976) Hydrochemistry of the Lake Magadi basin, Kenya (in press).
- LERMAN, A. (1967) Model of a chemical evolution of a chloride lake. The Dead Sea. *Geochim. Cosmochim. Acta* **31**, 2309–2330.
- LERMAN, A. (1970) Chemical equilibria and evolution of chloride brines. *Mineral. Soc. Amer.*, Spec. Paper **3**, 291–306.
- LERMAN, A. and JONES, B. F. (1973) Transient and steady state salt transport between sediments and brines in closed lakes. *Limnology and Oceanography* **18**, 72–85.
- LOTZE, F. (1957) *Steinsalz und Kalisalz*. I. Teil: *Gebrüder Bonträger*, Berlin, Nikolasssee, 465 pp. (2nd ed., 1960).
- PHILLIPS, K. N. and VAN DENBURGH, A. S. (1971) Hydrology and geochemistry of Abert, Summer and Goose lakes and other closed basin lakes in South Central Oregon. *U.S. Geol. Surv., Prof. Paper*, 502 B, 86 pp.
- TARDY, Y., CHEVERRY, C. and FRITZ, B. (1974) Néof ormation d'une argile magnésienne dans les dépressions interdunaires du lac Tchad. Application aux domaines de stabilité des phyllosilicates alumineux, magnésiens et ferrières. *C. R. Acad. Sci., Paris* **278**, série D, 1999–2002.
- TRUESDELL, A. H. and JONES, B. F. (1969) Ion association in natural brines. *Chem. Geol.* **4**, 51–62.
- VANT'HOFF, J. H. et al. (1962) *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen, insbesondere des stabfurter Salzlagerns*, Leipzig, Akademische Verlagsgesellschaft, 374 pp.
- WOOD, J. R. (1972) Prediction of mineral solubilities in concentrated brines: a thermodynamic approach. Ph.D., Baltimore, 121 pp.

Discussion

R. A. BERNER:

Why didn't you consider dolomite in your model?

B. KUBLER:

Same remark as for Berner's paper: the crystallographic control could change drastically the behavior of the elements (Mg-calcite with different amount of substitution for the pair Mg and Ca) aragonite, H_2S and so on for Iron monosulfide.

J. Y. GAC:

We did not calculate the solubility of different Mg-calcite because we could not have a field control of the Mg variation in calcites (mixed with many minerals) and because we are not yet able to simulate solid solution precipitation. Furthermore, we simply simulated a highly soluble calcite ($\log K_{ps} = -7.37$) and magnesite for taking into account of paragenesis calcite-dolomite-magnesite.

E. N. PENTCHEVA:

(a) Le modèle est-il appliqué pour l'étude des saumures marines où les stades concentration-cristallisation diffèrent de votre exposé?

(b) Le comportement hydrochimique simultané des éléments tels que Ba, Sr, Rb, Cs, Li a-t-il été observé par les auteurs?

J. Y. GAC:

Oui, le modèle est tout à fait applicable (et déjà appliqué) aux saumures d'origine marine. Non les éléments comme le baryum, le strontium, le lithium n'ont pas été pris en compte.

Reprinted from

ORIGIN AND DISTRIBUTION OF THE ELEMENTS

Edited by

L. H. AHRENS



B 316 ex 1