

Nucleation Kinetics of the Gypsum-Anhydrite System

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ABSTRACT

Although there are clear instances of post-depositional hydration and dehydration changes in the system $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ it has never been clearly established under what conditions, if any, anhydrite can occur as a primary precipitate. Marked inconsistencies occur between solubility measurement data, thermodynamic predictions of stability and the experimental data obtained from precipitation studies of CaSO_4 phases from aqueous solutions.

This is due primarily to the metastability of gypsum which precipitates readily outside its own stability field. Even within the stability field of anhydrite, nucleation kinetics in the system normally favor the nucleation of gypsum as a primary phase.

Conditions of high supersaturation (i.e. high concentrations of calcium or sulfate) can be shown both theoretically and experimentally to induce the nucleation and growth of anhydrite rather than metastable gypsum. The nucleation kinetics are not affected appreciably by high concentrations of NaCl, and gypsum is always the metastable phase under these conditions.

Near surface formation of anhydrite by direct precipitation or alteration of gypsum probably occurs in nature by reaction of high sulfate continental waters with calcium carbonate or gypsum or by mixing of these waters with solutions containing calcium.

INTRODUCTION

Gypsum and anhydrite both occur in extensive amounts in sedimentary evaporitic sequences.

These beds are often composed entirely of either gypsum or anhydrite, with or without other evaporite minerals, and occasionally the two minerals are interbedded with each other.

Because of the ease of hydration of anhydrite to gypsum in the near surface environment gypsum is normally seen at the surface. Under conditions of burial the dehydration of gypsum to anhydrite can occur and in the deeper subsurface anhydrite is the only phase present.

It has been maintained that gypsum is the primary form of calcium sulfate and that all anhydrite is probably the result of dehydration of original gypsum.

Even though anhydrite can be seen at the surface in saline and arid environments such as the Trucial Coast (Kinsman, 1965; Butler, 1969) and the deserts of Southwest Africa (Cagle and Cruft, 1969) it has never been clearly established whether anhydrite can form as a primary precipitate in nature. The geological evidence is unclear, and unfortunately the laboratory evidence has been similarly so.

Thermodynamic and solubility data.

Calculations by MacDonald (1953) involving the free energy changes in the dehydration reaction and solubility determinations by numerous workers (i.e., Posnjak, 1938) have indicated that gypsum should be the stable phase below 40 to 42°C in water saturated only with calcium and sulfate, and anhydrite the stable phase above this temperature. From thermodynamic arguments MacDonald (1953) showed that the addition of NaCl (to approximate the conditions in an evaporating basin of sea water) should lower the transition temperature to the point where primary

anhydrite could reasonably be expected to precipitate from water of high salinities. Marshall and Slusher (1966) also determined the transition curve from careful solubility measurements and this transition curve is compared with the curve derived by MacDonald (1963) in Figure 1.

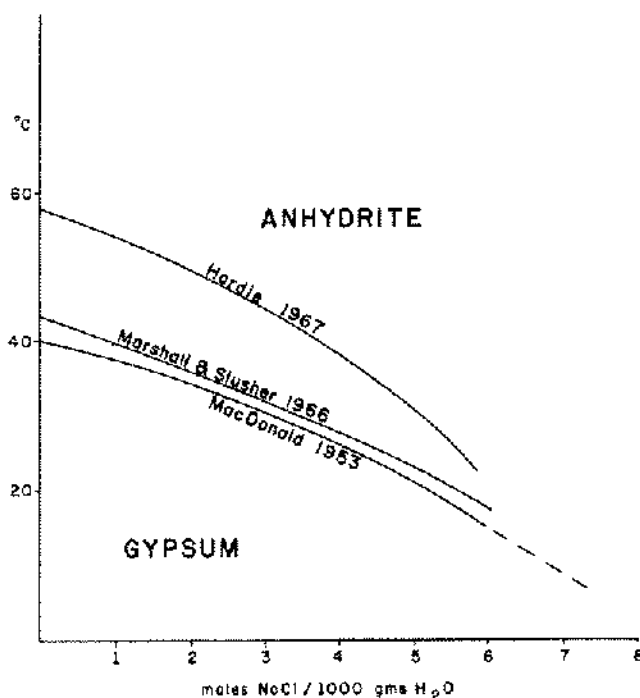


Figure 1. Transition temperature of gypsum-anhydrite at one atmosphere pressure as a function of sodium chloride in solution according to various workers.

Numerous other investigators i.e., Bock (1961), have investigated this system, and most of the solubility measurements indicate transition curves within a few degrees centigrade of the curves of MacDonald and Marshall and Slusher.

Difficulty of anhydrite precipitation.

Notwithstanding these predictions of the gypsum and anhydrite stability fields from the above arguments, the experimental data on the actual precipitation of gypsum or anhydrite in the laboratory is both conflicting and confusing. Although thermodynamic and solubility data predict the lower transition curves of Figure 1 it was not possible to precipitate anhydrite from aqueous solution in its predicted stability field. Metastable gypsum is usually the result of such an experiment. There are several possible reasons for this:

(1) the use of solubility data to predict phase transformations in the system does not give correct answer because either (a) supersaturation the system has not been adequately measured or controlled, or (b) during the measurement of solubility of an unstable phase i.e., anhydrite can be converted to a stable phase i.e., gypsum immediately in solution or during the partial reprecipitation process when the phases are at solubility equilibrium. In this regard it is interesting to note the data of Power, Fabuss and Satterfield (1965) on transient solute concentrations in the system $\text{CaSO}_4\text{-H}_2\text{O}$. Transient solute measurements show offer some degree of control on the problem of conversion of one phase to another during solubility measurements, and the data of these latter workers is in essential agreement with the transition curves of the workers noted previously. It appears likely, therefore, that the true thermodynamic equilibrium transition curve is in fact in the region of the curves defined by MacDonald, Marshall and Slusher and other workers, although this still does not solve the problem as to why anhydrite did not precipitate within its own stability field.

(2) The thermodynamic data is incorrect, or inadequate, in that it does not take into account surface energy term of the crystallizing phase. This latter term is generally unimportant in considering macro-crystals, but becomes of particular significance in determining the ΔG of the reaction for very small precipitating particles the size of critical nuclei. This parameter has been discussed by Fink and Bischoff (1965) in considering the calcite-aragonite transition. It is doubtful, however, if this effect is of sufficient magnitude to alter markedly the position of the transition curve.

(3) The kinetics of the precipitation process has not been evaluated, and the problem becomes one of defining a metastable region for gypsum due to the greater probability of gypsum nucleation than anhydrite nucleation. This is the most probable explanation for the discrepancy between the predicted stability fields of these minerals from thermodynamic evidence and the experimental data on the synthesis of anhydrite.

Recently several workers have attempted to define the phase transition from studies involving conversion of one phase to another in solutions of different ionic strengths. Zen (1965) noted that in the ternary system $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$ there was no formation of new authigenic anhydrite anywhere in the system, even within the predicted stability field of anhydrite. However, it is important to note that primary anhydrite was apparently formed

one instance, and from a solution saturated with calcium chloride at 70°C.

Hardie (1967) has been able to convert gypsum to anhydrite in solutions containing Na_2SO_4 or H_2SO_4 at various temperatures depending on the concentration of SO_4^{2-} ion, although he prefers to consider the "activity of water" rather than the activity of the specific solute as being the critical parameter. Hardie proposed a new equilibrium curve, which is also plotted in Figure 1. It can be seen that it is markedly higher than the previous curves, and it is important to note that the curve was extrapolated to NaCl solutions although the actual data were obtained in high sulfate solutions. The reason that Hardie considered his transition curve could be extrapolated to the sodium chloride solutions even though the experiment was carried out in H_2SO_4 solutions is that the only factors affecting the transition are pressure, temperature, and the activity of water, $a_{\text{H}_2\text{O}}$. This is based on the reaction:



$$\text{Hence } (K)_{P,T} = a^2 \text{H}_2\text{O}.$$

This reaction, however, is a conversion or dehydration reaction, and it has never been demonstrated that the reaction proceeds in solution by simple dehydration. Hardie agrees that the "evidence is unclear" in this regard. It appears more likely that the reaction is a solution-precipitation reaction, particularly in the light of transient solubility studies.

The significance of the fact that the transformation can occur in solutions high in either Ca^{2+} or SO_4^{2-} ion (highly supersaturated solutions) is that the reaction is kinetically controlled and that high supersaturations reduce the size of the anhydrite critical nucleus and increase the probability of anhydrite nucleation.

KINETIC CONSIDERATIONS

It is possible to show from kinetic considerations that an important parameter governing the nucleation of either gypsum or anhydrite is the degree of supersaturation of the solution, S , defined as:

$$S = \frac{\text{Ionic activity product}^{1/2}}{K_{sp}}$$

where K_{sp} is the thermodynamic solubility product for gypsum or anhydrite.

From Vollmer-Becker-Doring nucleation theory formulated by Nielsen (1964) the size of the critical nucleus, n^* (i.e., the minimum size of nucleating particle above which the particle will grow and below which it will tend to dissolve), is related to the degree of supersaturation of the solution, S , by the relation:

$$n^* = \frac{2\beta\sigma^3 v^2}{(kT \ln S)^3}$$

where β is a shape factor for the critical nucleus, σ is the surface tension, v is the molecular volume, k is Boltzmann's constant and T is the absolute temperature.

Assuming spherical nuclei the simpler Kelvin expression showing the relation between the radius of the critical nucleus, r^* and surface energy can also be used,

$$r^* = \frac{2}{kT \ln S}$$

From this relation it is apparent that the size of the nucleus will be different for anhydrite and gypsum crystallizing from solutions of the same degree of supersaturation because of the difference in surface energy of the two phases.

Surface energy determinations.

In order to predict theoretically the relative ease of nucleation within the system it is necessary to know the shape factor, β , molecular volume, v , and surface tension, σ , for both gypsum and anhydrite in aqueous solution. There are indications that many of the early literature values obtained from solution studies for the surface energy of crystalline phases were too high, and indeed this is a difficult parameter to measure in solution. It has been determined for gypsum from nucleation experiments by Nielsen (1964) who obtained a best value of 95 ergs/cm².

Inasmuch as anhydrite is not readily precipitated in the laboratory there are no good values for anhydrite, but an approximation, γ can be obtained as follows, using the Born-Sterns approximation for the surface tension of ionic crystals in vacuo:

$$\gamma = \frac{0.1166z^2 e^2}{4v}$$

where z is the number of electronic charges, e is the charge on electron, and v is the molecular volume. Comparing the calculated Born-Sterns approximation for dry, vacuum conditions, γ , with

the measured surface tension in aqueous solutions for barite and gypsum, σ , an approximate value of σ for anhydrite can be obtained. The higher surface

Table 1. Determination of Approximate Value of σ for Anhydrite.

	γ , calculated	σ , measured	γ/σ
BaSO ₄	312	126	2.48
CaSO ₄ · 2H ₂ O	220	95	2.32
CaSO ₄	350	—	2.33
γ gypsum	220	95	
γ anhydrite	350	anhydrite	

whence σ anhydrite = 150.

tension of anhydrite is also compatible with the greater surface hardness of anhydrite to gypsum. Surface tension or surface energy is related to Moh-scale surface hardness and in view of the greater hardness of anhydrite it is believed the surface energy term obtained above is a minimum figure.

Using the above approximate values it is possible to estimate the critical nuclei sizes, n^* , at different degrees of supersaturation in solution. A small difference between n^* gypsum and n^* anhydrite means that the free energy considerations will cause the most stable phase to nucleate and become stable, and a large difference will mean it will become increasingly difficult to nucleate the phase requiring the greatest number of particles to cluster together to reach the n^* . Table 2 gives some calculations of n^* for different degrees of supersaturation. It is important to realize that because of the difficulties of obtaining very accurate data on surface energies of the phases these figures are only of general accuracy to illustrate the effect of supersaturation on n^* .

The ease of nucleation is dependent on the number of atomic particles necessary to form n^* , and the number of molecular collisions in the media. At high values of S the collision probability is greater, the number of nuclei required to form n^* is less and more nuclei are able to form. This explains why rapid homogeneous precipitation of a large number of crystalline particles of small size occurs under conditions of high supersaturation. At low values of S the induction period before onset of crystallization can be very long (i.e., several hours) and a few large crystals form.

Table 2. Calculations of n^* for Different Degrees of Supersaturation.

S	n^* anhydrite	n^* gypsum	n^* anhydrite-gypsum
2	61,000	40,300	20,700
5	4,800	3,200	1,600
10	1,020	680	340
20	690	460	230
50	330	220	110

From Table 2 it can be seen that as S increases the probability of sufficient particles coming together to form anhydrite critical nuclei rapidly increases. A "nucleation barrier" at low values of S occurs which causes the precipitation of gypsum a long while before sufficient particles can agglomerate to form anhydrite nuclei.

EXPERIMENTAL

In order to test the above conclusions laboratory experiments were performed to determine which phases precipitated from aqueous solutions containing Ca^{2+} and SO_4^{2-} ions at various degrees of supersaturation. The experimental details are more fully described by Chao (1969).

Methods.

Concentrated sulfuric acid, sodium sulfate, calcium chloride and sodium chloride solutions were prepared. Precipitation of solid phases were obtained by mixing CaCl_2 solutions with Na_2SO_4 or H_2SO_4 solutions, both with or without NaCl , and in various ways in a 250 ml. Erlenmeyer flask. The flask and solutions before mixing were held in constant temperature bath at 1 atmosphere pressure. No seeds of gypsum or anhydrite were used. Details of the individual runs are given in Table 3.

Precipitation occurred immediately upon mixing of solutions because of the high concentrations used, and the flasks were manually shaken three times a day. The solid and liquid phases were held in contact at various times up to 14 days maximum.

The solid phases were removed and filtered through a millipore suction filter, rinsed in acetone and oven-dried at the same temperature. The identification of solid phases was made by immediate microscopic examination and by X-ray powder diffraction.

Under the microscope, gypsum generally could be seen as thin, tabular crystals, sometimes with fish-tail or polysynthetic twinning. Hemihydrate

Table 3. Experimental Runs.

Run No.	Solution		Temperature °C	Days	Precipitate Identified
	CaCl ₂	Na ₂ SO ₄			
31	0.1M 100ml	0.1M 100ml	30	7	large gypsum
51	0.1M 100ml	0.1M 100ml	50	7	large gypsum
61	0.1M 100ml	0.1M 100ml	60	7	large gypsum
71	0.1M 100ml	0.1M 100ml	70	7	large gypsum
81	0.1M 100ml	0.1M 100ml	80	3	large gypsum
32	0.5M 100ml	0.5M 100ml	30	7	large gypsum
52	0.5M 100ml	0.5M 100ml	50	7	large gypsum
62	0.5M 100ml	0.5M 100ml	60	7	small gypsum + small hemihydrate
72	0.5M 100ml	0.5M 100ml	70	7	small gypsum + small hemihydrate
82	0.5M 100ml	0.5M 100ml	80	3	large gypsum + small hemihydrate
33	1M 10ml	sat. 100ml	30	7	small gypsum
53	1M 10ml	sat. 100ml	50	7	thenardite
53A	1M 10ml	sat. 100ml	50	7	medium gypsum
63	1M 10ml	2M 100ml	60	7	thenardite
63A	1M 10ml	sat. 100ml	60	7	small hemihydrate
73	1M 10ml	2M 100ml	70	7	thenardite
73A	1M 10ml	17% 100ml	70	7	small hemihydrate
34	1M 10ml	17% 100ml	30	7	small gypsum*
54	1M 10ml	17% 100ml	50	7	small gypsum*
64	1M 10ml	17% 100ml	60	7	medium gypsum*
74	1M 10ml	17% 100ml	70	7	large gypsum*
84	1M 10ml	17% 100ml	80	3	large gypsum* + large anhydrite
35	6M 100ml	0.5M 20ml	30	7	minute gypsum + minute hemihydrate
55	6M 100ml	0.5M 20ml	50	7	minute hemihydrate

Run No.	Solution		Temperature °C	Days	Precipitate Identified
	CaCl ₂	Na ₂ SO ₄			
65	6M 100ml	0.5M 20ml	60	7	minute hemihydrate + minute anhydrite
75	6M 100ml	0.5M 20ml	70	7	minute anhydrite
85	6M 100ml	0.5M 20ml	80	3	minute anhydrite
81M	1M 50ml	0.5M 10ml	80	1	gypsum
82M	2M 50ml	0.5M 10ml	80	1	gypsum
83M	3M 50ml	0.5M 10ml	80	1	gypsum
84M	4M 50ml	0.5M 10ml	80	1	hemihydrate, anhydrite
85M	5M 50ml	0.5M 10ml	80	1	anhydrite, hemihydrate
72M	2M 50ml	0.5M 10ml	70	4	gypsum
73M	3M 50ml	0.5M 10ml	70	4	gypsum, hemihydrate
74M	4M 50ml	0.5M 10ml	70	4	hemihydrate
75M	5M 50ml	0.5M 10ml	70	4	anhydrite, hemihydrate
63M	3M 50ml	0.5M 10ml	60	3	gypsum
64M	4M 50ml	0.5M 10ml	60	3	gypsum
65M	5M 50ml	0.5M 10ml	60	3	hemihydrate
66M	6M 50ml	0.5M 10ml	60	3	hemihydrate
67M	7M 50ml	0.5M 10ml	60	3	hemihydrate
53M	3M 50ml	0.5M 10ml	50	7	gypsum
54M	4M 50ml	0.5M 10ml	50	7	gypsum
55M	5M 50ml	0.5M 10ml	50	7	hemihydrate, gypsum
56M	6M 50ml	0.5M 10ml	50	7	hemihydrate
57M	7M 50ml	0.5M 10ml	50	7	hemihydrate
56MB	6M 50ml	0.5M 10ml	50	14	hemihydrate
57MB	7M 50ml	0.5M 10ml	50	14	hemihydrate
58MB	8M 50ml	0.5M 10ml	50	14	hemihydrate

Run No.	Solution		Temperature °C	Days	Precipitate Identified
	CaCl ₂	Na ₂ SO ₄			
51C	3M 50ml	25% 5ml	50	7	gypsum
52C	4M 50ml	25% 5ml	50	7	gypsum, hemihydrate
53C	5M 50ml	25% 5ml	50	7	hemihydrate, anhydrite
54C	6M 50ml	25% 5ml	50	7	hemihydrate, anhydrite
55C	7M 50ml	25% 5ml	50	7	hemihydrate, anhydrite
71D	5M 50ml	5% 5ml	70	4	anhydrite, hemihydrate
72D	5M 50ml	20% 5ml	70	4	anhydrite, hemihydrate
73D	5M 50ml	50% 5ml	70	4	anhydrite, hemihydrate

minute = > 0.05mm in length

large = 1mm in length

small = 0.25-0.5mm in length

medium = 0.5-1mm in length

small = 0.25-0.5mm in length

small = 0.25-0.5mm in length

medium = 0.5-1mm in length

large = >1mm in length

*gypsum converting to anhydrite in air

occurred as thin, small needles with parallel extinction, and moderate birefringence. No attempt was made to distinguish hemihydrate and soluble anhydrite. Anhydrite appeared as a mass of minute, birefringent grains when precipitated in concentrated CaCl₂ solutions. Anhydrite formed in H₂SO₄ solutions occurred as large, prismatic to equant crystals with parallel extinction and rhombohedral cleavage.

RESULTS

Mixing of dilute CaCl₂ and Na₂SO₄ solutions resulted in the precipitation of large (>1mm) gypsum plates at all temperatures. If 30 gm of NaCl was first added to dilute CaCl₂ solutions before mixing with dilute Na₂SO₄ solution, gypsum was formed at 30° and 50°C, while gypsum and hemihydrate were precipitated together at higher temperatures.

When saturated (>3M) Na₂SO₄ solution was mixed with dilute CaCl₂ solution, the precipitate was gypsum at 30°C, but at higher temperatures, thenardite (Na₂SO₄) was precipitated. If 2M Na₂SO₄ solution was used instead of a saturated one, hemihydrate was formed at 60° and 70°C, while gypsum was formed at lower temperatures. The crystals from this solution were small (0.25 to 0.5 mm). It seems that saturation of Na₂SO₄ in solution does not favor anhydrite precipitation because of thenardite precipitation and inability to obtain sufficiently high supersaturations.

When 17 percent sulfuric acid solution was reacted with small amounts of 1M CaCl₂ at 80°C large (> 1mm), prismatic to equant anhydrite crystals were found in association with gypsum plates. At lower temperatures however only gypsum was formed, even after 7 days.

If concentrated (6M) CaCl₂ solution was mixed with a small amount of dilute Na₂SO₄ solution

then gypsum and hemihydrate were formed at 30°C; hemihydrate alone at 50°C; hemihydrate and anhydrite at 60°C, and anhydrite alone at 70° and 80°C.

A series of runs were made increasing the degree of supersaturation by adding 50 ml of 1M, 2M, 3M, 4M, 5M, 6M and 7M CaCl_2 solutions separately to 10 ml of 0.5M Na_2SO_4 solutions at 50°, 60°, 70° and 80°C. The results showed that anhydrite was formed in 4M CaCl_2 solution at 80°C, in 5M CaCl_2 solution at 70°C, but not in any CaCl_2 solution up to 7M, at 60° and 50°C. An earlier run however, which had lasted for 7 days did show the formation of anhydrite in 6M CaCl_2 solution. Hence it was apparent that as well as forming anhydrite immediately on precipitation, it was possible to convert precipitated gypsum or hemihydrate to anhydrite at somewhat lower concentrations than those used for direct precipitation.

An experiment using time as a variable was conducted (Table 4). Immediate examination of the precipitate showed the existence of hemihydrate only. Every few hours, a small amount of precipitate was taken out from the flask, examined under the microscope, and verified by X-ray diffraction. Anhydrite was not found until 79 hours had elapsed. It was associated with hemihydrate until 165 hours after the mixing of the solutions, the whole precipitate then being converted to anhydrite.

Table 4. The Relationship Between Time and Conversion of Hemihydrate in a Solution of 100 ml of 6M CaCl_2 plus 20 ml of 0.5M Na_2SO_4 at 60°C.

Time, hrs	Solid phase
instant	hemihydrate
2	hemihydrate
4	hemihydrate
22	hemihydrate
30	hemihydrate
46	hemihydrate
52	hemihydrate
70	hemihydrate
79	hemihydrate + anhydrite
93	hemihydrate + anhydrite
104	hemihydrate + anhydrite
118	hemihydrate + anhydrite
124	hemihydrate + anhydrite
141	hemihydrate + anhydrite
165	anhydrite

Geological considerations.

From the preceding results it is possible to show on a two-dimensional diagram of temperature vs. degree of supersaturation the field in which the nucleation kinetics will favor the formation of anhydrite over gypsum or hemihydrate.

This is obviously not an equilibrium phase diagram in that the phase boundary does not represent an equilibrium transition between phases in different stability fields. It cannot be deduced thermodynamically, and at the present time its presence can only be predicted from the nucleation kinetics as was done earlier, although theory does not permit us to predict its position or shape.

Such a diagram is shown in Figure 2 using CaCl_2 concentration on the composition axis. Figure 3 incorporates all the experimental data irrespective of starting solutions and as a function of supersaturation (either high Ca^{2+} or high SO_4^{2-}) and temperature. Obviously it is not reasonable to have natural solutions as supersaturated as fifty times the solubility product of calcium sulfate if almost equal ionic proportions of Ca^{2+} and SO_4^{2-} are available, as instantaneous precipitation would occur reducing the supersaturation. It is possible, however, to have highly supersaturated solutions in

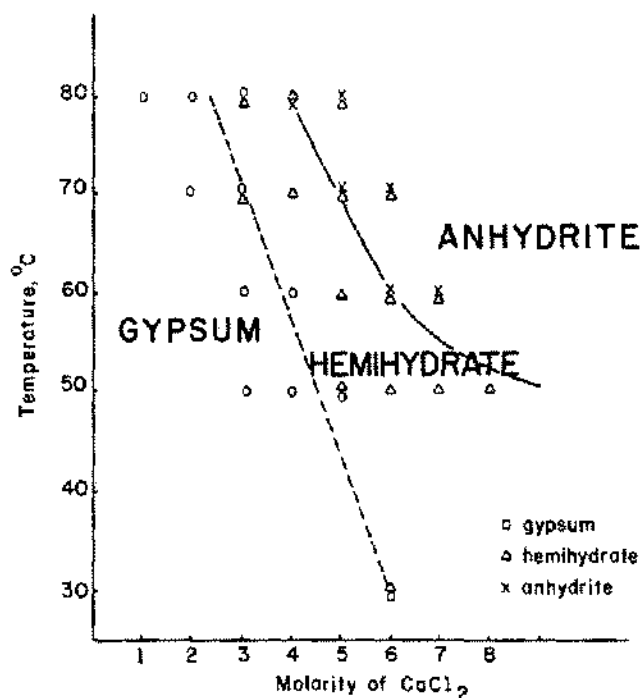


Figure 2. Dependence of transition temperature on concentration of CaCl_2 solution.

which an initial precipitate (i.e., gypsum) is in contact with high Ca^{2+} or high SO_4^{2-} solutions. Under these conditions new anhydrite nuclei would form and the gypsum would be converted. That this does occur is good evidence for the gypsum-anhydrite conversion being a solution-precipitation mechanism.

Direct precipitation of anhydrite could occur by mixing of water containing high sulfate or calcium with solutions or rocks containing the other anion. This would result in immediate anhydrite precipitation if the temperature and degree of supersaturation was sufficiently high. This could explain the formation of surface anhydrite in desert areas such as Southwest Africa, where high sulfate water comes in contact both with calcium carbonate in the soils and as extensive caliche deposits and earlier gypsum. Also if evaporation concentrates high sulfate waters in pore fluids at temperatures of 50°C or greater, anhydrite would readily form and earlier gypsum would be converted.

However, there does not seem to be any way in which normal modern sea water can be concentrated by evaporation such that a composition able to give anhydrite precipitation could occur. Even saturated NaCl solutions will not appreciably enhance the nucleation kinetics of the phases in the system. If in fact, true marine anhydrite precipitation ever does occur it appears that it must involve some abnormally high sulfate (or, less likely, high calcium) waters somewhere in the system either prior to or on initial burial. In the near shoreline areas of mixing of ground and marine waters, high sulfate solutions reacting with concentrated marine waters which contain calcium could possibly produce sufficient degrees of supersaturation for anhydrite formation. It has been proposed that the anhydrite in the Trucial Coast sabkha environment is near the present zone of mixing (Butler, 1969).

CONCLUSIONS

(1) The curves derived from thermodynamic and solubility determinations for the gypsum-anhydrite equilibrium transition by MacDonald (1953), Bock (1961), Marshall and Slusher (1966) and others and shown in Figure 1, probably are correct. However they cannot be used alone to predict the formation of anhydrite or gypsum as the nucleation kinetics in the system causes gypsum to precipitate metastably throughout the anhydrite stability field.

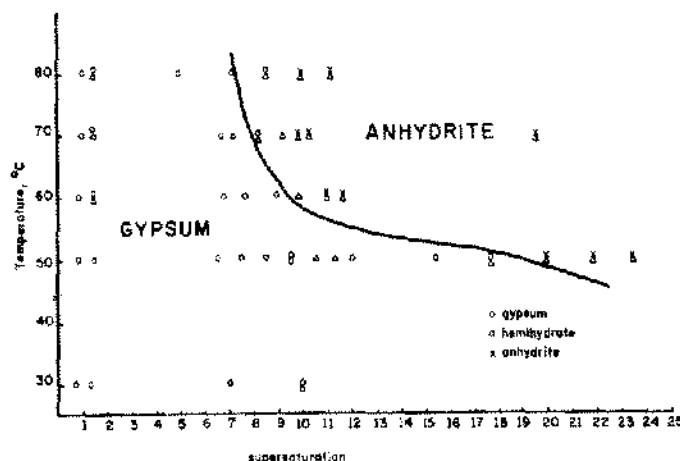


Figure 3. Dependence of transition temperature on supersaturation.

(2) The kinetics becomes favorable for the precipitation of anhydrite within its own stability field under conditions of high supersaturation i.e., high calcium or sulfate concentration in solution (Figs. 2, 3). Concentrated NaCl solutions are not able to alter the nucleation kinetics and gypsum will continue to precipitate under these conditions.

(3) In high concentrations of calcium or sulfate in solution at temperatures greater than 50°C (Fig. 3) it is also possible to rapidly convert hemihydrate or gypsum to anhydrite. This and other evidence from transient solubility studies suggest the conversion is a solution-precipitation mechanism.

(4) High calcium natural waters, or the much more likely high sulfate waters will cause conversion of gypsum to anhydrite under near surface conditions. A likely mechanism for near-surface continental anhydrite formation is reaction of high sulfate waters with earlier gypsum or CaCO_3 in soils, caliche and rocks.

(5) It is unlikely that modern seawater could ever obtain a composition by natural evaporation processes from which anhydrite would precipitate.

If anhydrite can form in the marine environment it would require contact of the solid phases with high sulfate (or calcium) waters, perhaps in deep brine pools or interstitially in sediments. Reaction of high sulfate ground waters with marine waters could lead to anhydrite formation.

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