

## MINERAL–SOLUTION EQUILIBRIA IN SPARINGLY SOLUBLE MINERAL SYSTEMS

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### ABSTRACT

Recent solubility, electrokinetic, spectroscopic and flotation studies in our laboratory on apatite and calcite in aqueous electrolytes indicate complex mineral–solution interactions which can alter surface characteristics of these minerals markedly in the presence of each other. In the case of systems containing such sparingly soluble minerals, understanding of the mineral–solution chemical equilibria under different physico-chemical conditions becomes important for developing schemes for processing them.

The chemical equilibria in heterogeneous systems involving salt-type minerals are investigated in this work. Stability relations have been analysed on the basis of bulk equilibria for calcite, apatite, magnesite, calcite–apatite, calcite–dolomite, apatite–dolomite, gypsum–anhydrite, calcite–gypsum, calcite–apatite–dolomite and calcite–magnesite–dolomite systems. The role of atmospheric carbon dioxide, which under most laboratory experimental conditions cannot be avoided, has been emphasised. Theoretical results have been correlated with experimental data reported in the literature.

### INTRODUCTION

Difficulties are often encountered in processing heterogeneous mineral systems under conditions predicted on the basis of single mineral tests. In systems containing minerals such as calcite and apatite which dissolve to a significant extent in water, the effect of dissolved species on the behavior of these minerals can be severe. In this study, chemical equilibria in selected single and mixed mineral systems are examined in order to determine the role of the dissolved species. The dissolution characteristics that take place in calcite–water [1–3] and apatite–water [4–7] single mineral systems have been studied in detail in the past. The results for the solubility of apatites [8, 9] and other phosphates are, however, not in agreement with each other [8–10].

Much of the work on the apatite–aqueous solution system has been centered upon obtaining reliable solubility constants for hydroxyapatite, fluorapatite and other phosphates. Difficulties encountered in this have been attributed to the existence of a non-stoichiometric solid phase. Several authors,

dissolved mineral species and surfactants. Adsorption of surfactants on particulates is the governing parameter in a number of interfacial processes such as flotation, flocculation, tertiary oil recovery using surfactant flooding, lubrication, detergency, comminution, chromatography and clarification for waste treatment, etc. The role of dissolved mineral species in surfactant abstraction (depletion) in these systems can be influenced significantly, in addition to solution properties such as pH, salinity and temperature, also by the mineral type [16]. Minerals such as calcite, gypsum, magnesite and limestone can be present in most reservoir rocks and systems, and recent experiments [17] have shown their predominating influence on sulfonate depletion in these systems. A knowledge of the equilibria in salt-type minerals is also important for the understanding of the interfacial processes in enhanced oil recovery. The role that dissolved mineral species play in determining the surface charge generation and thereby adsorption has been discussed by several investigators [4–8, 18, 19].

An understanding of the influence of the factors discussed above on the solubility and hence the chemical equilibria in heterogeneous mineral/aqueous system will therefore prove beneficial in developing capabilities to predict and control the behavior of minerals during interfacial processes such as adsorption, flotation and flocculation. The chemical equilibria in heterogeneous systems involving salt-type minerals are examined in this work. Stability relations have been discussed on the basis of bulk equilibria.

#### MINERAL–SOLUTION EQUILIBRIA

The equilibria in selected salt-type mineral systems with special reference to calcite and apatite are examined below. Theoretical results are correlated with experimental data.

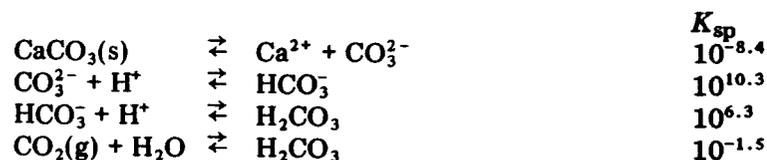
##### *Calcite equilibria*

The following are the major situations in which calcite equilibria could be considered [2, 3]:

- (1) Closed system: system closed to atmospheric  $\text{CO}_2$ .
- (2) Open system: system open to atmospheric  $\text{CO}_2$ .

Although these are two extreme cases most often realized in practice, other intermediate conditions can also be obtained.

When calcite is brought in contact with water, its dissolution will be followed by pH-dependent hydrolysis and complexation of the dissolved species. The following are the equilibria that will control the system [1, 18].



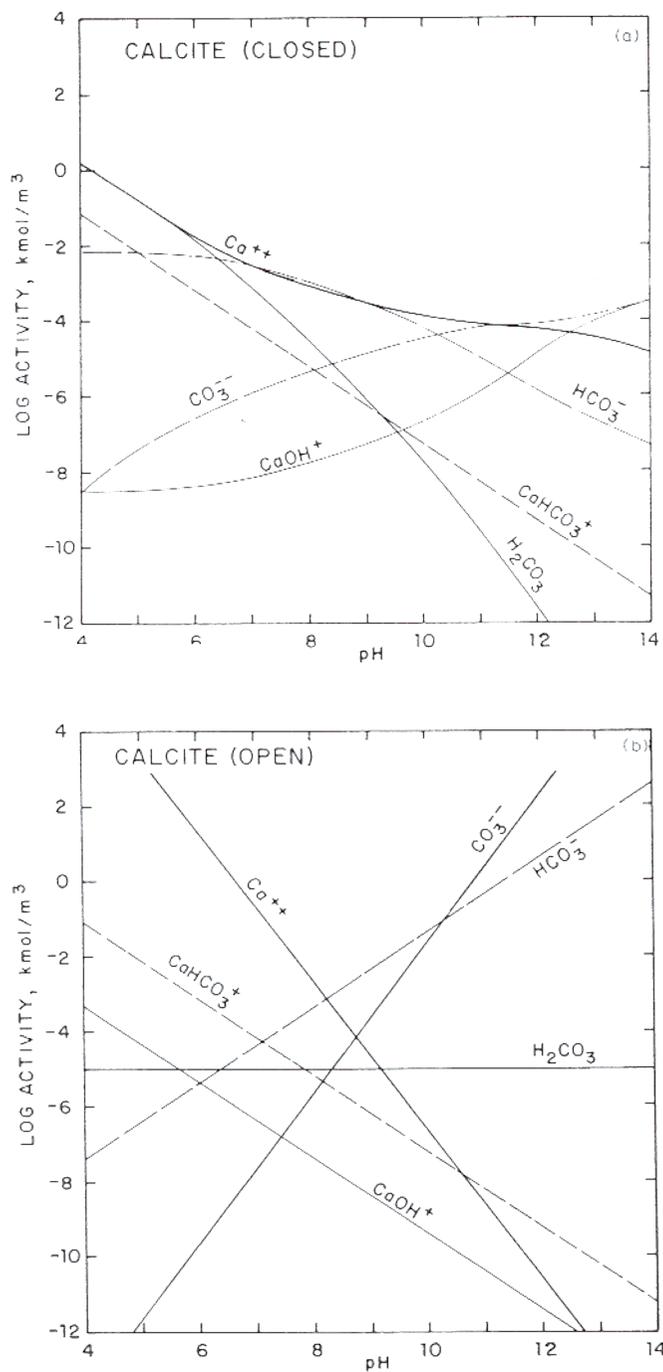


Fig. 1. Species distribution diagrams for calcite-water systems: (a) closed, (b) open.

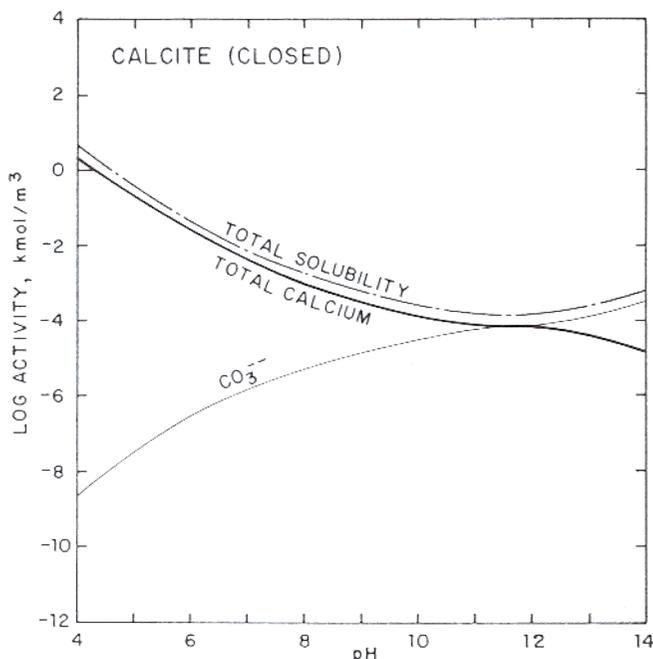
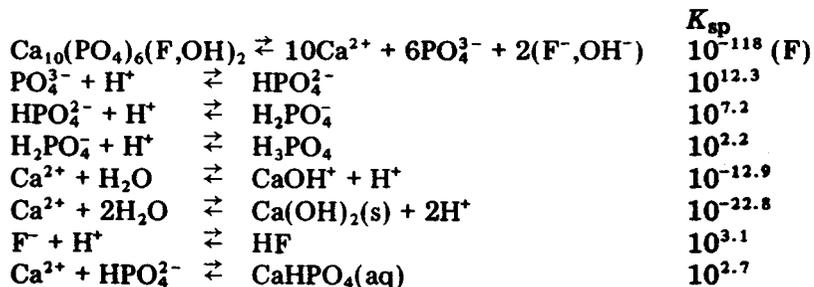


Fig. 3. Solubility of calcite in water (closed system) as function of pH.

solubility. As seen from Fig. 3, Beck's theory predicts an IEP of about 11.3 for the calcite closed system. This implies that values ranging from 8.2 (completely open systems) to 11.3 (completely closed systems) can be obtained for the IEP of calcite depending on the partial pressure of carbon dioxide in equilibrium with the system. Experimental values ranging from 8.0 to 10.8 reported in the literature [18] can at least partly be attributed to the differences in the partial pressure of carbon dioxide.

#### Apatite equilibria

The equilibria that control the dissolution of apatite in water are given below [5–7, 18].



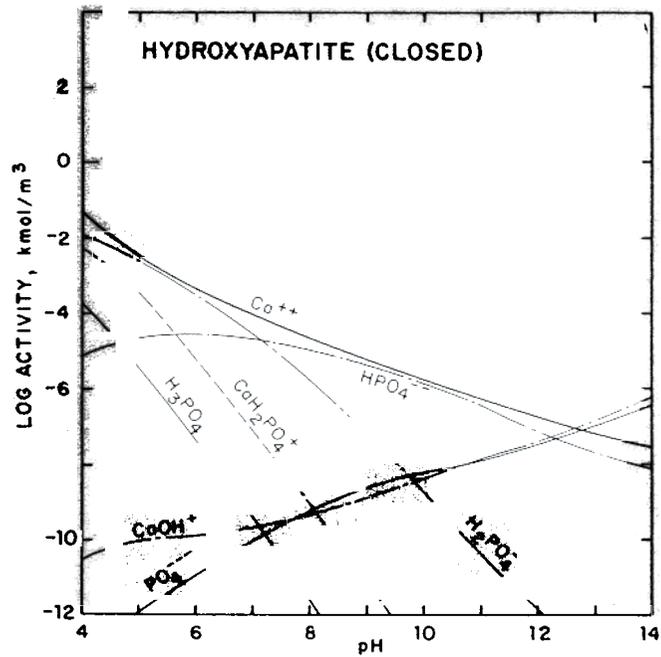
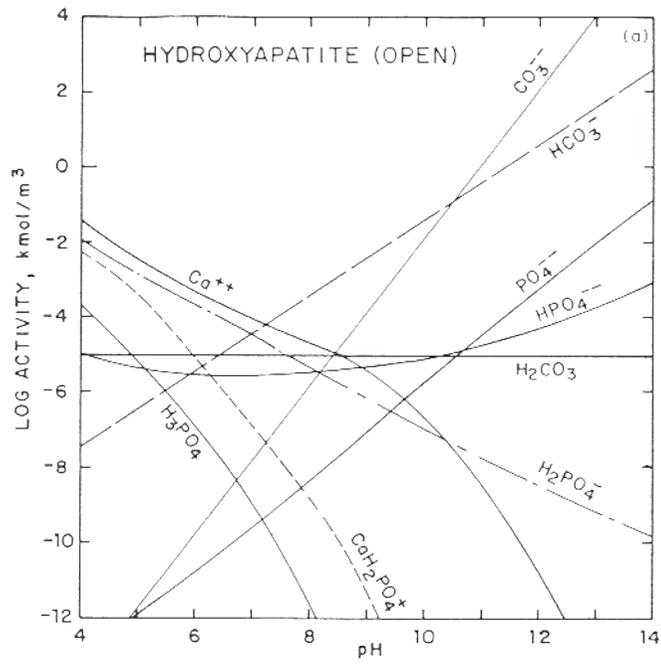


Fig. 4. Species distribution diagram for hydroxyapatite-water system: (a) open, (b) closed.

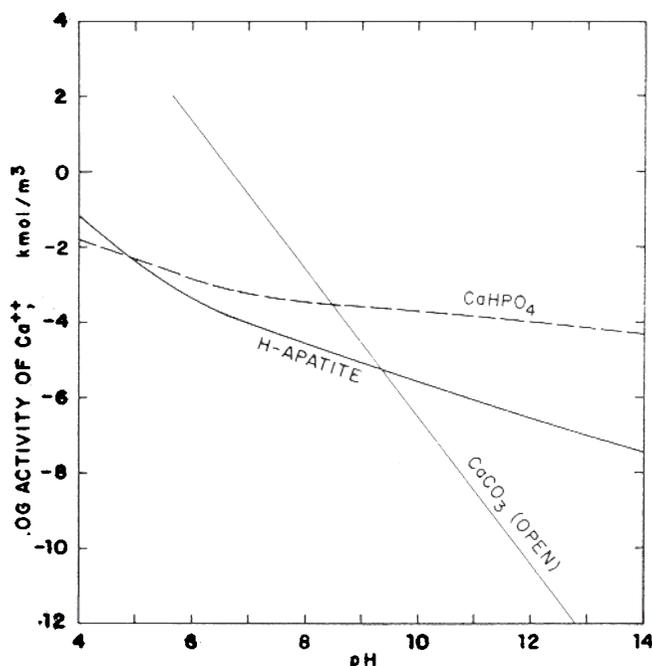


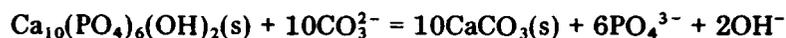
Fig. 6. Solubility isotherms at 25°C for monetite ( $\text{CaHPO}_4$ ), apatite and calcite.

- (1) The more stable phase, monetite, could precipitate from solution with the formation of a coating on the surface of the apatite particles, or
- (2) the surface of the apatite particles could undergo appropriate chemical reactions to convert to monetite [9].

In either case, the apparent solubility behavior of apatite in a solution more acidic than the singular point may be quite different from what one would expect for apatite. The formation of the most acidic phosphate in the form of a coating on apatite surface can lead to apparent low solubilities for apatite [8, 9].

It can also be seen from Fig. 6 that, above the singular point of 9.3, calcite is more stable than apatite. This implies that, if the apatite system is open to atmospheric  $\text{CO}_2$ , calcite can either precipitate from solution and subsequently form a surface coating on apatite, or the surface of apatite particles could be converted to calcite through surface precipitation or various surface reactions. Reactions involving organic and inorganic species leading to surface precipitation have been examined in detail elsewhere [25].

The conditions for the conversion of apatite to calcite can be more readily identified by considering the chemical reaction responsible for the process:



It can be seen from this reaction that, depending on the pH of the solution, apatite can be converted to calcite if the total carbonate in the solution

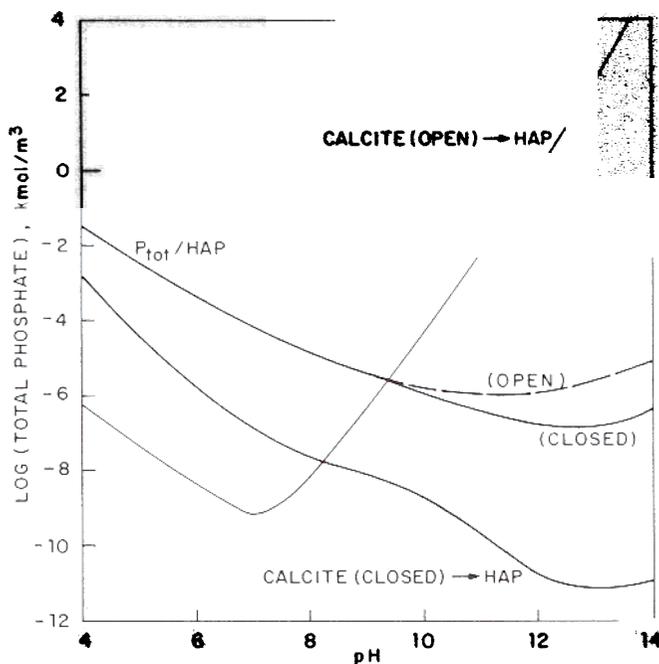


Fig. 8. Illustration of the possibility of the conversion of calcite to apatite.

calcite supernatant prepared above this pH could contain more than enough carbonate to convert apatite to calcite. Zeta-potential measurements conducted with calcite and apatite in water and in the supernatants of each other have shown that, indeed, these processes do occur [22]. Figure 9 presents the results of zeta-potential measurements in water and in supernatants. It can be seen that the two minerals have almost interchanged their points of zero charge (PZC). Additional electrokinetic experiments in relevant organic solutions, as well as solubility [26] and spectroscopic (ESCA) [27] studies have shown the surface conversion of apatite to calcite and vice versa under appropriate solution conditions. The ESCA results in Fig. 13 (Ref. [22]) clearly show the surface conversion process. Apatite conditioned in the supernatant of calcite at about pH 12 exhibits spectroscopic properties characteristic of both calcite and apatite, an indication of the conversion of the surface of the apatite to calcite [27].

Another aspect that is important from a surface chemical point of view is the transformation that hydroxyapatite can undergo in inorganic solutions. The solubility of various calcium minerals is shown in Fig. 10 as a function of pH. Comparison of the hydroxyapatite (HAP), fluorapatite (FAP) and fluorite ( $\text{CaF}_2$ ) solubilities shows that  $\text{CaF}_2$  is the most stable phase below about pH 5 and that FAP is the most stable mineral in the intermediate pH range while HAP is stable at high pH. This implies that, if systems in equilibrium with hydroxyapatite are brought in contact with a sufficiently high

concentration of fluoride ions, the apatite will be converted to fluorite under acidic pH conditions. In fact, numerous data reported in the literature [7, 28, 29] support this conclusion. Results of fluoride uptake and zeta-potential measurements presented in Fig. 11 indicate the occurrence of these

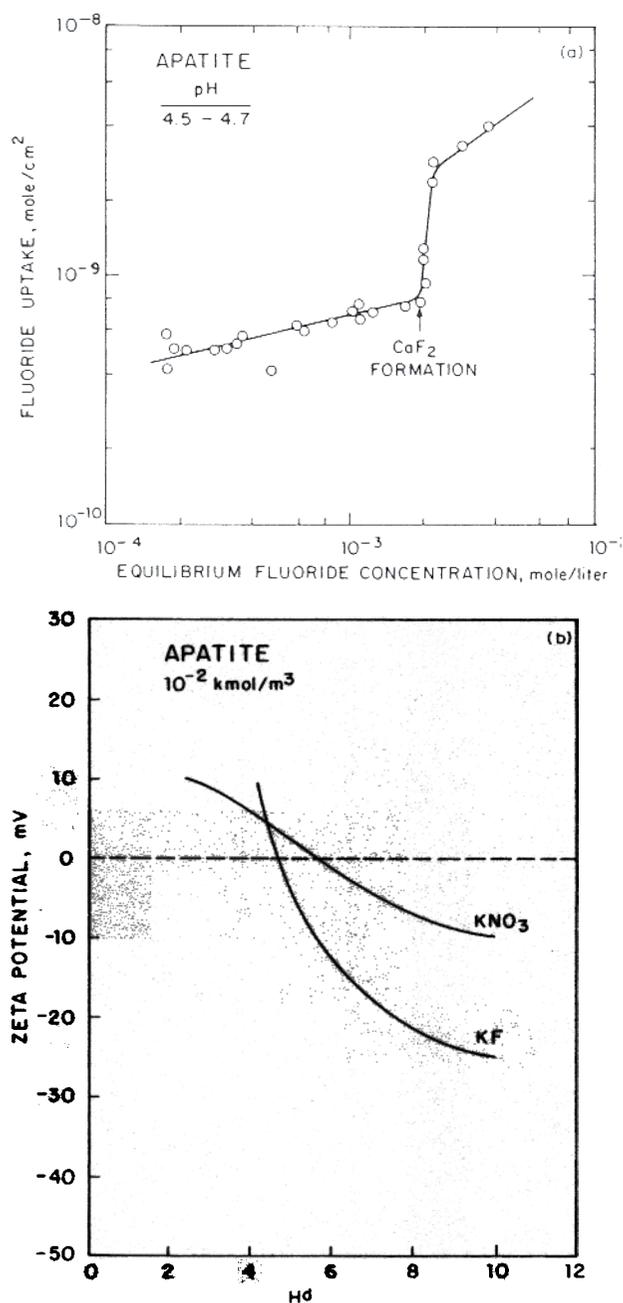


Fig. 11. Illustration of surface conversion of hydroxyapatite to fluorite: (a) fluoride uptake [28], (b) electrophoretic mobility [7].

in the Mg-CO<sub>2</sub>-H<sub>2</sub>O system. Table 1 illustrates this problem by comparing the free energy and equilibrium constant values from various sources for the most common minerals in this system at 25°C. The results obtained by using Langmuir [30] and Latimer [31] data, and Stumm and Morgan [2] data for the closed system are given in Figs 13(a) and 13(b), respectively. Comparison of the data in the two figures shows that magnesite is not stable in the pH range examined if Langmuir and Latimer data are used. However, on the basis of Stumm and Morgan data, magnesite is the most stable solid below about pH 10.7. Furthermore, using the data reported by Robie and co-workers [32] a value of 8.2 is obtained for the solubility product ( $pK_{sp}$ ) of magnesite, which is quite different from the values reported by Stumm and Morgan [2] and Langmuir [30] (see Table 1). The problems that can arise resulting from the differences in the interpretation of system behavior due to the use of such different data are obvious. It is to be noted that the Stumm and Morgan data are in close agreement with those reported elsewhere in the literature [3]. Figure 13(b) shows that, when magnesite is equilibrated with water in a closed system at sufficiently high pH (> 10.7), brucite (Mg(OH)<sub>2</sub>), which is the more stable phase, can form and thus convert the magnesite surface to brucite.

TABLE 1

Illustration of the variance in solubility data for some minerals in the Mg<sup>2+</sup>-CO<sub>2</sub>-H<sub>2</sub>O system at 25°C

Mineral	Formula	$pK_{sp}$		
		Langmuir [30] and Latimer [31]	Stumm and Morgan [2]	Robie et al. [32]
Magnesite	MgCO <sub>3</sub>	4.9	7.5	8.2
Brucite	Mg(OH) <sub>2</sub>	11.6	11.6	
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O	5.4	4.7	
Hydromagnesite	Mg <sub>4</sub> (CO <sub>3</sub> ) <sub>3</sub> (OH) <sub>2</sub> ·3H <sub>2</sub> O	29.5	29.5	

#### CALCITE-APATITE-DOLOMITE EQUILIBRIA

As mentioned earlier, the problem of separation of apatite from carbonates can be exemplified by the beneficiation of dolomitic phosphates in Florida where conventional flotation techniques have not been able to yield a concentrate with an acceptable MgO level of less than 1% [33]. Since dolomite is in most respects like calcite and it is found in significant ratios with apatite, dissolved species can be expected to play an important role in this system also.

The stability of dolomite under various conditions can be examined in the following manner. Consider the situation in which calcite or apatite is con-

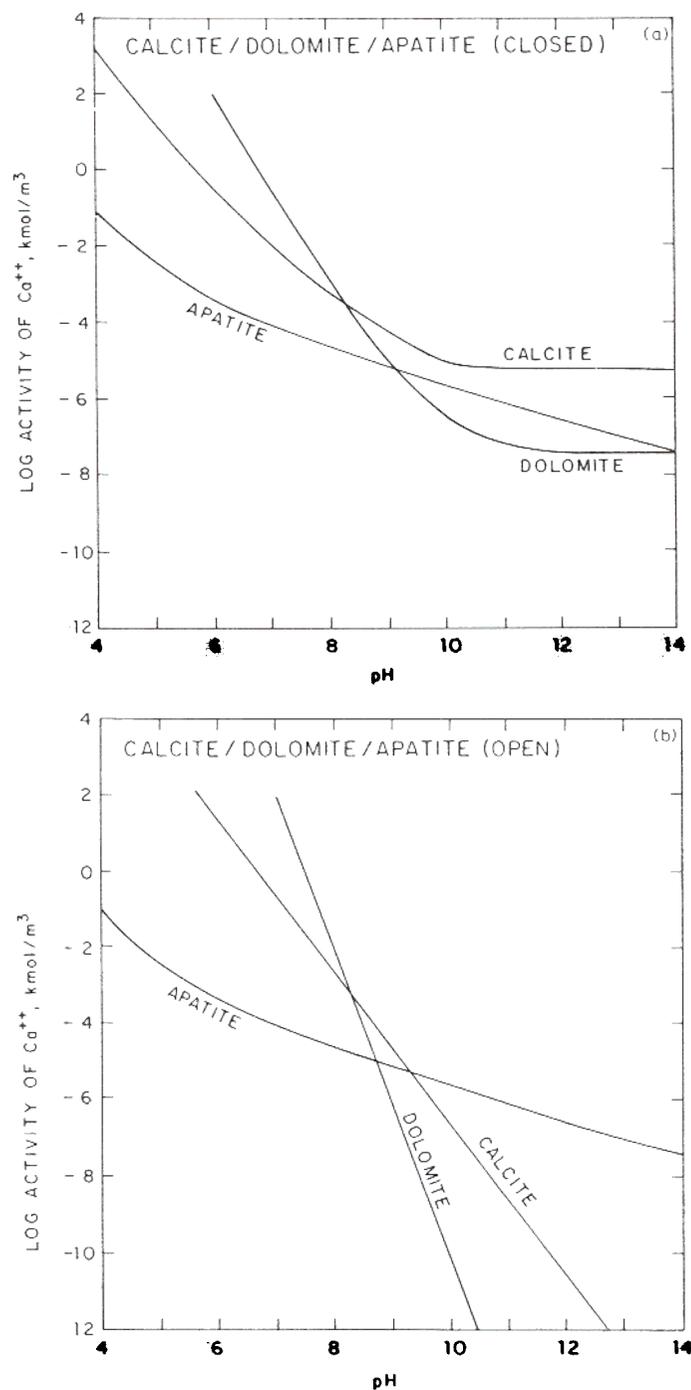


Fig. 14. Stability relations in calcite-apatite-dolomite system at 25°C.  $[\text{Mg}^{2+}] = 5.0 \times 10^{-4} \text{ kmol m}^{-3}$ , (a) closed ( $[\text{carbonate}] = 10^{-3} \text{ kmol m}^{-3}$ ), (b) open.

ferent investigators which range from  $10^{-16.5}$  to  $10^{-19.5}$  [2]. The difficulty in devising a scheme for the beneficiation of Florida dolomite phosphates and other phosphates in general can be attributed at least partly to the lack of understanding of the chemical equilibria governing the apatite–dolomite system. The surface conversion of apatite to dolomite and vice versa should be of major concern when considering such schemes.

#### CALCITE–MAGNESITE–DOLOMITE SYSTEM

Figure 15 shows the relative stability of calcite, magnesite, dolomite and brucite. The conversion of magnesite to dolomite and then to calcite is seen to be possible at various calcium/magnesium ratios. If dolomite is equilibrated with water in the presence of negligible amounts of  $\text{CO}_2$ , brucite will precipitate in the system. From the data in Figs 14 and 15, the conversion of dolomite to magnesite or calcite has minimal dependence on the partial pressure of carbon dioxide if the level is above about  $10^{-6}$  atm. Below this value, however, brucite will be the most stable phase.

#### SYSTEMS INVOLVING GYPSUM

##### *Calcite–gypsum equilibria*

Since gypsum is one of the most soluble salt-type minerals, the high level of  $\text{Ca}^{2+}$  activity in the gypsum–water systems will lead to the precipitation

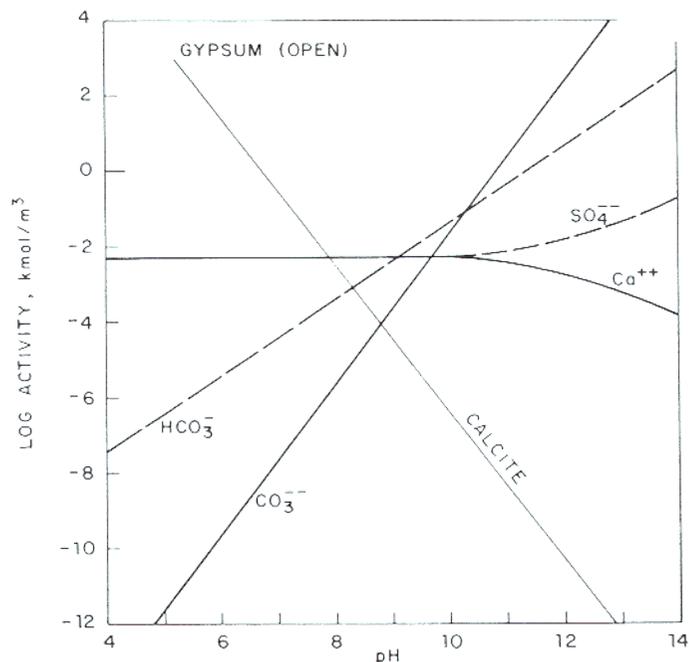


Fig. 16. Illustration of the possibility of conversion of gypsum to calcite [17]

when sparingly soluble minerals are contacted with water. Furthermore, the nature of the precipitate is markedly dependent in many systems upon the pressure of carbon dioxide in the environment. It is evident that many chemical alterations can take place in aqueous systems containing minerals such as calcite, apatite, magnesite, dolomite or gypsum in the presence of each other. The conversions are due not only to the presence of carbon dioxide in the system, but also to pH and pH alterations during the equilibration. It is in fact to note the serious effects of such surface conversion reactions in determining the efficiency of various interfacial processes such as adsorption, flotation, flocculation and leaching.

#### SUMMARY

The major findings from this investigation are summarized below:

(1) Atmospheric carbon dioxide affects the species equilibrium activity distribution in  $\text{MeCO}_3$  systems significantly. Stability relations in calcite—water, magnesite—water and dolomite—water systems are markedly dependent on the partial pressure of carbon dioxide.

(2) The theoretical points of zero charge of calcite, apatite and magnesite are in good agreement with experimentally determined values. If apatite is conditioned with water at  $25^\circ\text{C}$  in the presence of atmospheric carbon dioxide, calcite can precipitate in the system at pH values above 9.3.

(3) If apatite is conditioned in the supernatant of calcite, calcite may reprecipitate under certain pH conditions to convert the surface of apatite to calcite. Similarly, the precipitation of apatite from apatite supernatants that are contacted with calcite is also possible under certain other pH conditions.

(4) While relatively larger amounts of carbonate are required for the conversion of apatite into calcite, the conversion of calcite to apatite is possible even in the presence of micromolar concentrations of phosphate.

(5) Solid phases such as fluorite or fluorapatite can precipitate from apatite—fluoride systems depending upon fluoride concentration and pH level.

(6) At pH of about 8.6, if dolomite is equilibrated with excess  $\text{Ca}^{2+}$ ,  $\text{CaCO}_3$  can precipitate in the system. In the presence of excess  $\text{Mg}^{2+}$ , it may be converted to  $\text{MgCO}_3$ .

(7) If apatite is brought in contact with solutions containing  $5 \times 10^{-4} \text{ kmol m}^{-3} \text{ Mg}^{2+}$  under open or closed ( $10^{-3} \text{ kmol m}^{-3}$  carbonate) system conditions at the natural pH, the apatite surface can be converted to dolomite above pH 8.8 for the open systems and above pH 9.2 for closed systems.

(8) The conversion of calcite to dolomite under such solution conditions is also possible above pH 8.2 for both the open and closed systems. Conditioning both calcite and apatite in high concentration of magnesium solution in the open system makes calcite unstable in the entire pH range.

(9) If gypsum is present in a magnesium—carbonate system, favorable

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