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MINERAL EQUILIBRIUM STUDIES OF THE PSEUDOMORPHISM OF PYROMORPHITE BY HINSDALITE

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ABSTRACT

A pseudomorph of hinsdalite, $PbAl_3(PO_4)(SO_4)(OH)_6$ after pyromorphite, $Pb_5(PO_4)_3Cl$, has been noted from Dundas, Tasmania. Mineral equilibrium studies of the two species involved yield free energy of formation values of -842.8 k.cal./mole. for pyromorphite and -1116.8 k.cal./mole. for hinsdalite. Substitution of these values in an equation written to satisfy the volume requirements gives a free energy change of -802.5 k.cal. This high value suggests that the reaction as written would proceed spontaneously as required by the occurrence of the pseudomorph.

INTRODUCTION

The recognition of a pseudomorph after pyromorphite from Dundas, Tasmania, as hinsdalite (Baker, 1963) led to a study of the replacement process. Comparison of the formulas of pyromorphite, $Pb(PO_4)_3Cl$, and hinsdalite, $PbAl_3(PO_4)(SO_4)(OH_6)$, shows that the replacement would probably proceed in the presence of a solution containing aluminum, sulfate and hydroxyl ions. Refluxing of finely powdered pyromorphite in such a solution changed the colour of the solids present from an original yellow to white in less than 12 hours. *X*-ray diffraction data for the reaction product showed it to be identical with hinsdalite from the original locality in Colorado (Table 1). No trace of pyromorphite appeared in the diffraction pattern.

The occurrence of hinsdalite as a pseudomorph places a volume restriction on any equation written to represent its formation from pyromorphite. The latter mineral crystallizes with hexagonal symmetry with a unit cell volume of 630 Å^3 whilst hinsdalite is trigonal with a unit cell volume of 236 Å^3. From these figures the closest approach to a constant volume equation occurs when 3 unit cells of pyromorphite are replaced by 8 of hinsdalite. In both minerals the unit cell contains a single formula weight and the equation may be written:

$$3Pb_5(PO_4)_3Cl + 24Al^{3+} + 8SO_4^{2-} + 48OH^- \rightleftharpoons 8PbAl_3(PO_4)(SO_4)(OH)_6 + 7Pb^{2+} + PO_4^{3-} + Cl^-$$

This equation considers only the ions essential in the alteration. In the natural environment the system is open and since the average rainfall of western Tasmania is of the order of 100 inches per annum, very large volumes of dilute solutions must move rapidly through the weathering zone. It is assumed that with such volumes only a small degree of dissociation of water would be necessary to supply the 6 hydroxyl ions needed for the formation of each formula weight of hinsdalite. Consideration of the system on the basis of the law of mass action suggests that the reaction would proceed as the necessary ions are supplied. The ions released in the reaction which would normally oppose it are removed from the system in the mobile ground water.

In order to assess the validity of the proposed equation the mineral equilibria of the two species concerned were investigated.

TABLE 1. *X*-RAY POWDER DIFFRACTION DATA FOR PYROMORPHITE AND HINSDALITE

Pyromorphite (ASTM Card 2-0609)		Reaction Product		Hinsdalite Colorado	
d	I/I_1	d	I/I_1	d	I/I_1
4.31	60	5.70	60	5.70	90
4.09	90	5.55	10	5.57	30
3.63	20	4.91	10	4.90	3
3.34	60	3.50	40	3.51	45
3.24	60	3.46	15	3.43	20
2.95	100	2.97	100	2.97	100
2.86	60	2.93	2	2.93	5
2.25	5	2.84	5	2.85	10
2.18	20	2.79	5	2.79	15
2.14	10	2.45	10	2.45	10

MINERAL EQUILIBRIA

The determination of the equilibrium concentration of constituent ions in a solution in contact with the solid mineral enables the calculation of the free energy of formation of that mineral. This is achieved by first determining the solubility products of the mineral at various ionic strengths, plotting of the relationship between these variables and extrapolating the resulting curve to infinite dilution. This yields the value of the equilibrium constant from which the free energy can be obtained. The theoretical basis for this approach is discussed in most text books of physical chemistry such as Glasstone (1951) and an excellent condensed treatment is given by Garrels (1960).

It is not proposed to give more than a summary of the basic relationships. Taking pyromorphite as an example and using the standard symbols throughout the required relationships are:

(1) *Equilibrium Equation*

$$Pb_5(PO_4)_3Cl \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + Cl^-$$

(2) *Solubility Product*

$$K_{\text{pyromorphite}} = (m_{Pb^{+2}})^5(m_{PO_4^{3-}})^3(m_{Cl^-})$$

(3) *Equilibrium Constant*

$$k_{\text{pyromorphite}} = (a_{Pb^{2+}})^5(a_{PO_4^{3-}})^3(a_{Cl^-})$$

(4) *Concentration—Activity Relationship*

$$m = \frac{a}{\gamma}$$

(5) *Debye-Hückel Equation* (simplified for solutions of low ionic strength)

$$\log \gamma_i = -Az_i^2\sqrt{\mu}$$

(6) *Ionic Strength*

$$\mu = \tfrac{1}{2}\Sigma cz^2$$

(7) Combination of (2), (3) and (4) yields:

$$k_{\text{pyromorphite}} = K_{\text{pyromorphite}}(\gamma_{Pb^{2+}})^5(\gamma_{PO_4^{3-}})^3(\gamma_{Cl^-})$$

By taking logs of (7) and substituting values determined from (5) there results:

$$\log k_{\text{pyromorphite}} = \log K_{\text{pyromorphite}} - 24\sqrt{\mu}$$

From this it is seen that at low ionic strengths the solubility product is a function of the square root of the ionic strength and, in the case of pyromorphite, has a limiting gradient of −24. By a similar process the relationships in the case of hinsdalite result in the equation:

$$\log k_{\text{hinsdalite}} = \log K_{\text{hinsdalite}} - 22\sqrt{\mu}$$

By plotting solubility products versus the square root of ionic strength and extrapolating to infinite dilution (zero ionic strength), the value of the equilibrium constant for the dissociation of a mineral into its constituent ions can be obtained. The extrapolation can be guided by use of the theoretical limiting gradients.

PYROMORPHITE STUDY

Pyromorphite slowly crystallizes from a solution containing its constituent ions. In the study described here these ions were made available from solutions of lead chloride and disodium hydrogen phosphate at various concentrations. Reactant solutions, the compositions of which are given in Table 2, were prepared in triplicate and allowed to age for several months at 25° C. before being analyzed. Details of analytical procedures will not be given. Lead was determined by polarography, phos-

TABLE 2. REACTANT SOLUTION COMPOSITION FOR PYROMORPHITE EQUILIBRIUM STUDY

Soln. No.	H_2O ml	$PbCl_2$		Na_2HPO_4	
		ml	gm	ml	gm
1	80	100	1.0040	20	0.3039
2	110	75	0.7530	15	0.2279
3	140	50	0.5020	10	0.1519
4	170	25	0.2510	5	0.0759

phate by colorimetry and chloride by volumetric analysis. The analytical results and values of log K and $\sqrt{\mu}$ calculated from these are given in Tables 3 and 4.

A plot of log K versus $\sqrt{\mu}$ (Fig. 1) gives an array of points along a curve which becomes asymptotic to the Debye-Hückel limiting gradient at an ionic strength of about 0.01. Extrapolation of the curve at the limiting gradient (−24) to zero ionic strength gives a value of log K of −34.5. This figure should be close to the value of log k. Two factors may be involved in the deviation of the curve from a linear relationship at the higher concentrations in the range studied. The Debye-Hückel limiting law is not generally accepted as being applicable to solutions of ionic strengths in excess of 0.01. It is also possible that the system was not completely at equilibrium at the time of analysis.

At 25° C. the free energy change for a reaction is related to the equilibrium constant by the equation:

$$\Delta F^\circ_R = -1.364 \log_{10} k$$

This yields a value for the free energy of dissociation of pyromorphite into its constituent ions of 47.1 k.cal. The free energy change for any reaction is given by:

$$\Delta F^\circ_R = \Delta F^\circ_{\text{products}} - \Delta F^\circ_{\text{reactants}}$$

The free energies of formation of ions are available from a number of

TABLE 3. AVERAGED ANALYTICAL DATA FOR PYROMORPHITE EQUILIBRIUM STUDY (mg/100 ml)

Soln. No.	Pb	PO_4	Cl
1	17.75	0.425	110.75
2	14.70	0.310	84.10
3	13.05	0.275	57.55
4	11.70	0.205	31.05

TABLE 4. LOG K AND $\sqrt{\mu}$ VALUES FOR PYROMORPHITE EQUILIBRIUM STUDY

Soln. No.	1	2	3	4
Log K	−29.91	−30.73	−31.40	−32.21
$\sqrt{\mu}$	0.168	0.146	0.122	0.090

sources (*e.g.* Rossini *et al.*, 1952). Substitution of these data in the equilibrium equation for pyromorphite yields a value for the free energy of formation of this mineral of −842.8 k.cal./mole.

HINSDALITE STUDY

Procedures for the study of hinsdalite were similar to those used for pyromorphite. The ions necessary were made available from solutions of lead nitrate, disodium hydrogen phosphate and aluminium sulphate. Reactant solutions were prepared at various concentrations (Table 5) and were left for several months at 25° C. before being analysed. Lead and phosphate were determined as in the pyromorphite study, aluminum by colorimetry, sulphate by turbidimetry and hydroxyl ion by pH measurement. Analytical results, log K and $\sqrt{\mu}$ values are given in Tables 6 and 7.

The plot of log K versus $\sqrt{\mu}$ (Fig. 2) gives an array of points on a curve,

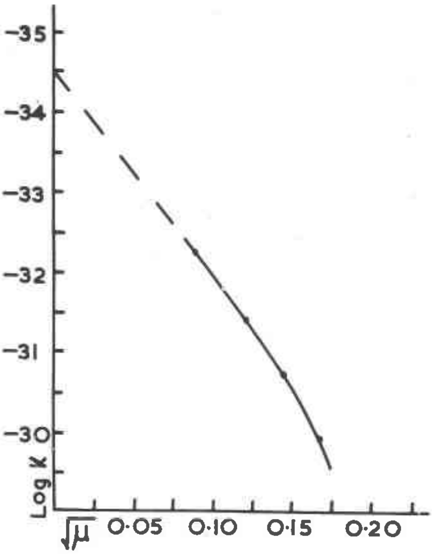

FIG. 1. Solubility product—ionic strength relationship for pyromorphite reaction.

TABLE 5. REACTANT SOLUTION COMPOSITION FOR HINSDALITE EQUILIBRIUM STUDY

Soln. No.	H_2O ml	$Pb(NO_3)_2$		Na_2HPO_4		$Al_2(SO_4)_3\cdot 9H_2O$	
		ml	gm	ml	gm	ml	gm
1	2	40	0.1947	4	0.0568	4	0.3026
2	14	30	0.1491	3	0.0426	3	0.2269
3	26	20	0.0994	2	0.0284	2	0.1513
4	38	10	0.0497	1	0.0142	1	0.0757

TABLE 6. AVERAGED ANALYTICAL DATA FOR HINSDALITE EQUILIBRIUM STUDY (mg/100 ml)

Soln. No.	Pb	Al	PO_4	SO_4	pH
1	2.20	35.8	8.68	32.70	2.82
2	3.00	25.0	5.50	24.00	2.88
3	3.10	17.2	3.30	16.40	2.96
4	3.20	5.5	1.36	7.80	3.14

which as in the pyromorphite study, becomes asymptotic to the limiting gradient (−22) at the lower concentrations in the range studied. Extrapolation to zero ionic strength gives a value of $\log_{10}k = -86.5$ for the dissociation of hinsdalite. By calculations similar to those used for pyromorphite this figure yields a value for the free energy of formation of −1116.8 k.cal./mole.

THE ALTERATION OF PYROMORPHITE

It is of interest to apply the data obtained from the above studies to the volume constant reaction proposed for the alteration of pyromorphite. The equation is repeated below with free energy data printed above the relevant constituents.

$$\begin{array}{cccc} 3x-842.8 & 24x-115.0 & 8x-177.34 & 48x-37.595 \\ 3Pb_5(PO_4)_3Cl \;+ & 24Al^{3+} \;+ & 8SO_4^{2-} \;+ & 48OH^- \end{array}$$

$$\begin{array}{cccc} 8x-1116.8 & 7x-5.8 & -245.1 & 3x-31.35 \\ 8PbAl_3(PO_4)(SO_4)(OH)_6 \;+ & 7Pb^{2+} \;+ & PO_4^{3-} \;+ & 3Cl^-. \end{array}$$

TABLE 7. LOG K AND $\sqrt{\mu}$ VALUES FOR HINSDALITE EQUILIBRIUM STUDY

Soln. No.	1	2	3	4
Log K	−82.19	−82.50	−82.96	−83.88
$\sqrt{\mu}$	0.290	0.245	0.197	0.125

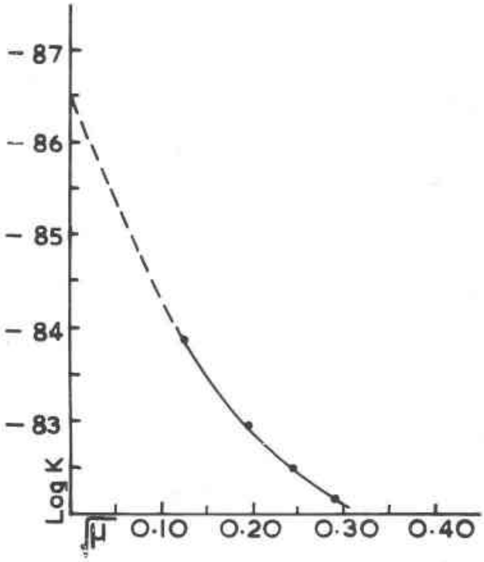

Fig. 2. Solubility product—ionic strength relationship for hinsdalite reaction.

The free energy change for this reaction is −802.5 k.cal. Hence in addition to satisfying the volume condition the reaction results in a large decrease in free energy and it could be expected to proceed spontaneously as required by the formation of hinsdalite in the natural environment.

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