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## **EXAMINATION OF $PbCO_3$ SOLUBILITY USING DIRECT AND COMPETITIVE CHELATION METHODS**

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### **ABSTRACT**

Competitive chelation method may be used to determine or examine the solubility product of a mineral. This method has the advantage of being independent of chemical conditions of the system. Direct and competitive chelation methods as well as XRD analysis were employed to examine the solubility product and mineralogical identity and purity of two  $PbCO_3$  samples. One of these samples has been used as the pure cerussite mineral for controlling activity of  $Pb^{2+}$  in several studies. Both direct and competitive chelation method indicated that  $\log K_{SP}$  value of -13.5 previously chosen for cerussite is smaller than its actual value. A mean value of -13.33 from direct method and an average value of -12.75 from chelation studies were obtained for  $\log K_{SP}$  of two  $PbCO_3$  samples. The XRD results indicated that one of the samples contains hydrocerussite as an impurity.

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## بررسی حلالیت $PbCO_3$ با روش مستقیم و رقابت کلاتی

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### چکیده

روش رقابت کلاتی را می توان برای تعیین یا بررسی حاصلضرب حلالیت کانی ها بکار برد. مزیت این روش مستقل بودن آن از شرایط شیمیایی شناسی و درجه خلوص دو نمونه کربنات سرب مورد استفاده قرار گرفت. یکی از این نمونه ها قبلاً\* به عنوان کانی خالص کربنات سرب (Cerussite) در سیستم می باشد. دو روش ((مستقیم)) و ((رقابت کلاتی)) برای مطالعه حاصلضرب حلالیت و همچنین روش تفرق اشعه ایکس (XRD) برای بررسی کانی مطالعات متعددی به منظور کنترل فعالیت  $Pb^{2+}$  در محلول بکار رفته بود. هر دو روش مستقیم و رقابت کلاتی نشان دادند که  $\log K_{sp} = -13/5$  که قبلاً\* برای حلالیت کانی مذکور انتخاب شده بود، کوچکتر از مقدار واقعی آن است. در روش مستقیم میانگینی برابر  $13/33$  - و در روش رقابت کلاتی میانگینی برابر  $12/75$  - برای لگاریتم حاصلضرب حلالیت کانی فوق الذکر به دست آمد. نتایج مطالعات به وسیله تفرق اشعه ایکس نشان داد که در یکی از نمونه ها مقداری کانی هیدروسروسیت (Hydrocerussite) به عنوان ناخالصی وجود دارد.

## INTRODUCTION

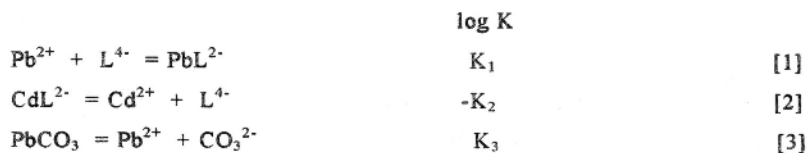
The competitive chelation method described by Workman and Lindsay (15) has been used to determine the activity of  $\text{Cd}^{2+}$  (2, 8, 15),  $\text{Zn}^{2+}$  (7, 8, 10),  $\text{Fe}^{3+}$  (8, 13) and  $\text{Ni}^{2+}$  (8) both in contaminated and uncontaminated soils. This method normally requires use of a well-defined pure mineral containing the counter metal ion to maintain the activity of this ion in solution as a function of an easily measurable parameter such as pH(15).

Commercially available analytical grade  $\text{PbCO}_3$  has been used as the pure mineral controlling the solution activity of  $\text{Pb}^{2+}$  (12) (counter ion) in studies aimed at determination of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  activities (2, 8, 15). The solubility product of  $\text{PbCO}_3$  used in these studies was not determined experimentally but was calculated from thermodynamic constants compiled by Sadiq and Lindsay (11) or Lindsay (5).

In the course of a study using competitive chelation to measure  $\text{Pb}^{2+}$  activity in lead-arsenate contaminated soils of central Washington, we observed that Pb solubility from an analytical grade  $\text{PbCO}_3$  sample obtained from Aldrich Chemical Company was substantially higher than that calculated from the solubility product  $\text{pK}_{\text{SP}} -13.5$  used by the above-mentioned authors. It was, therefore, the purpose of this work to use both direct and competitive chelation methods and X-ray diffraction analysis to examine the solubility and mineralogical purity of two  $\text{PbCO}_3$  samples.

### Theory

Competitive Chelation Method. The appropriate equilibrium reactions involving a chelating agent,  $\text{PbCO}_3$  and  $\text{CdCO}_3$  are:





where L is the chelation ligand,  $K_1$  and  $K_2$  are log of formation constants for  $\text{PbL}^{2-}$ ,  $\text{CdL}^{2-}$  and  $K_3$  and  $K_4$  are log of dissociation constants of  $\text{PbCO}_3$  and  $\text{CdCO}_3$ , respectively. Combining reactions [1] to [4] gives reaction [5] with log of equilibrium constant ( $K_5$ ) equal to  $(K_1 - K_2) + (K_3 - K_4)$ .

At equilibrium [5] is:

$$\frac{(\text{PbL}^{2-}) (\text{CdCO}_3)}{(\text{CdL}^{2-}) (\text{PbCO}_3)} = 10^{(K_1 - K_2) + (K_3 - K_4)} \quad [6]$$

Assuming that the activities of  $\text{CdCO}_3$  and  $\text{PbCO}_3$  as finite solids are unity, and that the activity coefficients of  $(\text{PbL}^{2-})$  and  $(\text{CdL}^{2-})$  are equal, Eq. [6] reduces to:

$$\frac{[\text{PbL}^{2-}]}{[\text{CdL}^{2-}]} = 10^{(K_1 - K_2) + (K_3 - K_4)} \quad [7]$$

where the brackets indicate concentration.

Equation [7] indicates that the concentration ratio of  $\text{PbL}^{2-}$  to  $\text{CdL}^{2-}$  is a constant independent of pH, ionic strength and partial pressure of  $\text{CO}_2$ . The exponential term on the right hand side of Eq. [7] is composed of a chelate-dependent constant,  $K_1 - K_2$  (difference between formation constants of the chelating ligand with Pb and Cd) and a chelate-independent component,  $K_3 - K_4$  (the difference between solubility products of  $\text{PbCO}_3$  and  $\text{CdCO}_3$ ).

The advantage of this method is that the concentration ratio of  $\text{PbL}^{2-}$  to  $\text{CdL}^{2-}$  for a system containing  $\text{PbCO}_3 + \text{CdCO}_3$  and a chelating agent is

independent of pH, ionic strength and CO<sub>2</sub> partial pressure. As it will be explained in the materials and methods the above ratio could be measured experimentally.

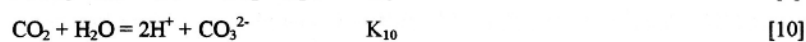
**Direct Method.** Effect of equilibrium pH and partial pressure of CO<sub>2</sub> on Pb<sup>2+</sup> activity from PbCO<sub>3</sub>, according to Lindsay (5), may be written as follows:



where K<sub>8</sub> is the log of equilibrium constant of reaction [8]. Assuming unit activity for H<sub>2</sub>O :

$$\frac{(\text{Pb}^{2+}) (\text{CO}_2)}{(\text{H}^+)^2} = 10^{K_8} \quad [9]$$

If K<sub>8</sub> is combined with K<sub>10</sub>, log K of reaction [10], K<sub>11</sub> or log K<sub>SP</sub> of PbCO<sub>3</sub> will be obtained from reaction [11]. Equilibrium Pb<sup>2+</sup> activity is determined and CO<sub>3</sub><sup>2-</sup> is assumed in equilibrium with CO<sub>2</sub> partial pressure at normal atmospheric pressure and K<sub>SP</sub> is taken as the product of Pb<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> activities.



## MATERIALS AND METHODS

Two samples of analytical grade  $\text{PbCO}_3$  and one sample of analytical grade  $\text{CdCO}_3$  were used in this study. The  $\text{CdCO}_3$  sample and one of the  $\text{PbCO}_3$  sample (sample No.1) were purchased from Aldrich Chemical Co.(Lot. KZ05026MX and AZ06615AY, respectively) for our laboratory. The other  $\text{PbCO}_3$  sample (No.2) was a Baker Chemical Co.(Lot. 37147) production and was used by Workman and Lindsay (15) in the competitive chelation studies.

Solubility of  $\text{CdCO}_3$  sample and  $\text{PbCO}_3$  samples was examined by both a direct method and a competitive chelation method. X-ray diffraction analysis was also used to identify the kind of mineral and the existence of possible impurities.

**Direct Method.** A small amount of each sample was separately equilibrated with 20 ml aliquots of dilute HCl or NaOH ( $10^{-4}$  to  $10^{-3}$  M HCl or NaOH). Equilibration was obtained by shaking 40 mg of sample with 20 ml of solution in 125 ml Erlenmeyer flasks cover with parafilm that was perforated to allow gas exchange with the atmosphere. The pH was measured in the suspension immediately at the end of the 5d shaking period, and the suspensions were filtered under vacuum through  $0.45 \mu\text{m}$  nylon membrane filters. The filtrates were then analyzed for Pb and/or Cd by direct-coupled plasma spectroscopy (DCP). Electrical conductivity (EC) was also measured in the filtrates to calculate ionic strength (I) from equation  $I=0.013 \text{ EC}$  (3).

**Competitive Chelation Method.** The method depends on reacting batches of  $\text{PbCO}_3$  and  $\text{CdCO}_3$  with a series of chelate solutions having different mole fractions of Pb and Cd. Upon reacting, solutions with low Pb mole fraction

gain Pb and lose Cd as  $\text{PbCO}_3$  dissolves. From these results and by graphical method (Figs. 4 and 5), it is possible to determine the unique mole fraction of Pb or Cd on the chelate that neither gains nor loses Pb or Cd. This unique mole fraction reflects equilibrium conditions and provides the required information to calculate the ratio  $[\text{PbL}]/[\text{CdL}]$  necessary for the Eq. [7].

Twenty-ml aliquots of  $10^{-4}$  M ethylenedinitrilotetraacetic acid (EDTA) or N-(2-hydroxyethyl) ethylenedinitrilotetraacetic acid (HEDTA) solution containing various  $[\text{PbL}]/[\text{PbL}+\text{CdL}]$  mole fractions (PbMF) were shaken with 20 mg  $\text{CdCO}_3$  and 20 mg of each of the  $\text{PbCO}_3$  samples. The solutions were prepared by adding 8.0 ml of 250  $\mu\text{M}$  of a series of chelate stock solution containing different  $[\text{PbL}]/([\text{PbL}]+[\text{CdL}])$  plus 12 ml of 1.0  $\mu\text{M}$  NaOH + 4 ml  $\text{H}_2\text{O}$  for HEDTA to  $\text{PbCO}_3 + \text{CdCO}_3$  in 125 ml Erlenmeyer flasks covered with parafilm that was perforated to allow gas exchange with the atmosphere. Reagent-grade  $\text{Na}_2\text{EDTA}$  and  $\text{Na}_3\text{HEDTA}$ , supplied by the Baker Co. (Phillipsburg, NJ), and  $\text{CdCl}_2$  and  $\text{Pb}(\text{NO}_3)_2$ , supplied by the Aldrich Co. (Milwaukee, WI) were used.

The NaOH was added to maintain the pH in alkaline range and prevent dissolution of  $\text{PbCO}_3$  and/or  $\text{CdCO}_3$  more than total chelate in solution (100  $\mu\text{M}$ ). For each series, a control solution containing both  $\text{PbCO}_3$  and  $\text{CdCO}_3$ , but no chelate and adjusted to the final pH of chelate containing solutions by 1.0  $\mu\text{M}$  NaOH was run. The final pH was measured in the suspension immediately after shaking period. The initial PbMF were 0.0, 0.4, 0.6 and 1.0 for EDTA and 0.0, 0.3, 0.6 and 1.0 for HEDTA.

**Data Analysis and Calculations.** The concentration of Pb or Cd in the control solutions were very low compared to the chelated solutions in the alkaline final pH range (7.62-7.89) obtained. Concentration of the chelated Pb or Cd ( $[\text{PbL}]$  or  $[\text{CdL}]$ ) was calculated by subtracting the Pb or Cd concentration of the control solutions from the chelated solutions. The

equilibrium PbMF was obtained by plotting the initial PbMF of the chelated solutions against their final PbMF and solving the linear equation obtained with 1:1 line for the crossing point (Fig. 4 and 5).

The measured total concentration of Pb and/or Cd in the chelation method were also speciated by MINTEQA2 (1) using the modified database by Lindsay and Ajwa (6). The concentration of PbL and CdL were obtained from MINTEQA2 output files. The equilibrium PbMF calculated graphically and those obtained from MINTEQA2 output files were almost identical, therefore only the experimentally determined equilibrium PbMF's were reported in Table 1. These values were used to calculate the equilibrium [PbL]/[CdL] ratios as follows:

$$\begin{aligned}\text{PbMF} &= [\text{PbL}] / ([\text{PbL}] + [\text{CdL}]) \\ 1 - \text{PbMF} &= 1 - [\text{PbL}] / ([\text{PbL}] + [\text{CdL}]) = [\text{CdL}] / ([\text{PbL}] + [\text{CdL}]) \\ \text{PbMF} / (1 - \text{PbMF}) &= [\text{PbL}] / [\text{CdL}]\end{aligned}$$

The equilibrium [PbL]/[CdL] was also calculated theoretically by MINTEQA2 using  $\text{PbCO}_3$  and  $\text{CdCO}_3$  as infinite solids and 100  $\mu\text{M}$  EDTA or HEDTA as chelate in 0.6  $\mu\text{M}$  NaOH for EDTA or 0.4  $\mu\text{M}$  NaOH for HEDTA. The equilibrium pH obtained from MINTEQA2 were 7.64 for EDTA and 7.65 for HEDTA, respectively. The results of these calculations were also included in Fig. 4 and 5 and reported in Table 1. The independency of the equilibrium [PbL]/[CdL] ratio from pH, ionic strength and partial pressure of  $\text{CO}_2$  in the above system (chelation method) was also tested by putting various pH's, ionic strength and  $\text{CO}_2$  partial pressure into the input files of MINTEQA2. The results always gave identical value for [PbL]/[CdL] ratio confirming the Eq. [7].

The measured total concentration of Pb or Cd in the direct method were also speciated by MINTEQA2 using measured pH, calculated ionic strength and the concentration of  $\text{Na}^+$  or  $\text{Cl}^-$  added as NaOH or HCl to each solution.



The activity of  $Pb^{2+}$  or  $Cd^{2+}$  obtained from MINTEQA2 output files was plotted against pH (Fig. 1 and 3) and mean solubility product for each sample was calculated using  $CO_3^{2-}$  activities obtained from MINTEQA2 output files.

## RESULTS AND DISCUSSION

### Direct Method

The experimentally determined total dissolved Cd concentration conformed closely with those predicted by MINTEQA2 for the equilibrium total Cd concentration for octavite (Fig. 1). The  $\log K_{SP}$  value of -11.99 used by MINTEQA2 data base, therefore, is a correct value.

X-ray diffraction analysis (XRD) of the  $CdCO_3$  sample shows close agreement with the d-values for octavite (Fig. 2a). All peaks were accounted for by XRD and ASTM powder diffraction data indicated that the sample, indeed, is an octavite with no detectable impurity.

Solubility data for two  $PbCO_3$  samples (No. 1 and 2) determined by the direct method are plotted against pH in Fig. 3. Equilibrium lines for cerussite ( $PbCO_3$ ) were constructed the same way as described for octavite.

The values for experimentally determined total dissolved Pb concentration for both  $PbCO_3$  samples fall on a single line (Fig. 3). This line lies above that by predicted MINTEQA2 for cerussite, suggesting that the  $\log K_{SP}$  value used by MINTEQA2 to construct the equilibrium concentration line is incorrect or the  $PbCO_3$  samples are not pure cerussite. The  $\log K_{SP}$  value in MINTEQA2 data base for cerussite is -13.50, taken from Sadiq and Lindsay (11). The average  $\log K_{SP}$  value calculated from our data is -13.33. The maximum and minimum  $\log K_{SP}$  calculated from  $\Delta G_f^\circ$  values reported in literature [Woods and Garrels (16), Wagman *et al.* (14), Karapet'yant and Karapet'yant (4)] are -12.83 and -13.44, respectively.

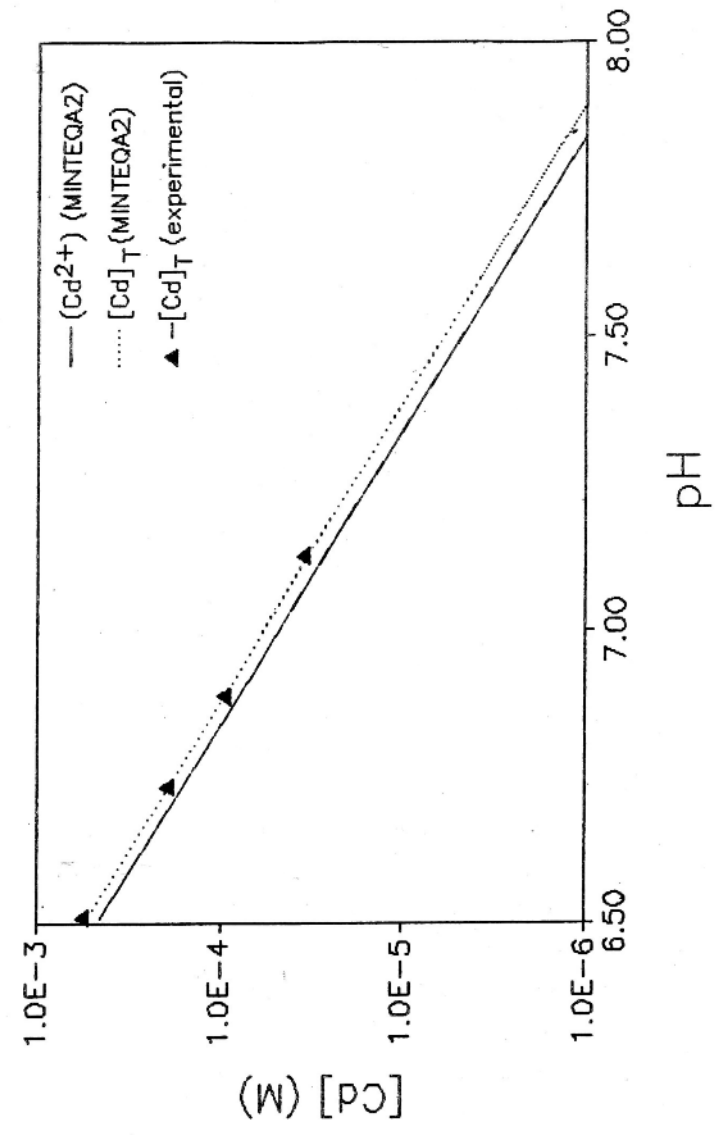


Fig.1. Solubility of  $\text{CdCO}_3$  as a function of pH at  $\text{PCO}_2=0.0003$  atm for a  $\text{CdCO}_3$  sample.

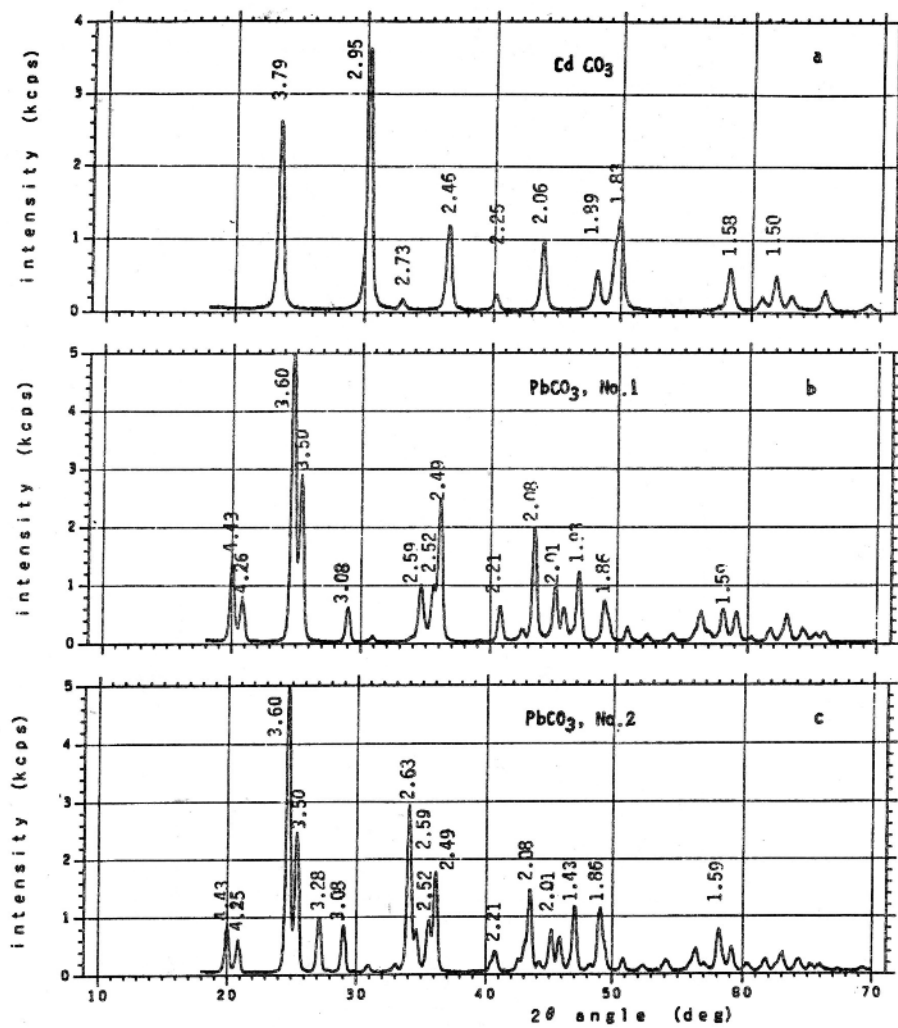


Fig. 2. XRD diagrams and "d" values for: (a) the  $\text{CdCO}_3$  sample, (b)  $\text{PbCO}_3$  sample No. 1, and (c)  $\text{PbCO}_3$  sample No. 2.

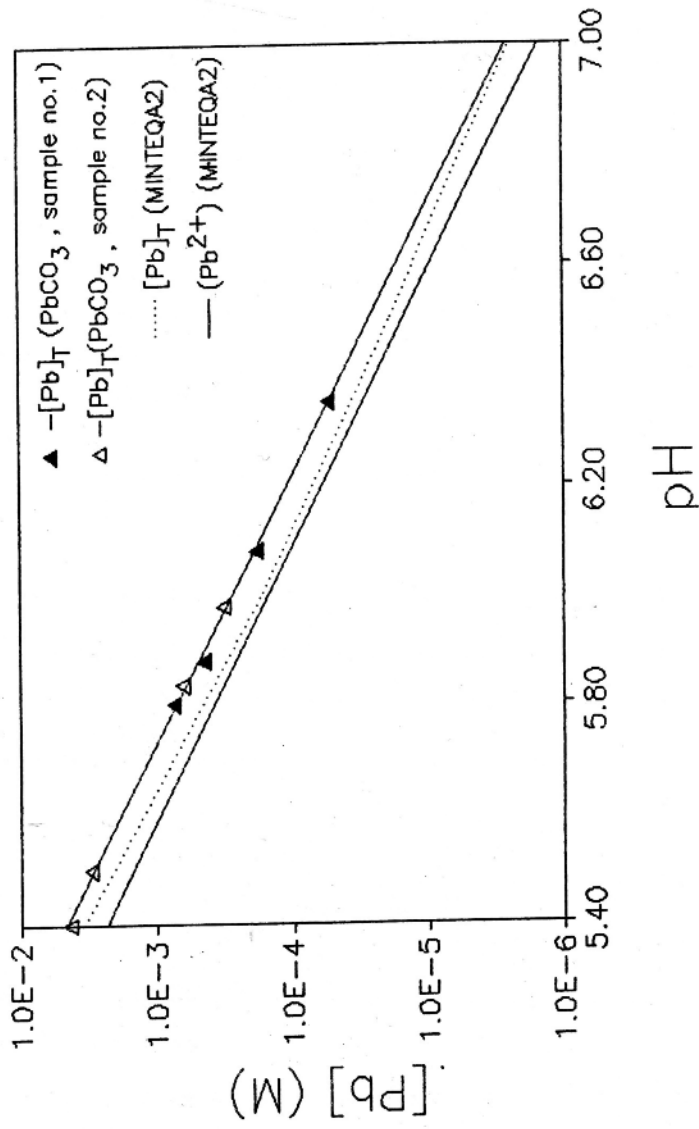


Fig. 3. Solubility of  $\text{PbCO}_3$  as a function of pH at  $\text{PCO}_2=0.0003$  atm for two  $\text{PbCO}_3$  samples.

Results of XRD analysis of the  $\text{PbCO}_3$  sample No.1 is shown in Fig.2b. The d values measured by XRD for this sample match with ASTM diffraction data for cerussite. The XRD results of sample No.2 (Fig. 2c), however, show, in addition to the peaks for cerussite, a few peaks that match the hydrocerussite  $[\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2]$  ASTM diffraction data. According to MINTEQA2 (6) hydrocerussite has a higher solubility as compared to cerussite, therefore its existence in the cerussite sample may increase the overall solubility of the mixture.

#### **Competitive Chelation Method**

Changes in Pb mole fraction ( $[\text{PbL}]/[\text{PbL}+\text{CdL}]$ ) after reacting solutions of EDTA or HEDTA with one of  $\text{PbCO}_3$  samples and  $\text{CdCO}_3$  sample are shown in Fig. 4 and 5, respectively. The equilibrium PbMF values predicted by MINTEQA2 are also included.

The final equilibrium PbMF for  $\text{PbCO}_3$  sample No.1 is 0.89 for EDTA and 0.72 for HEDTA. The equilibrium PbMF for  $\text{PbCO}_3$  sample No.2 is 0.91 for EDTA and 0.75 for HEDTA. The equilibrium PbMF obtained from MINTEQA2 output files are 0.51 and 0.44 for EDTA and HEDTA, respectively.

Table 1 summarizes the results of the competitive chelation study with three chelates (EDTA, HEDTA and DTPA). The studies with EDTA and HEDTA are from our lab and the results for DTPA (diethylenetrinitrilopentaacetic acid) were calculated from the data obtained by Workman and Lindsay (15). Table 1 also contains  $K_1$ ,  $K_2$ ,  $K_3$  and  $K_4$  values for calculation of  $\log K_{\text{SP}}$  of  $\text{PbCO}_3$  samples as explained in theory.

The large difference between equilibrium  $[\text{PbL}]/[\text{CdL}]$  ratio predicted by MINTEQA2 and experimentally determined values is consistent for all three chelates. This difference is greater for EDTA No.2 as compared to  $\text{PbCO}_3$  sample No.1. The reason for this apparent discrepancy is not quite clear. The following possibilities will be, however, considered:

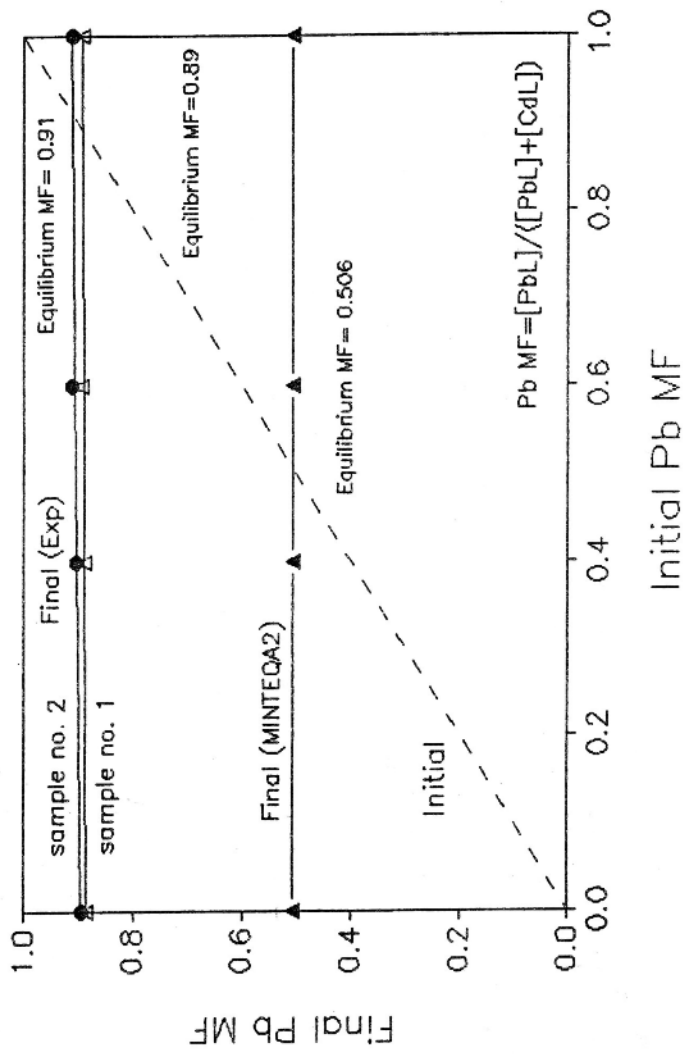


Fig. 4. Changes in PbMF after reacting EDTA solutions with CdCO<sub>3</sub> and two PbCO<sub>3</sub> samples.

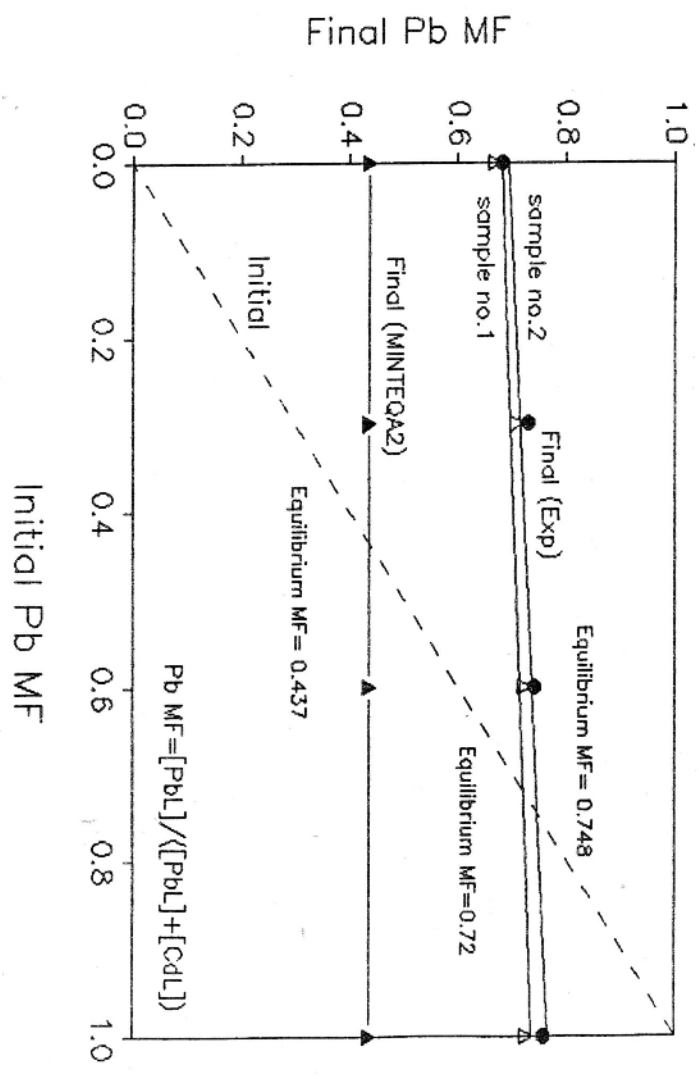


Fig.5. Changes in PbMF after reacting HEDTA solutions with CdCO<sub>3</sub> and two PbCO<sub>3</sub> samples.

Table 1.  $\log K_{sp}$  of  $PbCO_3$  samples from experimentally determined equilibrium PbMF of 3 chelating agents with  $CdCO_3$  and  $PbCO_3$ .

Predicted by MINTEQA2						Experimentally determined			
Chelate	$K_1^*$	$K_2^*$	$K_3^*$	$K_4^*$	$[PbL]/[CdL]^*$	PbCO <sub>3</sub> sample	Equilibrium PbMF	Equilibrium $[PbL]/[CdL]$	$\log K_{sp}^1$ of PbCO <sub>3</sub>
EDTA	19.59	18.07	-13.50	-11.99	1.02	1	0.89	0.89	-12.60
						2	0.91	10.11	-12.21
HEDTA	16.90	15.5	-13.50	-11.99	0.776	1	0.72	2.57	-12.98
						2	0.75	2.97	-12.92
DTPA <sup>††</sup>	20.80	21.14	-13.50	-11.99	0.014	2	0.109	0.122	-12.56



(Table 1., continued)

\*  $K_1$  and  $K_2$  stability constants at zero ionic strength for Pb and Cd with chelating ligand, Martell and Smith (9)

†  $K_3$  and  $K_4$ , Log  $K_{SP}$  of cerussite and octavite, Sadiq and Lindsay (11)

§  $[PbL]/[CdL] = 10^{(K_1 - K_2) + (K_3 - K_4)}$

@  $[PbL]/[CdL] = \frac{PbMF}{1 - PbMF}$

¶  $\log K_{SP} = \log \frac{[PbL]}{[CdL]} - K_1 + K_2 + K_4$

†† From data by Workman and Lindsay (15)

1) The  $\log K_{SP}$  value for  $CdCO_3$  (octavite) in MINTEQA2 data base may be inaccurate. This is unlikely since the results of the direct measurement of  $\log K_{SP}$  for  $CdCO_3$  indicates a very close agreement between the measured and predicted Cd total concentration.

2) The stability constants of Cd and/or Pb with EDTA, HEDTA or DTPA ( $K_1$  and  $K_2$  values) in the MINTEQA2 data base may be off. The chelate-metal formation constants in MINTEQA2 data base are taken from Martell and Smith (9). The possibility of the formation constants being off can not be ruled out, however, it is unlikely that the stability constants of all three chelating agents with both metals are off in the same direction. Workman and Lindsay (15) found similar discrepancy when they equilibrated DTPA with the  $PbCO_3$  samples from their lab. They attributed this difference to the inaccuracy of the published stability constants ( $K_1$  and  $K_2$ ) of DTPA with Pb and Cd. Our results, however, show that the discrepancy is more likely due to an inaccurate  $\log K_{SP}$  for added  $PbCO_3$ .

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3) The  $\log K_{SP}$  value for  $PbCO_3$  (cerussite) in MINTEQA2 data base, chosen from Sadiq and Lindsay (11) compilation may be too low. This possibility is very likely because the  $\log K_{SP}$  of  $PbCO_3$  calculated from  $\Delta G_f^\circ$  values reported in literature (4, 14, 16) ranges from -13.46 to -12.79, the  $\log K_{SP}$  measured in the direct method was -13.33 and the  $\log K_{SP}$  values calculated from the results of the competitive chelation experiment (Table 1) range from -12.98 to -12.51. All these values are consistently larger than -13.51 used in several publications (2, 8, 15) and in the MINTEQA2 data base.

4) The  $PbCO_3$  samples used in this study were not pure cerussite. This possibility is true for sample No.2. The XRD results of this sample (Fig. 2c) show some additional peaks, as compared to Fig. 2b and as compared to the ASTM XRD data, which could be attributed to hydrocerussite. The results of competitive chelation method (Fig. 4 and 5) consistently show a slightly higher solubility for  $PbCO_3$  sample No.2 as compared to sample No.1. It is, therefore, possible that the solubility of Pb in the sample No.1 was governed by cerussite and in sample No.2 by hydrocerussite. The difference between the solubility of these two mineral is too small to be picked up in the direct method.

The consistent and higher experimentally determined  $[PbL]/[CdL]$  ratio for all three chelates indicates that  $PbCO_3$  samples are more soluble than predicted from its  $\log K_{SP}$  of -13.50. An average value of -13.33 from the direct method and a mean value of -12.75 from the chelation method was obtained for  $K_{SP}$  of cerussite in this study.

The chelation method is independent of pH, ionic strength and partial pressure of  $CO_2$  (Eq.7) while the direct method is very sensitive to all these factors specially pH (Eq.9) which makes it less reliable as compared to the chelation method. The average  $K_{SP}$  value obtained from the chelation method is, therefore a more accurate value and agrees better with -12.83 reported by Wagman *et al.* (14).

## CONCLUSION

Competitive chelation method may be used to determine or examine  $K_{SP}$  of some minerals and has the advantage of being independent of pH, ionic strength and other chemical conditions of the system. The  $\log K_{SP}$  of cerussite used in several research works and in MINTEQA2 data base is not accurate, the accurate value is probably higher up to one unit. Based on the results of this study we suggest a value of -12.75 for the  $\log K_{SP}$  of cerussite.

## LITERATURE CITED

1. Allison, J.D., D.S. Brown and K.J. Novo-Gradac. 1991. MINTEQA2 / PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 . EPA, Athens, GA.
2. El-Falaky, A.A., S.A. Abouloos and W.L. Lindsay. 1991. Measurement of cadmium activities in slightly acidic to alkaline soils. *Soil Sci. Soc. Am. J.* 55:974-979.
3. Griffin, R.A. and J.J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. *Soil Sci.* 116:26-30.
4. Karapet'yants, M.K. and M.L. Karapet'yants. 1970. Thermodynamic constants of inorganic and organic compounds. Ann. Arbor, Humphry Science Publishers, Ann. Arbor, MI.
5. Lindsay W.L. 1979. Chemical Equilibria in Soils. Wiley-Interscience, New York, NY . 449p.
6. Lindsay, W.L. and H.A. Ajwa. 1992. Use of MINTEQA2 in teaching soil chemistry. In: Chemical Speciation Symposium, San Antonio, TX, Soil Sci. Soc. Am., Madison, WI.

7. Ma, Q. and W.L. Lindsay. 1990. Divalent zinc activity in arid-zone soils obtained by chelation. *Soil Sci. Soc. Am. J.* 54:719-722.
8. Ma, Q.Y. 1991. Measurements of  $Zn^{2+}$ ,  $Fe^{3+}$ ,  $Cd^{2+}$  and  $Ni^{2+}$  activities and Franklinite solubility in soils. Ph.D. Thesis, Colorado State University, Fort Collins, Co.
9. Martell, A.E. and R.M. Smith. 1974. *Critical Stability Constants*. Vol. 1: Amino Acids. Plenum Press, New York, NY.
10. Sachdev, P., W.L. Lindsay and D.L. Deb. 1992. Activity measurements of zinc in soils of different pH using EDTA. *Geoderma* 55:247-257.
11. Sadiq, M. and W.L. Lindsay. 1979. Selection of standard free energies of formation for use in soil chemistry. *Tech. Bull.* 134, Colorado State Univ. Exp. Sta.
12. Santillan-Medrano, J. and J.J. Jurinak. 1975. The chemistry of lead and cadmium in soil: Solid phase formation. *Soil Sci. Soc. Am. Proc.* 39:851-856.
13. Vlek, O.L.G., T.J.M. Blomm, J. Beek, and W.L. Lindsay. 1974. Determination of the solubility product of various iron hydroxides and Jarosite by the chelation method. *Soil Sci. Soc. Am. Proc.* 38:429-432.
14. Wagman, D.D., W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailery, K.L. Churney and R.L. Nuttall. 1982. The NBS tables of chemical thermodynamic properties : Selected values for inorganic and C1 and C2 organic substances in SI units. *J. Physic. and Chemic. Ref. Data*, 11, supplement No.2, 392 p.
15. Workman, S.M. and W.L. Lindsay. 1990. Estimating divalent cadmium activities measured in arid-zone soils using competitive chelation. *Soil Sci. Soc. Am. J.* 54:987-993.
16. Woods, T.L. and R.M. Garrels. 1987. *Thermodynamic values at low temperature for natural inorganic materials: An uncritical summary*. Oxford Univ. Press, Oxford, UK.