

HYDROTALCITE-LIKE MINERALS ($M_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5}\cdot X\text{H}_2\text{O}$, WHERE $M = \text{Mg, Zn, Co, Ni}$) IN THE ENVIRONMENT: SYNTHESIS, CHARACTERIZATION AND THERMODYNAMIC STABILITY

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Abstract—Hydrotalcite-like layered double hydroxides (LDH), of the formulation $M_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5}\cdot\text{H}_2\text{O}$, where $M = \text{Mg, Zn, Co, Ni}$, have been prepared, the products characterized and their solubility products measured at ionic strengths of 0.0065 and 0.0128 M and at 25°C. Steady-state solubility was reached after 100 days. The solubility products have been formulated according to the following reaction: $M_2\text{Al}(\text{OH})_6\cdot 0.5\text{CO}_3\cdot\text{H}_2\text{O} + 6\text{H}^+ \rightarrow 2M^{2+} + \text{Al}^{3+} + 0.5\text{CO}_3^{2-} + \text{H}_2\text{O}$ where

$$K_{\text{so}} = \frac{[M^{2+}]^2[\text{Al}^{3+}][\text{CO}_3^{2-}]^{0.5}}{[\text{H}]^6}$$

Average values of K_{so} for $I = 0$, estimated using the Davies equation, are 25.43, 20.80, 22.88 and 20.03 for Mg, Zn, Co and Ni, respectively. Model calculations reveal that the thermodynamic stability of the LDHs is greater than that of the corresponding divalent hydroxides for Zn, Co and Ni below a pH of ~10, 9 and 8, respectively, and at least up to pH 12 for Mg.

Key Words—Cobalt, Hydrotalcite, Magnesium, Nickel, Solubility, Zinc.

INTRODUCTION

Minerals of the hydrotalcite group have been known for ~100 years but their structure and classification had to await the development of X-ray structural crystallography. For an account relating composition and structure see Reichle (1986). Gaines *et al.* (1997) used a structural classification and recognized two mineral phases corresponding to the formula $\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$: manasseite; hexagonal, $P6_3mmc$, $a = 6.12$, $c = 15.324$ and hydrotalcite, $R3m$, $a = 6.15$, $c = 46.5$. The latter is perhaps a superstructure of the former. Gaines *et al.* (1997) noted that it is expected that other representatives of this group are yet to be discovered as natural minerals.

While the Mg/Al ratio of minerals is either 5:1 or 3:1, synthetic preparations appear to yield hydrotalcite-like phases at the 2:1 ratio (*e.g.* Thevenot *et al.*, 1989). The product which forms spontaneously in blast furnace slag-Portland cements also has ratios in the range 2:1–2.5:1 (Taylor, 1997). Consequently the synthetics, while composed of brucite-like and gibbsite-like sheets with intercalated CO_3 and H_2O , appear not to be isostructural with the natural counterparts. Hence the term, layer 'double hydroxides' (LDH), embraces both groups, although the synthetics are best described as hydrotalcite-like. While LDHs are readily recognized from

their characteristic diffractions, compositions and optical properties, exact mineralogical characterization is more difficult because of similarities in diffraction patterns even of LDHs differing in M^{2+}/M^{3+} ratio (Taylor, 1997).

Layered double hydroxides form spontaneously in a wide range of environments, *e.g.* in suspensions of clays equilibrated together with heavy metal ions in the laboratory (*e.g.* Co-Al LDH, Thompson *et al.*, 1999a), in weathered bottom ash arising from combustion (Mg-Al LDH, Schweizer, 1999) or in contact zones between Mg-rich rocks and concrete (Roy *et al.*, 1991). However, there are no reliable thermodynamic data on their solubility and stability. These data are desirable because LDHs may control contaminant mobility in soils and wastes. The LDHs have a flexible structure capable of accommodating a wide range of M^{2+} and M^{3+} ions: *e.g.* Mg, Zn, Ni, Co, Fe and Cr in natural minerals and Cd, Cs, Li and Cu in synthetics, the latter finding application in the production of catalysts (*e.g.* Chisem and Jones, 1994; Vichi and Alves, 1997; Yamaoka *et al.*, 1989). Ion size appears to play an important role in stabilizing LDH structures and an ion as large as Pb^{2+} cannot form LDHs. For other cations, such as Cu^{2+} or Cd^{2+} , LDHs can be at least partially synthesized, but they are thermodynamically unstable in comparison to common solids, such as simple (hydr)oxides or carbonates, that may form in environmental systems and are, therefore, not found in nature.

This paper reviews the preparation and characterization data and presents solubility products for single phases containing Mg, Ni, Zn and Co. The data will be

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used to determine under which conditions LDHs are likely to be thermodynamically stable in environmental systems.

METHODS

Synthesis

The general procedure described by Reichle (1986) was followed. An aqueous solution of the appropriate M^{2+} and M^{3+} nitrate salts was prepared at an $M^{2+}:M^{3+}$ ratio of 2:1. This mixture was added dropwise to a basic carbonate solution containing NaOH (approximately twice the divalent and three times the trivalent cation concentration in moles) and a Na_2CO_3 solution (1.5 times the concentration of the trivalent cation). In these experiments the divalent cations chosen were Mg^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} and the trivalent cation was Al^{3+} . Approximately 0.25 mole batches of LDH were prepared in a 2 L suspension. The suspensions were kept at 70–80°C for a week and subsequently centrifuged and the supernatant solution removed. Deionized water was added, the mixture shaken and centrifuged. This washing procedure was repeated 10 times. The solids were then dried at room temperature under vacuum. Residual nitrate concentrations were determined to be 0.17, 0.4, 0.15 and 1% w/w for the Mg-, Zn-, Co- and Ni-containing minerals, respectively.

It should be noted that preliminary experiments showed that the purest solids had an $M^{2+}:M^{3+}$ ratio of 2:1 according to transmission electron microscopy (JEOL 2000X EX Temscan) and X-ray powder diffraction (Philips PW 1410) analysis. Metal hydroxide impurities were detected when the proportion of divalent and trivalent cations was significantly altered.

Characterization

Mineral d spacings were determined from XRD ($\text{CuK}\alpha$, 1.5406 Å, 45 kV, 40 mA). Surface area was determined using the Brunauer, Emmett and Teller (BET) method (Quantochrome) and infrared (IR) spectra were obtained using Biorad FTS 475.

Mineral water content was determined by thermogravimetry (Stanton-Redcroft STA 781). The temperature was increased at 10°C min^{-1} to 50, 200 and 650°C. At the last two of these temperatures, indistinct plateaux were observed. The total weight loss at 650°C was assumed to correspond to the loss of 3H₂O and 0.5CO₂ as $M_2\text{Al}(\text{OH})_6(\text{CO}_3)_{0.5}$ decomposed to MO and 0.5Al₂O₃. The weight loss not due to CO₂ was assumed to correspond to structural water. The elemental composition of the minerals was determined in duplicate by dissolution of the synthesized minerals (1 g) in concentrated HNO₃ (1, 1, 4 and 15 mL for the Mg-, Zn-, Co- and Ni-containing minerals, respectively). Analysis of Al, Mg, Zn, Co and Ni was carried out after filtration (0.45 µm, Sartorius) by atomic absorption spectrometry (AAS, Perkin Elmer 5100 PC). Carbon analyses were

carried out once using a Total Organic Carbon (TOC) Analyzer (Shimadzu, TOC-5000A) and repeated by coulometric titration (Coulometric Inc. 5011).

Determination of solubility products

All equipment was cleaned in acid solutions (1% HNO₃). A preliminary experiment (following the procedure described below) was carried out to determine the time required to equilibration using the Mg mineral. For this, 10 samples were equilibrated in a solution containing 0.83 mM Na₂CO₃ and 4 mM NaNO₃ (10 mg C L⁻¹, $I = 6.5$ mM) for 8, 37, 70, 98 and 135 days at 25°C. The duplicate samples were then filtered (0.45 µm, cellulose nitrate, Sartorius), acidified (1 mL concentrated 'Suprapure' HNO₃) and the Al concentrations determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectroflame M, Spectra, calibrated down to 20 µg L⁻¹). Single blank solutions were also prepared and treated in the same way as the suspensions for each time step. Tests were made to assess the suitability of 0.45 µm filters. It was found that there was no significant difference in results when 0.1 µm filters were used. The solution pH was not adjusted in either the preliminary or subsequent experiments.

Suspensions (10 g L⁻¹) of the LDH minerals were prepared and equilibrated in 100 mL high-density polyethylene bottles. Four suspensions of each of the Mg-, Zn-, Co- and Ni-containing minerals were prepared, equilibrated for 147 days and treated as described above. A total of 16 suspensions (4 of each) containing higher carbonate concentrations (4.16 mM Na₂CO₃ and 0.31 mM NaNO₃, NaNO₃: 50 mg C L⁻¹, $I = 12.8$ mM) were also treated as above. The equilibration time was also 147 days. Triplicate blank solutions were also prepared and treated in the same way as the suspensions.

A third set of 16 samples, prepared with the lower carbonate concentrations, was equilibrated for 147 days, then stored at 42±5°C for 37 days in order to displace the dissolved concentrations from their 25°C value without damaging the crystalline precipitate. The suspensions were then re-equilibrated at 25°C for a further 100 days. A blank solution was also prepared and treated in the same way as the suspensions. A fourth set of eight samples (duplicates), prepared with the higher carbonate concentrations, was pre-equilibrated at 25°C for 271 days, then stored at 42±5°C for 37 days and re-equilibrated at 25°C for a further 100 days.

After equilibration, the samples were filtered (0.45 µm, Sartorius). Subsequently, one portion was used for the measurement of carbonate content, measured using the TOC analyzer, and pH values. The electrode (Ross combination, Orion Model 81-72BN) was calibrated using a titration technique and a pH meter (Metrohm 713) and a titrator (Dosimat, Metrohm 665) controlled by an IBM personal computer. Standard

potentials and slopes were determined by linear regression from the calibration data over a pH range of 2 to 11, and the $\log [H^+]$ values of aqueous solutions were determined from the calibration constants. Such a calibration results in the direct determination of hydrogen ion concentration rather than hydrogen ion activity. The remaining solution (70–80 mL) was acidified (1 mL/100 mL concentrated HNO_3 , Suprapure) and later analyzed for Al and Mg using ICP-OES. Cobalt concentrations were determined by graphite furnace AAS and Zn concentrations by AAS. Nickel was determined by cathodic stripping voltametry employing a standard Metrohm method (693 VA processor, 694 VA Stand, Applications Bulletin 231/2 d) modified only with regard to the sorption step to 120 seconds.

Thermodynamic calculations

Thermodynamic equilibrium calculations were performed with the aid of the computer programs MQV40TIT (Furrer, 1995, based on MICROQL by Westall, 1986). The values were corrected for an ionic strength using activity coefficients calculated by the Davies Equation. The thermodynamic data used for the calculations are listed in Table 1.

RESULTS AND DISCUSSION

Characterization of the LDHs

The XRD spectra of the LDH minerals correspond to spectra found in the literature (*e.g.* Thevenot *et al.*, 1989; Kannan *et al.*, 1995). The d spacings listed in Table 2 show the characteristic values for hexagonal structures with symmetrical peaks assigned to the (003), (006), (110) and (113) planes and asymmetric peaks for the (102), (105) and (108) planes. The peaks of the Zn LDH are all symmetrical, indicating the high degree of crystallinity achieved. The most poorly crystalline LDHs are those of Co and Ni.

With the exception of the Co mineral, whose surface area is surprisingly low, the BET surface area reflected the degree of crystallinity, the most crystalline minerals having the lowest surface area (Table 3). The IR spectra of the minerals were similar (Figure 1). The broad peak at $\sim 3400\text{ cm}^{-1}$ can be ascribed to an O–H stretch, the peaks at ~ 1400 , 800 and $620\text{--}650\text{ cm}^{-1}$ to asymmetric stretching, out-of-plane deformation and in-plane bending of CO_3 respectively. The two peaks between 600 and 400 cm^{-1} are generally ascribed to $M\text{--Al--O}$ stretching and bending and $M\text{--O}$ stretching (Kannan *et al.*, 1995).

Table 1. Thermodynamic data used in calculations for $I = 0\text{ M}$ and $T = 25^\circ\text{C}$. Hydrolysis reactions are represented as $M^{2+} + H_2O = M(OH)^+ + H^+$.

		Aqueous species			Solids	K_{so}
		OH	CO_3	HCO_3		
Mg	MX	-12.7^a	3.15^a	11.33^a	$Mg(OH)_2$	16.85^a
					$Mg_2Al(OH)_6 \cdot 0.5CO_3$	25.43^d
Zn	MX	-8.96^b	4.8^c	12.53^c	$Zn(OH)_2$	12.45^a
	MX ₂	-16.9^b			$Zn_2Al(OH)_6 \cdot 0.5CO_3$	20.80^d
	MX ₃	-28.4^b				
	MX ₄	-41.2^b				
Co	MX	-9.65^b	4.41^c	12.53^c	$Co(OH)_2$	12.52^a
	MX ₂	-18.8^b			$Co_2Al(OH)_6 \cdot 0.5CO_3$	22.88^d
	MX ₃	-31.5^b				
	MX ₄	-46.3^b				
Ni	MX	-9.86^b	4.83^c	12.55^c	$Ni(OH)_2$	11.02^a
	MX ₂	-19.0^b			$Ni_2Al(OH)_6 \cdot 0.5CO_3$	20.03^d
	MX ₃	-30.0^b				
	MX ₄	-44.0^b				
Al	MX	-4.97^b	8.43^b		$Al(OH)_3$	8.50^a
	MX ₂	-9.30^b				
	MX ₃	-15.0^b				
	MX ₄	-23.0^b				
H	Carbonate					
	HX	10.33^a				
	H ₂ X	16.68^a				

The references are:

^a Smith and Martell (1976)

^b Turner *et al* (1981)

^c Fouillac and Criaud (1984)

^d this work, average value from Table 4

Table 2. X-ray data for the LDHs.

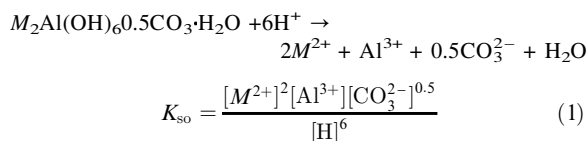
Mg		Zn		Co		Ni	
<i>d</i> Å	Intensity	<i>d</i> Å	Intensity	<i>d</i> Å	Intensity	<i>d</i> Å	Intensity
7.563	100	7.563	100	7.499	100	7.563	100
3.801	67	3.786	50	3.770	45	3.786	50
3.153	6	2.644	7	2.644	9	2.564	23
2.592	27	2.592	46	2.592	13	2.292	13
2.578	24	2.404	8	2.287	8	1.941	10
2.309	13	2.292	32	1.937	7	1.884	11
1.969	10	2.058	5	1.535	12	1.512	16
1.523	20	1.941	24	1.503	14	1.484	16
1.492	18	1.892	4	1.419	6	1.404	8
1.416	6	1.728	9				
		1.631	7				
		1.537	13				
		1.506	15				
		1.461	5				
		1.423	7				
		1.386	3				

Thermogravimetric measurements indicated that one water molecule per formula weight was bound in the crystalline structure (Table 3). The elemental analyses of the LDHs showed that the ratio of M:Al:CO₃ was ~2:1:0.5 in all cases. The relatively large error in the Co and the Ni contents was due to the difficulty in dissolving these minerals in concentrated acid. Large quantities of acid were required and this resulted in elevated blank values. However, it is possible that relatively amorphous (hydr)oxides of these elements had formed, but were not detected by XRD. The relatively small concentrations of all above-mentioned components in the Mg LDH are an indication of an elevated moisture content.

Solubility products

It took ~100 days to achieve steady-state solubilities, as preliminary experiments with Mg LDH showed (Figure 2). The samples were thus equilibrated for at least 147 days under the experimental conditions

described above. The values of the solubility products are given in Table 4. The solubility products have been formulated according to the following reaction:



All values are listed because, despite very careful work, there were significant differences in the calculated solubility products determined at the different ionic strengths. The influence of time or temperature upon solubility is not so clear. One of the most sensitive parameters is the measurement of pH because it enters in the solubility product to the power 6 and it is possible that small errors in the numerical values of this parameter were the cause of the variation of the results.

Table 3. Mineral characteristics of LDHs used.

Parameter	Mg	Zn	Co	Ni
BET surface area (m ² g ⁻¹)	53.9	22.2	23.3	97.8
Crystal water, mol/mol LDH	0.9	0.9	0.7	1.1
Elemental content, mol/mol LDH (standard deviation)				
Al	0.84 (0.12)	0.93 (0.04)	1.07 (0.16)	0.99 (0.12)
M (Mg, Zn, Co, Ni)	1.84 (0.05)	1.90 (0.04)	2.52 (0.32)	2.20 (0.18)
CO ₃	0.45 (0.02)	0.51 (0.00)	0.49 (0.00)	0.48 (0.02)
Formula weight <i>M</i> ₂ Al(OH) ₆ (CO ₃) _{0.5} ·H ₂ O	225.59	307.76	294.84	294.36

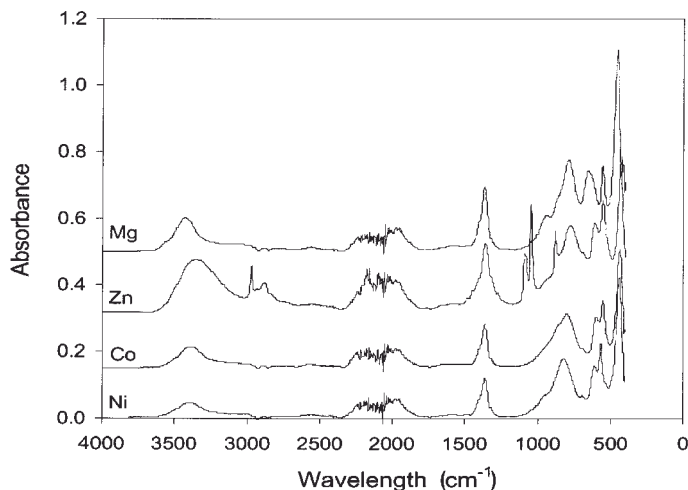


Figure 1. IR spectra of the LDH minerals.

There are few data with which to compare these results. Bocclair and Braterman (1999) report solubility products of LDH minerals $M_2Al(OH)_6Cl$ where M is Mg, Zn, Co and Ni of 20.42, 26.74, 25.56 and 26.09, respectively, for an ionic strength of 1.0. The values were obtained by the titration of solutions containing 2:1 mixtures of M :Al with base and by the linear fitting the consumption of hydroxide to pH. It is stated that up to 15 min were required for the attainment of constant pH at each titration point. Considering the differences in methodology and counter ion, the results are quite similar. Pfister (2001) obtained a solubility product of 24.40 from the supernatant of a 2:1 precipitate of a Zn-Al LDH with Cl as the anion at pH 7.5 after 10 to 14 h of equilibration. It is not practicable to contrast this K_{so} value with those obtained in the course of the title study on account of the difference in anion chemistry as well as the short equilibration times of a few hours. Thompson *et al.* (1999a) reported a solubility product for

a Co-containing LDH mineral with a Co:Al ratio of 3:1. The solubility product they obtain is 32.8 but requires 8 moles of protons instead of 6 to dissolve one mole of the LDH solid, hence differences arise in the formulation of K_{so} . They do state though, that there may be impurities in their products.

Implications for the occurrence of LDHs in the environment

The formation of the LDHs appears to be quite favorable at ambient temperature and pressure in the laboratory. The question is, under what conditions are LDH compounds likely to be formed in the environment? Understanding the stability of LDHs in relation to that of the simple hydroxides is a first step. Carbonate has a strong affinity to LDHs and its crystallochemical inclusion is believed to have a strong stabilizing action on the thermodynamic stability of the LDH phase in comparison to hydroxy LDHs (Taylor, 1997). The treatment of carbonate in thermodynamic calculations is thus critical. In Figure 3, the ionic strength was set to 0.1 M and the carbonate content to 0.001 M, which is the approximate concentration expected in an open system at ambient p_{CO_2} at pH 9. The following conditions were tested: (1) the solubility of the cations M^{2+} (where $M = Mg, Zn, Co$ and Ni) in equilibrium with their simple hydroxides assuming no Al to be present in solution; (2) the solubility of Al in equilibrium with gibbsite assuming no other metal cations to be present; (3) the equilibrium concentrations of the cations M^{2+} (where $M = Mg, Zn, Co$ and Ni) with LDH; and (4) the equilibrium concentrations of the cations in the presence of the corresponding LDH and gibbsite. The last case implies that Al is derived from a source other than the LDH. It should be noted that the model results using the LDH thermodynamic data are likely to be most accurate close to the experimental pH values at equilibrium. Depending on carbonate content, the pH ranged from

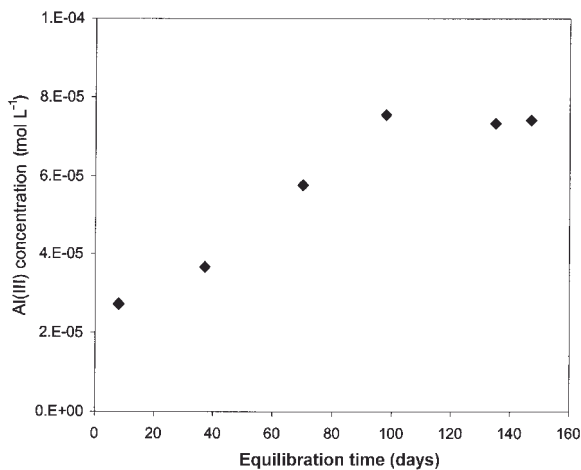


Figure 2. Concentration of Al(III) in solution as a function of time in suspensions of Mg LDH.

Table 4. Solubility products (K_{so}) of the LDH minerals corrected to $I = 0$. The experimental conditions under which the determinations were carried out are also listed.

<i>M</i>	K_{so}	sd	Ionic strength	Temperature (°C)	Time (days)	No. of replicates
Mg	24.98	0.49	0.0065	25	147	4
	24.94	0.18	0.0065	25*	284	4
	25.70	0.32	0.0128	25	147	4
	26.10	0.21	0.0128	25*	411	2
Zn	21.95	0.46	0.0065	25	147	4
	21.09	1.21	0.0065	25*	284	4
	20.30	0.88	0.0128	25	147	4
	19.85	0.02	0.0128	25*	411	2
Co	23.89	0.38	0.0065	25	147	4
	20.92	1.03	0.0065	25*	284	4
	23.04	0.44	0.0128	25	147	4
	23.09	0.70	0.0128	25*	411	2
Ni	19.37		0.0065	25	147	4
	19.71	0.34	0.0065	25*	284	4
	20.37		0.0128	25	147	4
	20.34	0.52	0.0128	25*	411	2

* equilibrated for 147 days at 25°C, followed by 37 days at 42°C and finally, 100 days at 25°C

9.15 to 9.8 for $[CO_3]_{tot} = 0.00083$ M and 10.13 to 10.41 for $[CO_3]_{tot} = 0.0042$ M in the equilibration experiments.

Figure 3 shows calculated solubility curves as a function of pH. The model calculations reveal that the thermodynamic stability of the LDHs is greater than that of the corresponding divalent hydroxides for Zn, Co and Ni below a pH of ~10, 7 and 7, respectively. It should be noted that congruent dissolution of the LDHs is assumed

and Al precipitation is ignored. A system containing both LDH and $Al(OH)_3$ is more realistic. Below a pH range of roughly 10 to 9, Al is more likely to be precipitated as $Al(OH)_3$. However, provided the concentration of available Al is in excess of that of the bivalent cations, which in most systems it invariably is, LDHs may still form. Evidence for the LDH formation of Zn, Co and Ni in environments such as soils or wastes contaminated with heavy metals is not common.

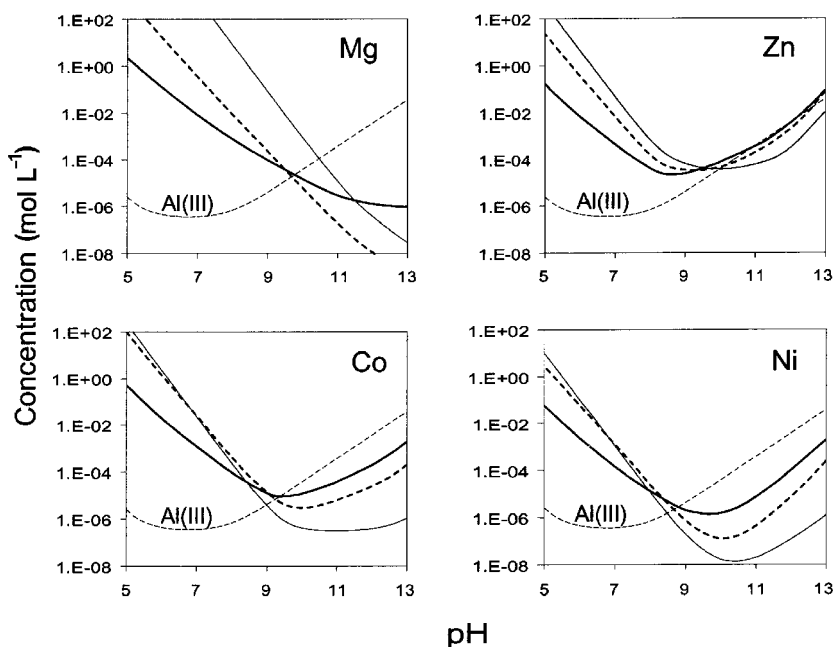


Figure 3. The solubility of Mg(II), Zn(II), Co(II) and Ni(II) at $I = 0.1$, $[CO_3]_{tot} = 0.001$ M and $T = 25^\circ C$ in equilibrium with their respective LDHs (—), hydroxides (---) and with their respective LDHs plus $Al(OH)_3$ (- · - · -) and the solubility of Al(III) in equilibrium with $Al(OH)_3$ alone (· · · ·).

However, they have been observed in laboratory experiments. The Ni LDHs are reported to have formed in cement pastes aged for 150 days (Scheidegger *et al.*, 2000) and have been observed to form at the surface of silicate minerals at pH 7.5 (Scheinost *et al.*, 1999). Cobalt LDHs have also been observed in laboratory experiments where Co was sorbed onto kaolinite at pH 4.2 for 24 h and then aged at pH 7.8 for several months (Thompson *et al.*, 1999b). Trainor *et al.* (2000) observed Zn LDH when they sorbed Zn(II) onto α -Al₂O₃ in a pH range of 7.0 to 8.2. The ageing of Zn-Al LDH precipitates in pyrophyllite-water suspensions results in more crystalline phases and it is postulated that Si may be incorporated in the interlayer leading to the transformation to a phyllosilicate-type phase (Ford and Sparks, 2000).

For Mg the LDH is the more stable form up to a pH value of at least 12. The imposition of Al(OH)₃ precipitation has the effect of increasing the solubility of LDHs in the neutral to acidic pH range, but decreasing the solubility as Al(OH)₃ dissolves under alkaline conditions. As long as sufficient concentrations of Al are available, Mg-Al LDH may form in slightly acid conditions. This mineral has been observed to form as an alteration product of synthetic glasses (Larsen *et al.*, 1991) or as the result of the interaction of alkaline solutions with rocks containing Mg (*e.g.* Roy *et al.*, 1991). The availability of Mg in rocks and soils and the pH range over which its formation is favorable is probably responsible for the fact that Mg LDH has been observed in field systems.

In natural systems a wide variation in composition is possible. As already suggested, the exchange of CO₃²⁻ for silicate may increase thermodynamic stability. Equally the solubility of LDHs may be higher in saline or highly alkaline systems: the effect of the exchangeable anion on the thermodynamic stability of LDHs also remains to be investigated. In addition, Fe(III) LDHs often appear in surficial deposits (Gaines *et al.*, 1997). Boclair and Braterman (1999) report the solubility products of LDHs with Fe in M³⁺ sites to be up to 4.5 logarithmic units lower than the equivalent Al series. Since Zn, Co and Ni solubility could be significantly affected by the formation of such LDHs, they should certainly be investigated. Finally, in many realistic situations, LDHs may contain mainly Mg²⁺ as the principal M²⁺ ion but with substituents such as Zn, Co, Ni and possibly even Cd in dilute solid solution. Where data are unavailable, and if Al is the main M³⁺ substituent, it is suggested that data for the Mg-Al LDH be used provisionally.

CONCLUSIONS

The greater thermodynamic stability of Zn, Co and Ni LDHs under investigation in comparison to the corresponding simple (hydr)oxides in the neutral pH range illustrates the potential importance of LDHs in environ-

mental systems. Magnesium-Al LDH is thermodynamically more stable than brucite at least up to pH 12 and is likely to be ubiquitous in alkaline systems where Al is sufficiently soluble. Other, potentially more stable LDHs containing Fe in the M³⁺ sites or silicate in exchange for CO₃²⁻, are likely to have a still greater significance and should be investigated.

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