as that of the comma plates. When no R plates are present, the S propellers repel one another, and above ω ~ 200 rpm they form open lattice structures, whereas at lower rotational rates, the hydrodynamic repulsions are weak and the plates form disordered structures. In the mixed ensembles of R and S isomers, however, the S propellers occasionally participate in aggregation and attach to large aggregates of R plates, especially when the rotation of the aggregate is not resonant with the external field. The selectivity improves with decreasing viscosity of the liquid. In pure water, even the large assemblies rotate fast, and we observed that in ~50% of experiments all the S propellers remained monomers.

We have described a rationally designed dynamic system in which the aggregation of macroscopic particles is mediated by chiral vortex-vortex interactions. We found that both chirality and the energetics of the components of this system are the key variables that control the formation of extended structures. We believe that this system and others analogous to it can be used to model certain aspects of stereoselective self-assembly in molecular ensembles. Indeed, recent results of Ribo *et al.* (*16*) suggested that stereoselective aggregation of certain chiral molecules in rotating liquids could have its origin in the vortex-vortex interactions between them. We also believe that our observations will stimulate research in fluid mechanics that will ultimately allow theoretical description of the forces acting between vortex patches (*17*, *18*) generated by rotating objects of complex shapes.

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15. For the typical rotational speeds ($\omega \sim 100$ to 600 rpm), particle radii ($a \sim 1$ mm), and fluid kinematic viscosities of our experiments ($\upsilon \sim 0.1$ cm^2/s), the Reynolds numbers on the scale of the rotating particles ($Re = \omega a^2/\upsilon$) were between 1 and 5.
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Thermochemistry and Aqueous Solubilities of Hydrotalcite-Like Solids

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Hydrotalcites are used in technology as catalysts and anion exchangers and are important sinks for environmental contaminants. Their compositional variability makes it important, but difficult, to estimate their aqueous solubility. We report calorimetric measurements of the heats of formation of cobalt-aluminum hydrotalcite phases. The heat and free energy of formation from the elements are equal to those of mechanical mixtures of binary compounds, namely hydroxides and carbonates. The interlayer anion is much more important than the cation in determining the solubility of the hydrotalcite phase and its ability to contain or release heavy metals to the environment. Because hydrotalcites do not have an unreactive polymer as a structural core, their aqueous stability will change dramatically with composition, particularly with anion content. This simple mechanical mixture model allows prediction of aqueous solubilities and trace metal retention in a variety of geochemical settings.

In 1995, d'Espinose de la Caillerie (*1*, *2*) showed that the uptake of divalent metals by aluminum (hydr)oxide minerals was commonly due to precipitation of hydrotalcite-like minerals and not to the formation of an adsorbate surface complex as previously thought. These results are now confirmed and extended (*3*–*8*) and are important to geochemistry because predictions of total metal concentrations in aquifers usually rely on the calculated solubilities of minerals with fixed composition in the natural water. The mineral phases considered are usually simple hydroxides, carbonates, sulfates, and so forth, for which thermodynamic data are available. Solids of variable composition, like those of the hydrotalcite class, are usually ignored because accurate thermodynamic data are missing or difficult to acquire (*9*). Because the rates of metal migration in soil and their bioavailability are usually proportional to the equilibrium concentration, it is important to identify trace mineral phases that might exert a disproportionate effect on the equilibrium metal concentration. Particularly important are minerals that reduce the total concentration of the dissolved metal in solution relative to equilibrium with simple phases, because these reactions directly influence our assessments of environmental safety.

Hydrotalcites have the general stoichiometry: $\mathrm{M(II)}_{1-x}\mathrm{M(III)}_x\mathrm{(OH)}_2[\mathrm{A}^{n-}]_{x/n}\cdot m\mathrm{H_2O}$ and a structure composed of positively charged brucite-type metal-hydroxide layers intercalated with anions [A^{n-}] and water molecules. The structures accommodate a number of cations, including Mn^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Al^{3+}, Fe^{3+}, Cr^{3+}; interlayer anions such as $\mathrm{CO_3}^{2-}$, $\mathrm{NO_3}^{-}$, Cl^{-}, and $\mathrm{SO_4}^{2-}$; and varying amounts of water (*5*, *10*). Thermodynamic data are not available because hydrotalcites exhibit wide compositional variations, are disordered, and readily exchange anions. A means of estimating thermodynamic data for many such compounds based on measurements for only a few would be very useful.

As a first step in obtaining thermochemical data and devising a systematic thermodynamic model, we measured enthalpies of for-

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mation of three cobalt-aluminum hydrotalcites: $Co_{0.68}Al_{0.32}(OH)_2\ (CO_3)_{0.16}\cdot 0.779H_2O$ (HT-1), $Co_{0.756}Al_{0.244}\ (OH)_2\ (CO_3)_{0.122}\cdot 0.805H_2O$ (HT-2), and $Co_{0.756}\ Al_{0.244}(OH)_2(CO_3)_{0.1202}(NO_3)_{0.0018}\cdot 0.810H_2O$ (HT-3), using high-temperature oxide-melt solution calorimetry (*11*). We chose the cobalt-aluminum materials because of their straightforward synthesis, their well-defined oxidation state [only Co(II)], the importance of ^{60}Co as a radionuclide, and some previous characterization (*5*–*8*). The drop-solution experiment consisted of dropping 15-mg pellets of the compound at room temperature into a molten lead-borate solvent ($2PbO\cdot B_2O_3$) at 973 K in a twin Calvet microcalorimeter (*11*, *12*). The samples dissolved to form a dilute solution of oxides (CoO and Al_2O_3) and evolved gaseous H_2O and CO_2 (*13*). Using appropriate thermochemical cycles, we calculated the enthalpies of formation of each compound from the oxides ($\Delta_f H^{ox}$), from mixtures of hydroxide and carbonate components ($\Delta_f H^c$), and from the elements ($\Delta_f H^\circ_{298}$) (Table 1).

The enthalpies of formation from hydroxide and carbonate components are between zero and –10 kJ/mol for the two pure hydrotalcites that contain carbonate in the interlayer (Table 1). This small value leads us to propose that, in general, thermodynamic properties can be estimated by treating hydrotalcites as a mixture of structurally similar binary compounds. For example, for a phase having the stoichiometry: $M(II)_{1-x}Al_x\ (OH)_2(CO_3)_{x/2}\cdot mH_2O$, the enthalpies and Gibbs free energies of formation from the elements ($\Delta_f H^\circ_{298}$ and $\Delta_f G^\circ_{298}$) can be estimated as a weighted sum of the components:

$$\Delta_f H^\circ_{298} = \Delta H_{\mathrm{HTlc}} = \frac{x}{2}\,\Delta H_{\mathrm{MCO_3}} + x\Delta H_{\mathrm{Al(OH)_3}} + \left(1 - \frac{3}{2}x\right)\Delta H_{\mathrm{M(OH)_2}} + m\Delta H_{\mathrm{H_2O}} \quad (1)$$

$$\Delta_f G^\circ_{298} = \Delta G_{\mathrm{HTlc}} = \frac{x}{2}\,\Delta H_{\mathrm{MCO_3}} + x\Delta G_{\mathrm{Al(OH)_3}} + \left(1 - \frac{3}{2}x\right)\Delta G_{\mathrm{M(OH)_2}} + m\Delta G_{\mathrm{H_2O}} \quad (2)$$

with the $M(OH)_2$ having the brucite structure, $Al(OH)_3$ having the gibbsite structure, and MCO_3 having the calcite structure.

In making this approximation, we ignore contributions to the $\Delta_f H^\circ_{298}$ and $\Delta_f G^\circ_{298}$ that are less than 5 kJ/mol, because these are smaller than experimental uncertainties. The entropy of these reactions can be considered to arise mainly from configurational entropy resulting from cation (Co and Al) disorder. The entropy contribution ($T\Delta S$) term at 298 K from such disorder would be about –2 kJ/mol. Positive excess Gibbs energies of mixing above 5 kJ/mol would cause a miscibility gap in the hydrotalcite minerals at room temperature (which is not seen in synthetic samples). Thus, we ignore deviations from ideality of this magnitude or smaller. We show that small changes in the composition of the anion in the hydrotalcite interlayer region exert an enormous effect on the solubility, much greater than could arise from 10 kJ/mol uncertainties in Gibbs energies of formation. Furthermore, when assessing the usefulness of such a prediction, it is important to consider the reliability of other thermodynamic measurements or estimates for complex phases. For example, few free energies of reaction ($\Delta_{rxn}G^\circ_{298}$) obtained from clay mineral solubilities are known to within ±10 kJ/mol (*14*, *15*). Such $\Delta_{rxn}G^\circ_{298}$ values are commonly determined by solubility experiments in which equilibrium is difficult to achieve and reversibility is not always demonstrated (*15*, *16*). Thus, the mechanical-mixture model proposed here for calculating $\Delta_{rxn}G^\circ_{298}$ values is simple, thermodynamically reasonable, and useful.

The mechanical-mixture approach is justified on the atomistic scale because the metal and anion coordination environments in the hydrotalcite are structurally similar, and therefore probably energetically similar, to those in the simple minerals used as components. The binary hydroxides and carbonates have layered structures. They combine to form a new ternary layered material, hydrotalcite, in which cations are located in a layer similar to that in their binary precursors, and the anions are located above or below these planes. Thus, the reactants (the hydroxide and carbonate) and the products (hydrotalcite) are structurally similar.

Compared to other complex ion-exchangeable minerals (clays, zeolites, and manganese- or uranium-oxide based phases), the hydrotalcites are unique in that all their constituents (divalent and trivalent cations and anions) are exchangeable with no sparingly soluble and relatively strongly bonded framework remaining intact and largely determining the solubility. Thus, one may expect the solubility of the hydrotalcite to be much more strongly affected by the nature of each of the exchangeable species. This is confirmed by the following solubility calculations.

With the approximations above, the estimated concentration of Co(II) in the aqueous solution in equilibrium with a hydrotalcite mineral of given composition is given by the weighted sum of the solubilities of each end member compositions. Using Eq. 2 to get the $\Delta_f G^\circ_{298}$ values for the pure hydrotalcite phases, the $\Delta_{rxn}G^\circ_{298}$ values for:

$$M(II)_{1-x}\ M(III)_x(OH)_2(CO_3)_{x/2}\cdot mH_2O + 2H^+\ (aq) = (1 - x)M^{2+}\ (aq) + xM^{3+}\ (aq) + \frac{x}{2}CO_3^{2-}\ (aq) + (m + 2)H_2O\ (1) \quad (3)$$

and hence the solubilities are easily calculated.

The usefulness of this approach is evident in calculations that demonstrate the sensitivity of the mineral solubilities to changes in composition. In most soils, the trivalent metal (in our case aluminum) will be sparingly soluble, so we can postulate equilibrium between the hydrotalcite and the soil mineral, gibbsite [$Al(OH)_3$ (s)] (*17*). For example, a mineral with both carbonate and nitrate in the interlayer and the nominal composition: $Co_{0.8}Al_{0.2}(OH)_2(NO_3)_{0.2x}(CO_3)_{0.1(1-x)}\cdot(0.7 - 0.3x)H_2O$ has a solubility simply given as a weighted sum of contributions from the end members:

Table 1. Enthalpies of drop solution at 973 K in $2PbO\cdot B_2O_3$ and enthalpies of formation from oxides, hydroxide and carbonate (nitrate) components, and elements. Error bars are calculated as two standard deviations from the mean value.

Sample	ΔH_{ds} (kJ/mol)	$\Delta_f H^{ox}$ (kJ/mol)	$\Delta_f H^\circ_{298}$ (kJ/mol)	$\Delta_f H^c$ (kJ/mol)
$Al(OH)_3$ (gibbsite)	184.56 ± 0.97	−31.46 ± 1.12	−1293.34 ± 1.30	
β-$Co(OH)_2$	147.16 ± 1.8	−20.93 ± 1.98	−544.70 ± 2.35	
$CoCO_3$	203.66 ± 0.73	−114.36 ± 1.10	−745.82 ± 1.68	
$Co(NO_3)_2$	484.5 ± 4.9*		−420.5†	
CoO	57.23 ± 0.84		−237.94 ± 1.255‡	
α-Al_2O_3	108.62 ± 0.99		−1675.7 ± 1.3‡	
CO_2			−393.51 ± 0.13‡	
H_2O			−285.83 ± 0.042‡	
HT-1	226.98 ± 1.24	−42.80 ± 1.50	−1044.17 ± 2.54	−5.05 ± 2.86§
HT-2	228.50 ± 1.25	−43.51 ± 1.42	−991.79 ± 1.72	−9.78 ± 2.07§
HT-3	226.31 ± 2.94		−967.89 ± 3.33	−13.64 ± 3.13‖

*Calculated from the following reaction: $Co(NO_3)_2\ (s) + Na_2CO_3\ (s) \rightarrow 2NaNO_3\ (s) + CoCO_3\ (s)$. †See (*14*). ‡See (*20*). §Calculated from the following reaction: $(1\text{–}3/2x)Co(OH)_2 + xAl(OH)_3 + x/2CoCO_3 + mH_2O \rightarrow Co_{1-x}Al_x(OH)_2(CO_3)_{x/2}\cdot mH_2O$. ‖Calculated from the following reaction: $0.634Co(OH)_2 + 0.244Al(OH)_3 + 0.1202CoCO_3 + 0.0018Co(NO_3)_2 + 0.710H_2O \rightarrow Co_{0.756}Al_{0.244}(OH)_2(CO_3)_{0.1202}(NO_3)_{0.0036}\cdot 0.710H_2O$.

$$\mathrm{Co_{0.8}Al_{0.2}(OH)_2(NO_3)_{0.2x}(CO_3)_{0.1(1-x)} \cdot (0.7 - 0.3x)H_2O\ (s)] + 1.4H^+\ (aq) + 0.6\mathit{H_2}O\ (1) = 0.2Al(OH)_3\ (s) + 0.8Co^{2+}\ (aq) + 0.1(1-x)CO_3^{2-}\ (aq) + 0.2xNO_3^-\ (aq) + (2.7 - 0.3x)H_2O\ (1)} \quad (4)$$

where x is the mole fraction of the nitrate-bearing hydrotalcite component. The variation in equilibrium constant ($\log K_4$) for this reaction with respect to x is shown in Fig. 1. If instead, Ni(II) is substituted for Co(II), the reaction is equally as direct:

$$\mathrm{(Ni_xCo_{1-x})_{0.8}Al_{0.2}(OH)_2(CO_3)_{0.1} \cdot 0.7H_2O\ (s) + 1.4H^+\ (aq) + 0.6H_2O\ (1) = 0.8(1 - x)Co^{2+}(aq) + 0.8xNi^{2+}\ (aq) + 0.2Al(OH)_3\ (s) + 0.1CO_3^{2-}\ (aq) + 2H_2O\ (1)} \quad (5)$$

where x represents the mole fraction of Ni(II) substituted in the hydrotalcite.

In both cases, the equilibrium constant increases exponentially (free energy changes linearly) with the substitution (Fig. 1). However, the change in solubility as Ni(II) substitutes for Co(II) exerts a relatively minor effect (less than one order of magnitude), whereas the effect of substitution of NO_3^- for CO_3^{2-} in an otherwise similar hydrotalcite structure is over two orders of magnitude. The ready exchange of anions in the hydrotalcite structure, one of the few phases in which this is possible, makes the anion chemistry of this phase, and of the coexisting aqueous solution, important in determining the solubility and hence the equilibrium concentration of the divalent metal. Calculations for Mg-Al, Zn-Al, Ni-Al, and Co-Al hydroxycarbonates predict equilibrium constants of 10^7 to 10^{11}. Thus, phases with multiple types of divalent cations, as have been observed (*18*), are predicted to be possible equilibrium phases.

Although the exact values of equilibrium constants may be somewhat different when one does detailed calculations, the major thermodynamic driving force is the free energy of formation, which differs somewhat for hydrotalcites containing different cations and widely for those containing different anions. The absence of an insoluble framework (e.g., aluminosilicate) makes hydrotalcite solubility much more sensitive to aqueous chemistry than is the solubility of minerals such as clays. This point may be important for the storage of contaminants as hydrotalcite phases in soil.

In natural systems, the major hydrotalcite phase is a magnesium-aluminum hydroxycarbonate. The distribution of heavy metals between the hydrotalcite and aqueous solution is governed by the stability of the end member (e.g., Pb, Co, Zn, or Ni) hydrotalcites, the thermodynamics of solid solutions, and the aqueous thermodynamics. Because the deviations from ideal mixing in both the solid and the aqueous phases are small compared to the large differences in free energies of the end members, the calculations here are directly applicable to the partitioning of trace metals between aqueous and solid phases.

These results have several important implications for environmental geochemistry. First, they indicate that the acquisition of experimental thermodynamic data for hydrotalcite minerals from aqueous solubility studies will be difficult because small amounts of carbonate contamination will affect the solubility. Second, trace amounts of hydrotalcite phases may play a key role in controlling the concentrations of metal contaminants in natural waters (*1*, *2*). Consider radioactive ^{60}Co, a contaminant of environmental concern. The metal concentration in equilibrium with a hydrotalcite phase is sensitive to anions in the aqueous phase that coprecipitate into the interlayer. Carbonate-bearing hydrotalcite phases may be a feasible means for sequestering toxic metals such as ^{60}Co in aqueous systems. Other anions, such as silicate and borate, can also enter the interlayer of these phases and decrease solubility further. Nitrate and sulfate entering the interlayer increase solubility. These effects can be estimated, using the mechanical-mixture model, from the thermodynamic properties of the binary silicate, borate, nitrate, and sulfate relative to the carbonate. Third, once formed, hydrotalcite phases commonly change interlayer compositions at measurable rates (complete exchange taking hours to days). Therefore, the equilibrium metal concentrations in equilibrium with a given mineral assemblage will change with time as well, as the hydrotalcite ages (*19*). The approach we outline here allows prediction of thermodynamic data for hydrotalcite phases to within 5 to 10 kJ/mol (corresponding to 1 order of magnitude in the solubility at 298 K), which can improve design calculations for the geologic storage of radioactive and metal-contaminated waste.

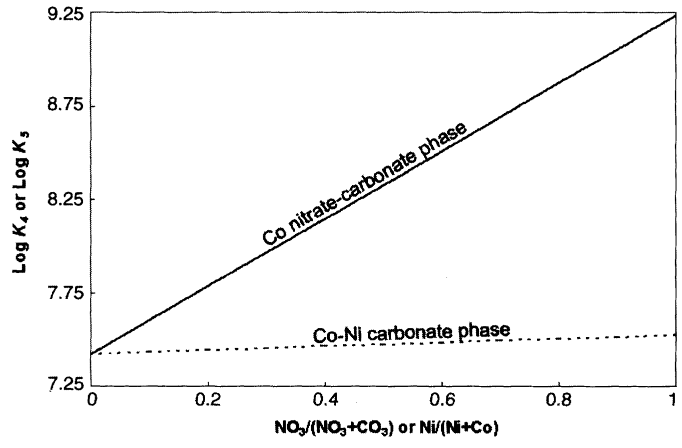

Fig. 1. Variations in the logarithm of the equilibrium constants for Eq. 4 and 5 as a function of hydrotalcite composition in neutral waters (at a pH of ~7). In both cases, the equilibrium constants vary exponentially with composition. The equilibrium constant for Eq. 5 (K_5) is affected by substituting Ni^{2+} for Co^{2+} (dashed line), and the equilibrium constant for Eq. 4 (K_4) is affected by substituting NO_3^- for CO_3^{2-} (solid line).

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