

The many ways of making anionic clays

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Abstract. Together with hydrotalcite-like layered double hydroxides, bivalent and trivalent metal hydroxides and their hydroxy salts are actually anionic clays consisting of positively charged hydroxide layers with anions intercalated in the interlayer region. The anionic clays exhibit anion sorption, anion diffusion and exchange properties together with surface basicity making them materials of importance for many modern applications. In this article, we discuss many different ways of making anionic clays and compare and contrast the rich diversity of this class of materials with the better-known cationic clays.

Keywords. Anionic clays; hydrotalcite; layered double hydroxides.

1. Introduction: Cationic clays

Cationic clays or smectite clays consist of a stacking of negatively charged aluminosilicate or magnesiosilicate layers and intercalate positive ions – primarily alkali metal ions, in the interlayer region¹. These well-known materials exhibit a number of properties such as cation diffusion and surface acidity, by virtue of which they find application as cation exchangers, sorbants and catalysts.

Smectite clays are derived from the minerals talc and pyrophyllite², which consist of a stacking of charge-neutral layers of the composition $Mg_6Si_8O_{20}(OH)_4$ and $Al_4Si_8O_{20}(OH)_4$ respectively. Each layer consists of a four-atom thick close-packing of oxide and hydroxide ions in which Si atoms occupy the tetrahedral sites on either flank (figure 1). In talc, the central plane of octahedral sites is occupied completely by Mg^{2+} ions, and in pyrophyllite, two-thirds of the octahedral sites are occupied by Al^{3+} ions.

There are two ways by which the neutral layers of these minerals can be rendered negatively charged to obtain cationic clays.

(1) By partial isomorphous substitution of Si(IV) ions by M(III) – usually Al – ions in the tetrahedral layers to give a layer composition of $[Mg_6(Si_{8-x}M^{III}_x)O_{20}(OH)_4]^{x-}$ or $[Al_4(Si_{8-x}M^{III}_x)O_{20}(OH)_4]^{x-}$.

(2) By partial isomorphous substitution of Mg(II) ions by M(I) ions (in the case of talc) or Al(III) ions by M(II) ions (in the case of pyrophyllite) in the octahedral layers to give a layer composition of $[(Mg_{6-x}M^I_x)Si_8O_{20}(OH)_4]^{x-}$ or $[(Al_{4-x}M^{II}_x)Si_8O_{20}(OH)_4]^{x-}$.

In all these cases, the negative charge is compensated for by the inclusion of positive ions in the interlayer region, by virtue of which this class of compounds is called cationic

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clays. Intercalated cations are often hydrated leading to swelling of the material. The cationic clays exhibit wide compositional flexibility with the x values ranging from 0.4 to 2. At low (0.4–1.2) values of x , the intercalated cations are exchangeable. However, when the extent of substitution is high ($x=2$) we get micas which do not exhibit cation exchange.

An alternative mechanism for generating negatively charged layers, though rare, is by creating vacancies in the cation sub-lattice within the layers. This mechanism is found in the chalcogenophosphates of divalent metals such as MPS_3 ($M = Cd, Ni$). By suitable soft chemistry these compounds can be transformed into phases of the type $Na_{2x}[M_{1-x}PS_3]$. In this compound the Na^+ ions together with their hydration spheres are intercalated between the metal-deficient chalcogenophosphate layers³. The intercalated cations can be exchanged for other simple cations, long chain alkyl ammonium ions and others.

2. Anionic clays

It would be of interest to design and synthesize anionic clays, with properties that are the exact inverse of those of the cationic clays. Such materials would consist of a stacking of positively charged layers with anions intercalated in the interlayer region together with water molecules.

The most well-known anionic clays are the hydrotalcite-like layered double hydroxides (LDHs)⁴. LDHs are derived from the structure of mineral brucite, $Mg(OH)_2$. Brucite consists of a hexagonal close-packing of hydroxyl ions in which alternate layers of octahedral sites are occupied by Mg^{2+} ions. This results in the stacking of charge-neutral hydroxide layers of the composition $[Mg(OH)_2]$, held together by van der Waal's interaction (see figure 2). Such a structure throws open the possibility of performing interesting intercalation chemistry similar to that observed in the cationic clays. However, $Mg(OH)_2$ is not known to exhibit any interlayer chemistry.

When a fraction, x , of the Mg^{2+} ions in brucite is substituted by trivalent cations such as Al^{3+} , the resultant hydroxide layers having the composition $[Mg_{1-x}Al_x(OH)_2]^{x+}$ acquire a positive charge and intercalate various anions, A^{n-} , in the interlayer region. This results in the expansion of the c -parameter from 4.8 Å seen in brucite to 7.6 Å observed in hydrotalcite ($x=0.25$, $A^{n-} = CO_3^{2-}$)⁴. Materials of this type exhibit anionic (hydroxyl ion) mobility⁵, anion exchange and sorption properties⁶ in addition to surface basicity, making them attractive catalysts for base-catalysed reactions⁷.

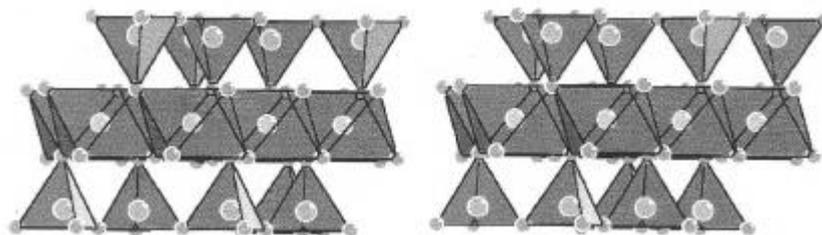


Figure 1. Schematic representation of a layer of mineral pyrophyllite/talc.

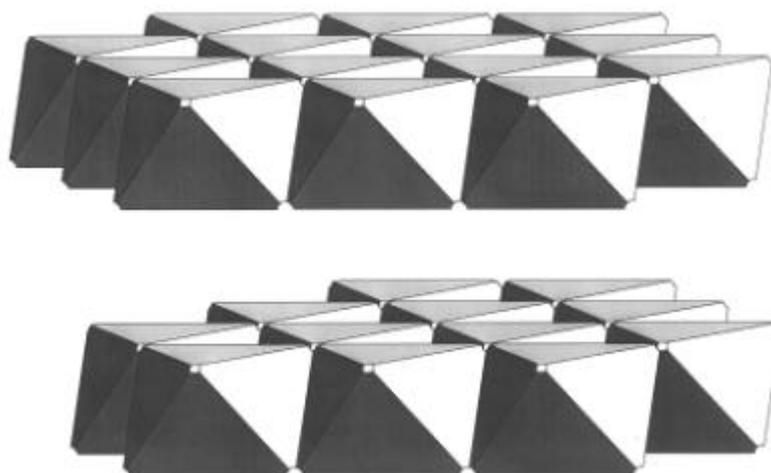


Figure 2. Schematic representation of the structure of the mineral brucite.

3. Brucite-based anionic clays

Considering the importance of this class of materials, it would be useful to explore the different chemical means by which a positive charge can be imparted to a brucite-like hydroxide layer. We list below a number of mechanisms, each of which leads to a different class of materials. Many of these have not been recognised as anionic clays although they exhibit many structural and functional features of clays. These mechanisms may be classified into two broad categories as below.

3.1 *Involving the modification of the hydroxyl sub-lattice*

(1) By the creation of hydroxyl vacancies, positively charged metal hydroxide layers of the composition $[M(OH)_{2-x}]^{x+}$ can be obtained. The vacancies are made good by the direct ligation of the anions to the metal ion, a mode of bonding known as “grafting”⁸. This results in layered compounds having the general formula $[M(OH)_{2-x}][A^{n-}]_{x/n}$ (see figure 3), which are otherwise known as basic salts. Illustrative examples of this class of compounds are the basic salts of Ni, such as $Ni(OH)(NO_3)$, $Ni_3(OH)_4(NO_3)_2$ and $Ni_2(OH)_3(NO_3)$, which correspond to $x = 1, 0.66$ and 0.5 respectively⁹. Basic salts of Cu(II) comprising a variety of anions such as chloride, nitrate, sulphate and others have been prepared and shown to exhibit anion exchange properties¹⁰. The basic salts of Co(II) have also been shown to intercalate large organic anions similar in character to the pillared clays¹¹.

(2) By partial protonation of the hydroxyl ions in keeping with the equilibrium



positively charged layers of the hydrated hydroxide can be generated. These layers intercalate anions to yield compounds of the type $[M^{II}(OH)_{2-x}(H_2O)_x][A^{n-}]_{x/n}$. The *a* hydroxides of Ni(II)¹² and Co(II)¹³ are the best examples of this class of materials. The *a* hydroxides can be synthesized under hydroxyl deficient conditions of moderately

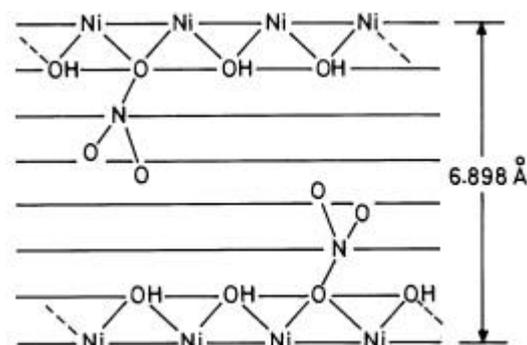


Figure 3. Schematic representation of the structure of a basic salt of Ni.

alkaline pH (8–9), by the addition of strong alkali or ammonia. A variety of anions ranging from Cl^- , NO_3^- , CO_3^{2-} to long chain alkyl carboxylates can be incorporated¹⁴.

3.2 Involving the modification of the cation sub-lattice

(1) Partial isomorphous substitution of the divalent ions of the brucite-like hydroxide by a trivalent cation yields positively charged layers of the composition $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$ which intercalate anions to yield hydrotalcite-like LDHs of the type $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$ (see figure 4). Among all the anionic clays, these are the most extensively studied. LDHs with $M^{II} = Mg, Ca, Co, Ni, Cu, Zn$; $M^{III} = Al, V, Cr, Mn, Fe, Co, Ga, In$ and $A^{n-} =$ organic anions¹⁵, inorganic anions and polyoxometallate ions¹⁶ are described in the literature¹⁷ together with their clay-like properties. Isomorphous substitutions are generally guided by considerations of ionic size. The LDH structure is sufficiently flexible to permit the substitution of trivalent ions varying in radius from 0.67 Å (Al^{3+}) to 0.93 Å (In^{3+}) in the octahedral voids defined by the packing of hydroxyl ions. However the composition as reflected by the x value is restricted by other considerations. As x increases, the positive charge on the layer increases to compensate which the anions need to be tightly packed in the interlayer region. There are inherent limits to the number of anions that can be packed in the interlayer region, and this restricts x to the range $0.2 \leq x \leq 0.33$ ¹⁸. At values of $x < 0.2$, the anions are insufficient to pillar the layers apart causing them to buckle. This gives rise to interstratified phases in which the LDH motifs grow within the matrix of brucite-like motifs¹⁹.

(2) A related mechanism to the one described in [1] above is the partial oxidation of brucite-like divalent metal hydroxides resulting in mixed valent (the same metal being in the divalent as well as trivalent states) hydroxide layers carrying positive charge and of composition $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}$, which intercalate anions leading to compounds having the general formula $[M(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$. Such materials are obtained when $M = Co$ ²⁰ or Fe ²¹. The clay-forming ability in this class of compounds competes with the acidity of the hydroxyl proton. If the proton is acidic, the increase in positive charge resulting from metal oxidation is compensated for by the loss of an equivalent number of protons leading to the formation of metal oxide–hydroxides having the formula $MO(OH)$ instead of anion incorporation in the interlayer region. This is observed in the nickel system, where phases of the type $Ni_3O_2(OH)_4$, $Ni_5O(OH)_9$ and others are observed²². These

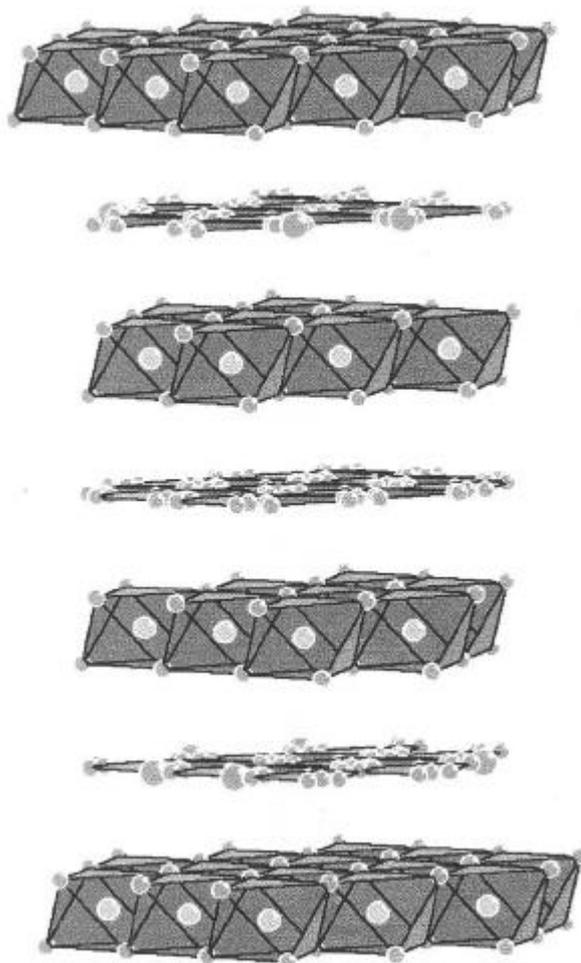


Figure 4. Schematic representation of the structure of hydrotalcite.

phases are actually partially oxidised brucite-like $\text{Ni}(\text{OH})_2$ phases and can be represented as $\text{Ni}(\text{OH})_2 \cdot 2\text{NiO}(\text{OH})$ and $4\text{Ni}(\text{OH})_2 \cdot \text{NiO}(\text{OH})$ respectively. Clearly, hydroxides with acidic protons do not form anionic clays.

(3) When the value of x in (1) above becomes 1, the limiting composition, $[\text{M}^{\text{III}}(\text{OH})_2][\text{A}^{n-}]_{1/n}$, in the LDH series is obtained. A model compound of this composition with a layered structure, $\text{La}(\text{OH})_2(\text{NO}_3)$ exists²³. Two factors affect the structure of this compound: (i) Such a high positive charge cannot be accommodated in brucite-like layers. (ii) Rare earth ions on account of their large size have a coordination higher than 6. These factors cause the layers in $\text{La}(\text{OH})_2(\text{NO}_3)$ to pucker. This puckering provides the La^{3+} ion with a tricapped prismatic coordination. The nitrate is grafted in one of the corners of the tricapped prism. Nevertheless the nitrate can be exchanged for other anions demonstrating its clay-like nature²³.

(4) Positively charged hydroxide layers can be obtained even in the absence of trivalent cations by generating cation rich layers where $n_{\text{cation}}/n_{\text{anion}} > 0.5$. This can be done by partial substitution of the octahedrally coordinated divalent cation in the brucite structure by twice the number of other divalent cations with a tetrahedral site preference, which occupy the tetrahedral sites on either sides of the octahedral vacancy. Such a substitution yields layers of the composition $[\text{M}^{\text{octa}}_{1-x}\text{M}^{\text{tetra}}_{2x}(\text{OH})_2]^{2x+}$ which then intercalate anions to yield layered hydroxides. Compounds of this type with $\text{M}^{\text{octa}} = \text{Ni}^{2+}$ and $\text{M}^{\text{tetra}} = \text{Zn}^{2+}$ with acetate anions have been synthesized and shown to participate in anion exchange reactions²⁴. We refer to these as II-II LDHs.

(5) A class of compounds related to those described in (4) above, but where the tetrahedrally coordinated cations are the same as the octahedrally coordinated ones, are also known. An illustrative example is mineral hydrozincite, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (see figure 5) which can be formulated as $[\text{Zn}^{\text{octa}}_3\text{Zn}^{\text{tetra}}_2(\text{OH})_8][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$, where $x = 0.25$ ²⁵. Tetrahedrally coordinated Zn is coordinated to three hydroxyl ions of the layer below and one water molecule of the interlayer region. These special positions of Zn^{2+} result in a thicker than usual hydroxide layer and a larger interlayer distance, 9.2 \AA for NO_3^- , compared to $\sim 8 \text{ \AA}$ observed for the same anion in related compounds. These compounds have recently been shown to exhibit anion-exchange properties²⁶.

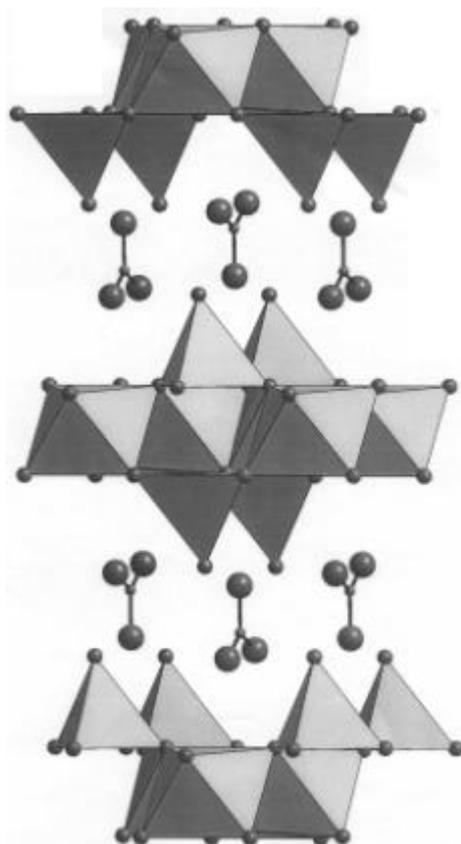


Figure 5. Schematic representation of the structure of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2$.

(6) Cation-rich hydroxide layers with more than one kind of octahedral site occupancies can be seen in another compound, $\text{Cd}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. In this compound the octahedral site vacancies in the brucite structure are compensated for by twice the number of Cd^{2+} ions which occupy octahedral sites above and below the hydroxide layer²⁷. These ions are coordinated to three hydroxyl groups in the layer below, and one water molecule and one nitrate in a bidentate manner.

4. Gibbsite-based anionic clays

Another layered hydroxide is mineral bayerite, $\text{Al}(\text{OH})_3$. Bayerite is similar to brucite except that $2/3$ of the octahedral vacancies in alternate layers of a hexagonally close-packed hydroxyl lattice are occupied by Al^{3+} ions. This results in the stacking of charge-neutral layers of composition $[\text{Al}_{2/3}\square_{1/3}(\text{OH})_2]$. The vacancies are ordered leading to tunnels parallel to the c -axis. A polymorphic modification of bayerite, with a stacking of hydroxyl ions in the pattern ABBA is also known in mineral gibbsite (see figure 6). Several anionic clay-type materials can be derived from the structure of gibbsite/bayerite.

4.1 By stuffing the vacancies

(1) The cation vacancies of the gibbsite structure can be filled by cations of a suitable size such as Li^+ to yield positively charged layers of composition $[\text{Al}_{2/3}\text{Li}_{1/3}(\text{OH})_2]^{1/3+}$. These layers intercalate anions for charge neutrality to yield a new class of gibbsite-based LDHs. A typical compound of this type is $[\text{LiAl}_2(\text{OH})_6]\text{Cl} \cdot 3\text{H}_2\text{O}$ ²⁸. We call this a I–III LDH. The Li–Al LDH participates in a variety of exchange reactions²⁹. Other I–III LDHs combining Li^+ with Cr^{3+} , Fe^{3+} , Ga^{3+} and In^{3+} can be visualised. But the authors' efforts at realizing these failed. This may be because (i) Cr and Fe do not crystallize as binary hydroxides, and (ii) $\text{Ga}(\text{OH})_3$ and $\text{In}(\text{OH})_3$ crystallise in the ReO_3 structure and

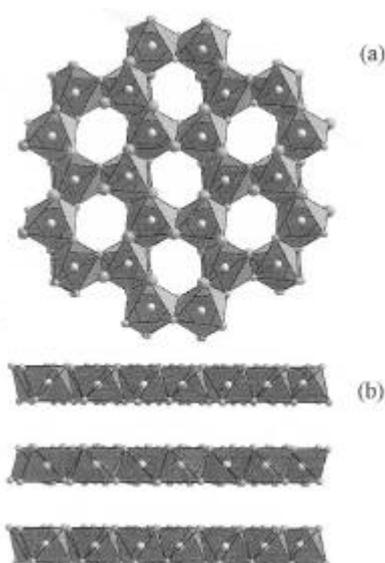


Figure 6. The structure of gibbsite viewed down the c (a) and b (b) axes.

have high solubilities in alkali, and these probably militate against the formation of I–III LDHs comprising these cations. Li–Al LDH is the only known compound in this class of materials.

(2) Although the nominal Li/Al ratio in (1) above is 0.5, it is not difficult to visualize compounds with other compositions, especially keeping in view the wide compositional flexibility of brucite-based LDHs. When the Li/Al ratio is >0.5 , a layer of composition $[\text{Li}_{1+x}\text{Al}_{2-x}(\text{OH})_6]^{(1-2x)+}$ can be formulated. The layer charge is lower than that found in the compound of the nominal composition. For $x=0.5$, charge-neutral layers of the composition $[\text{Li}_{1.5}\text{Al}_{1.5}(\text{OH})_6]$ or $\text{LiAl}(\text{OH})_4$ are obtained. While hydroxides corresponding to this composition have not been explicitly reported, there is a report of a layered hydrated oxide without anions having the formula $\text{Li}_2\text{Al}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ (PDF: 20-0618) which has been indexed to a hexagonal cell very similar to that of the Li–Al LDH. Although Li/Al ratios up to 0.58 in the Li–Al LDHs have been reported, the authors do not comment on the layer charge or its consequences³⁰.

When the Li/Al ratio is <0.5 , two possibilities arise:

- (i) The layers acquire the composition $[\text{Li}_{1-x}\square_x\text{Al}_2(\text{OH})_6]^{(1-x)+}$.
- (ii) The layers acquire the composition $[\text{Li}_{1-x}\text{Al}_{2+x}(\text{OH})_6]^{(1+2x)+}$.

In the former case, the layer charge is lower than that found in the compound of nominal composition, and in the latter, it is higher. These considerations have not been discussed in the literature. The Li–Al LDHs prepared by the authors exhibited a Li/Al ratio of 0.36³¹.

(3) The cation vacancies in bayerite/gibbsite can be occupied by higher valent cations such as Mg^{2+} or Cr^{3+} or even Al^{3+} . These ions can either (i) partially occupy the cation vacancies in gibbsite to yield a layer composition $[(\text{M}^{n+})_{1/n}\square_{1-1/n}\text{Al}_2(\text{OH})_6]^+$ or (ii) fully occupy all the vacancies to yield a layer composition $[(\text{M}^{n+})\text{Al}_2(\text{OH})_6]^{n+}$. On the basis of anion packing considerations, the latter seems unlikely, although mineral hydrocalcite having the formula, $\text{CaAl}_2(\text{OH})_4(\text{CO}_3)_2 \cdot 3\text{H}_2\text{O}$ (PDF: 42-0592) has been reported. There are other compounds with compositions $n\text{Al}(\text{OH})_3 \cdot m\text{AlCl}_3$. One of these, $\text{Al}_5(\text{OH})_{12}\text{Cl}_3 \cdot 7.5\text{H}_2\text{O}$ (PDF: 27-0011), is significant. This composition can be formulated as $[\text{Al}_{0.5}\square_{0.5}\text{Al}_2(\text{OH})_6]\text{Cl}_{1.5} \cdot 3.75\text{H}_2\text{O}$. This phase has been indexed on the rhombohedral cell (space group $R\bar{3}$) similar to the Li–Al LDH which has been indexed to a hexagonal cell²⁸. Efforts by authors to prepare LDHs of the former type with $\text{Mg}/\text{Al}=0.25$ did not result in a single-phase product.

4.2 By creating cation-rich layers

An alternative strategy is to leave the octahedral vacancies undisturbed and introduce cations with a tetrahedral site preference on either side of the octahedral vacancy to yield layers with the composition, $[(\text{M}^{\text{tetra}})_2\square\text{Al}_2(\text{OH})_6]^{2n+}$, where n is the charge of the ion. A basic sulphate with the formula $\text{Zn}_6\text{Al}_6(\text{OH})_{26}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$ is known in the literature (PDF: 41-1361), but its structure has not been described.

5. Conclusions

This article brings together a very diverse range of compounds into a single class defined by functionality. The functionality we have chosen is the exchangeability of anions. Since

most of these compounds have very similar formulae³², it is important to evolve definitions, which help to classify them in subclasses.

a) When all the crystallographically defined anion sites in the layers are occupied by hydroxyl ions, the compounds can be referred to as hydroxides. Hydroxides can be simple (comprising a single metal) or complex (comprising two or more metal ions). In the latter case, we have the (I–III), (II–III) and the (II–II) double hydroxides. In all these instances, intercalated anions merely balance the layer charge without being in the coordination sphere of the metal ion.

b) When some of the crystallographically defined anion sites in the layers are occupied by anions other than hydroxyl which are grafted to the metal, the compounds can be referred to as basic salts. Complex basic salts comprising two different cations have been referred to in the literature as hydroxy double salts (HDS)¹⁰.

These definitions do not cover all the compounds described and need further elaboration.

The exchange of anions can take place by two mechanisms:

- (i) by a purely activity driven topochemical reaction which conserves certain essential aspects of the structure between the parent and the product phase,
- (ii) by dissolution–reprecipitation, where the parent phase dissolves and reprecipitates with a different anion obtained from the solution.

While, in principle, the latter mechanism is not expected to conserve any structural relationship between the parent and product phases, in practice, the operation of Ostwald's "rule" as explained elsewhere³³, leads to crystallisation of products whose atomic positions are only slightly away from those in the parent phase. Many transformations among hydroxide materials have therefore been characterized to occur via the dissolution–reprecipitation mechanism^{31,34–35}. An unstated understanding seems to exist that while intercalated anions are exchanged topochemically, grafted ions are exchanged by dissolution–reprecipitation.

In conclusion, while the mechanisms of generating cationic clays are rather limited, there are numerous mechanisms that can be employed to synthesize anionic clays. Several minerals can be found in each variety showing that nature's laboratory has fully utilized all available mechanisms to generate a bewildering array of materials, all of which function as anionic clays.

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