

# The creation of neotypes for hydrotalcite

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## ABSTRACT

Two samples of hydrotalcite, probably worked on by Carl Christian Hochstetter, have been discovered in the Museum für Naturkunde Berlin and given neotype status by the IMA CNMNC (proposal 15-J). The two samples from Snarum, Norway, have been reanalysed and give  $\text{Mg}_{5.84}\text{Al}_{2.07}\text{Fe}_{0.09}(\text{OH})_{16}(\text{CO}_3)_{1.08}\cdot 4\text{H}_2\text{O}$  and  $\text{Mg}_{5.75}\text{Al}_{2.21}\text{Fe}_{0.04}(\text{OH})_{16}(\text{CO}_3)_{1.12}\cdot 4\text{H}_2\text{O}$ . Both samples have a mix of the two polytypes 3R/2H in the ratio of 69.2/30.8 and 69.5/30.5%. A discussion of hydrotalcite and hydrotalcite-like phase occurrences in the literature is also presented.

**KEYWORDS:** hydrotalcite, polytype, hydrotalcite supergroup, Snarum, Norway, LDH, layered double hydroxide.

## Introduction

HYDROTALCITE,  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}[\text{CO}_3]\cdot 4\text{H}_2\text{O}$ , is a common mineral and the archetype for a very large supergroup of minerals and synthetic compounds (Mills *et al.*, 2012). However, when it was first described by Hochstetter (1842), no designated type specimens for the mineral were deposited, since the ‘type’ concept (Dunn and Mandarino, 1987) was not widely adopted at the time. Given the historical difficulty of checking data accuracy when foreign languages and remote localities were involved, accounts of the discovery and documentation of old specimens can be prone to contain errors. For example, Foshag (1920) states that Hochstetter first described hydrotalcite from “the Shishimsk District in the Urals” whereas the locality was actually Snarum, Norway, and Foshag investigated a specimen in the United States Museum of Natural History (NMNH13191) that was labelled as from “Kongsberg”, Norway, whereas we have re-examined material from the same specimen and found it to be texturally and

compositionally identical to others that are known to be from Snarum. Furthermore, there is some confusion in the literature between hydrotalcite *sensu stricto* and other similar, closely related minerals. For example, the material from Věžná, Czech Republic, whose crystal structure was determined by Allmann and Jepsen (1969) was reported by them to have the composition  $\text{Mg}_4\text{Al}_2(\text{OH})_{12}[\text{CO}_3]\cdot 3\text{H}_2\text{O}$ , which would make it a 3R polytype of the mineral quintinite (Chao and Gault, 1997) rather than true hydrotalcite. In fact, there was a need to verify that material with the composition and structure assumed for hydrotalcite actually existed, as well as to locate suitable material to act as a neotype. Thus, we decided to try and track down original specimens worked on by Hochstetter. In the present study, we unravel some of the history of the original description and trace back original samples likely to have been deposited by Hochstetter.

## History

The first description of hydrotalcite by Carl Christian Hochstetter (1842) gives a complex provenance for the investigated specimens from

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Snarum, Norway, which were first given by Prof. Theodor Scheerer (1813–1875) to Dr. Richard Felix Marchand (1813–1859), who then passed the sample(s) for analysis to Hochstetter (1818–1880). The publication also mentioned that Gustav Rose (1789–1873) interpreted the chemical analysis by Hochstetter, so as to establish a chemical formula.

In the years leading up to 1842, (1) Marchand was a chemist and lecturer at the Artillereschule in Berlin (one of the precursors of the Technische Universität Berlin) and at the Friedrich-Wilhelms-Universität (now Humboldt Universität zu Berlin) (Ladenburg, 1884); (2) Hochstetter was, since 1841, a student in Berlin at the Friedrich-Wilhelms-Universität, but mainly working in the private physical laboratory of Gustav von Magnus (1802–1870) (Otruba, 1972); and (3) Gustav Rose was Professor of Mineralogy at the Friedrich-Wilhelms-Universität and curator of the Mineralogisches Museum of the Friedrich-Wilhelms-Universität under the director Christian Samuel Weiss (1780–1856) (Hoppe, 2001, 2003). Unfortunately, Hochstetter (1842) does not indicate at which laboratory or university the samples in question were analysed. Therefore, the samples could have found their way into several collections, that are today found within the mineralogical collections of the Museum für Naturkunde Berlin and the Technische Universität Berlin.

We conducted an intensive search in both collections for hydrotalcite samples that (1) were from the region and period in question, and (2) were connected directly to Scheerer, Marchand and/or Hochstetter. We found no samples in the mineralogical collection of Technische Universität Berlin (Dr. Susanne Herting-Agthe, personal communication, 4 May, 2015). Nevertheless, the mineralogical collection of the Museum für Naturkunde Berlin hosts two hydrotalcite samples from this region labelled by Gustav Rose, MFN\_MIN\_1998\_2751 from “Skutterud” and MFN\_MIN\_1998\_2758 from Snarum (Fig. 1). Both samples are of identical appearance, displaying an assemblage of hydrotalcite, serpentine and magnetite, consistent with them being from the same locality. Furthermore, the appearances of both are consistent with those of specimens from Snarum preserved in the collections of many museums. Skutterud is an amphibolite-hosted Co and Ni mine with no confirmed hydrotalcite, in which the rocks are quite different in composition and appearance. The distance between Skutterud and Snarum is only ~4 km, and it is probably the case that the locality Skutterud was better known at that time, hence the mistake. Such

historical errors are noted frequently in historical museum collections (e.g. Bridges *et al.*, 2008). There is an additional error on the label of MFN\_MIN\_1998\_2758 that gives as region “Schlesien” (Silesia), which was corrected to “Schweden” (Sweden) later by an unknown person, whose handwriting cannot be recognized. Neither label contains a date or accessioning data. In the context of labels written by Gustav Rose, this is typical for samples which were not self-collected but donated to him (based on experience during collection databasing in the mineralogical collection of the Museum für Naturkunde Berlin and accompanying provenance research). For historical reasons, the mineralogical collection of the Museum für Naturkunde Berlin has no inventory lists or books from this period available that could have been linked to these objects to give hints about their provenance.

Nevertheless, based on the reference of Gustav Rose in the publication of Hochstetter (1842) we know that Rose viewed the material analysed by Hochstetter, had discussions with him to establish the chemical formula given in the publication, and got samples from him for the collection of the Mineralogisches Museum of the Friedrich-Wilhelms-Universität.

### Comparison of hydrotalcite samples

Quantitative analyses of the two hydrotalcite samples (Table 1) were undertaken using a JEOL 6400 SEM with a Link ISIS quantification system (Oxford instruments) at the Australian National University, Canberra. Samples were mounted in an epoxy block, polished and coated with carbon. The operating conditions were: 15 kV accelerating potential, 1 nA probe current, 3 µm spot size and 100 live seconds counting time. Standards used were albite (Na, Al), MgO (Mg), sanidine (Si), pyrite (S), NaCl (Cl), diopside (Ca), Cr<sub>2</sub>O<sub>3</sub> (Cr), MnSiO<sub>3</sub> (Mn) and Fe<sub>2</sub>O<sub>3</sub> (Fe). Data are broadly consistent with the original analyses of Hochstetter (1842), although he reported 6.90 wt.% Fe<sub>2</sub>O<sub>3</sub>, which is much higher than found in this study, and may result from Fe oxide inclusions. The analytes Na, Si, S, Cl, Ca, Cr and Mn were below energy-dispersive spectroscopy detection limits in these samples (0.1 wt.% for most elements, 0.3 wt.% for Na<sub>2</sub>O), and so were excluded from the formula recalculations. The Fe content correlated positively with Mg but negatively with Al, implying Fe<sup>3+</sup> rather than Fe<sup>2+</sup>. Formulae were thus recalculated

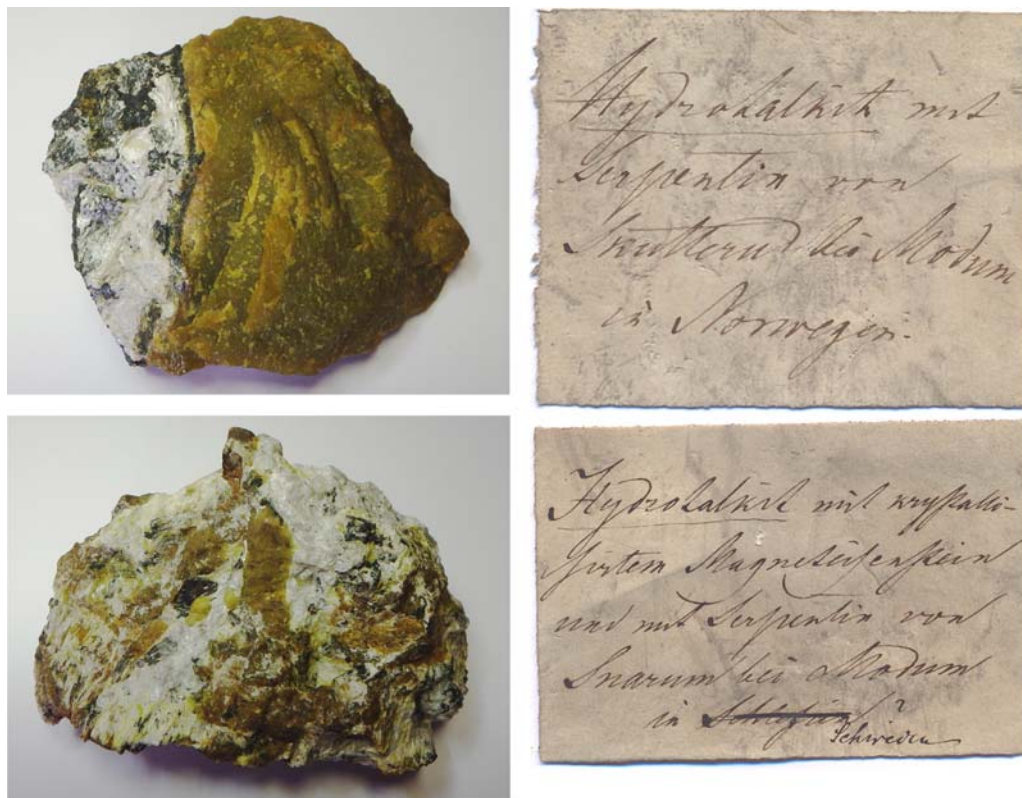


FIG. 1: (Top) Hydrotalcite specimen from “Skutterud”, Norway with label written by Gustav Rose (MFN\_MIN\_1998\_2751). (Bottom) Hydrotalcite specimen from Snarum, Norway with label written by Gustav Rose and a later change by an unknown person (MFN\_MIN\_1998\_2758).

on the basis of eight octahedral cations per formula unit, with the assumptions that (1) all Fe was ferric; (2) the positive layer charge was balanced exclusively by interlayer  $\text{CO}_3^{2-}$ ; and (3) there are 16  $\text{OH}^-$  and four interlayer  $\text{H}_2\text{O}$  per formula unit. Assumptions (2) and (3) allowed the calculation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  contents corresponding to the analysed components. Even including these components, the totals are still somewhat low (87–97 wt.%), which is unavoidable, given the relatively poor surface quality obtainable from these very soft, flexible and volatile-rich minerals.

The analyses give Mg:Al ratios which are very close to the 3:1 ratio of end-member hydrotalcite, with minor substitution towards pyroaurite ( $\text{Fe}^{3+}$  for Al) and no significant variation of  $M^{2+}:M^{3+}$  towards the 2:1 ratio characteristic of the quintinite group. It is clear that these samples are good examples of hydrotalcite, as defined in the report of Mills *et al.* (2012), and are suitable for neotype material.

### Crystallography

Minerals of the hydrotalcite group crystallize in several different polytypic varieties, which may occur as physically inseparable intergrowths (e.g. Frondel, 1941). The name ‘hydrotalcite’ applies historically to the 3R polytype; the corresponding 2H polytype was formerly known as ‘manasseite’, until this name was discredited in the nomenclature report of Mills *et al.* (2012). Crystallographically, both MFN\_MIN\_1998\_2751 and MFN\_MIN\_1998\_2758 consist primarily of hydrotalcite-3R, with a subordinate amount of the 2H polytype. Full-pattern Rietveld fitting gives a 3R/2H ratio of 69.2/30.8 and 69.5/30.5%, respectively for MFN\_MIN\_1998\_2751 and MFN\_MIN\_1998\_2758. The unit-cell parameters are:  $a = 3.05(1) \text{ \AA}$ ,  $c = 23.36(1) = 3 \times 7.79 \text{ \AA}$  and  $V = 188.04(1) \text{ \AA}^3$  for 3R and  $a = 3.07(1) \text{ \AA}$ ,  $c = 15.62(5) = 2 \times 7.81 \text{ \AA}$  and  $V = 127.85(5) \text{ \AA}^3$  for 2H. Similar intergrowths were

TABLE 1. Quantitative analyses (5 spots per sample) for hydrotalcite samples. Recalculation ignores components that were below detection limit, assumes all Fe is trivalent, calculates carbonate by charge balance and renormalizes to  $8(M^{2+} + M^{3+})$ ,  $16OH^-$  and  $4H_2O$  per formula unit.

		MFN_MIN_1998_2751				MFN_MIN_1998_2758			
		mean	std dev	min	max	mean	std dev	min	max
SiO <sub>2</sub>		0.14	0.08	0.06	0.27	0.14	0.05	0.06	0.17
Al <sub>2</sub> O <sub>3</sub>		15.58	0.75	14.98	16.78	16.55	0.30	16.15	16.93
Cr <sub>2</sub> O <sub>3</sub>		0.03	0.04	0.00	0.09	0.00	0.00	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>		1.11	0.06	1.03	1.19	0.43	0.04	0.38	0.48
MnO		0.03	0.06	0.00	0.13	0.03	0.03	0.00	0.05
MgO		34.83	1.39	33.40	37.09	33.99	0.66	33.29	35.03
CaO		0.01	0.02	0.00	0.04	0.01	0.02	0.00	0.05
Na <sub>2</sub> O		0.10	0.03	0.08	0.14	0.08	0.04	0.04	0.11
SO <sub>3</sub>		0.02	0.02	0.00	0.04	0.05	0.03	0.00	0.07
Cl		0.00	0.01	0.00	0.02	0.01	0.01	0.00	0.02
-O = Cl		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO <sub>2</sub> calc		7.02	0.34	6.76	7.57	7.23	0.13	7.09	7.42
H <sub>2</sub> O calc		31.98	1.34	30.69	34.16	31.70	0.60	31.02	32.62
Total		90.86	3.91	87.26	97.21	90.20	1.71	88.12	92.78
Atoms per formula unit:									
$M^{2+}$	Mg	5.84	0.02	5.82	5.87	5.75	0.01	5.73	5.76
$M^{3+}$	Fe	0.09	0.00	0.09	0.10	0.04	0.00	0.03	0.04
	Al	2.07	0.02	2.04	2.08	2.21	0.01	2.20	2.23
	Σ	2.16	0.02	2.13	2.18	2.25	0.01	2.24	2.27
Interlayer	C	1.08	0.01	1.06	1.09	1.12	0.01	1.12	1.13
Ratios									
	Mg/(Mg + Al + Fe)	0.73	0.00	0.73	0.73	0.72	0.00	0.72	0.72
	Fe/(Al + Fe)	0.04	0.00	0.04	0.05	0.02	0.00	0.01	0.02

observed by Mills *et al.* (2011) for the analogous Mg–Cr mineral stichtite, which showed 3R/2H polytype ratios of 79.2/20.2 for a sample from Dundas, Tasmania (with minor lizardite) and 54.4/45.6 and 46.5/53.5 for samples from Barberton, South Africa.

### Hydrotalcite–quintinite series (Mg–Al–CO<sub>3</sub>–OH–H<sub>2</sub>O system)

Synthetic Mg–Al–CO<sub>3</sub> phases with a layered double hydroxide structure have been made with a wide variety of Mg/Al ratios. Bellotto *et al.* (1996) used powder X-ray diffraction (XRD) data to refine structures for examples with Mg/Al = 2 and Mg/Al = 5. Both of these ‘hydrotalcite-like’ phases had the same space group  $R\bar{3}m$  as hydrotalcite-3R, and similar unit-cell parameters. With increasing Mg/Al ratio, the  $a$  parameter increased from 3.0460 to 3.0808 Å, while  $c$  increased from 22.772 = 3 × 7.591 Å (Mg/Al = 2) to 23.784 = 3 × 7.928 Å (Mg/Al = 5). Recently, Kim *et al.* (2015) have reported that Mg/Al ratios up to 16 are obtainable while keeping the 3R structure. Similar variation in layer spacing of layered double hydroxide (LDH) minerals was also attributed to change in Mg/Al ratio by Zhitova *et al.* (2015). The ~3 Å  $a$  parameter implies that there is one cation per unit mesh of the brucite-like octahedral layer of the structure, and hence that there is no long-range three-dimensional ordering of Mg and Al, concomitant with the unusual fractional unit-cell contents [e.g.  $Z = \frac{3}{8}$  for LDH Mg<sub>6</sub>Al<sub>2</sub>CO<sub>3</sub>·3R, to use the generalized LDH nomenclature of Mills *et al.* (2012)].

In nature, LDH Mg<sub>*m*</sub>Al<sub>*n*</sub>CO<sub>3</sub> phases usually have Mg/Al ratio  $m$  very close to 2 or 3, with intermediate values probably representing intergrowth of  $m = 2$  and  $m = 3$  phases (Stanimirova, 2001; Mills *et al.*, 2012). The bimodal distribution of compositions justifies the definition of mineral species on compositional grounds as hydrotalcite (Mg/Al = 3; ideally Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>[CO<sub>3</sub>]·4H<sub>2</sub>O) or quintinite (Mg/Al = 2; ideally Mg<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>[CO<sub>3</sub>]·3H<sub>2</sub>O), as in Mills *et al.* (2012). Stacking variation or the occurrence of superstructures due to three-dimensional Mg–Al ordering are not considered to be species-defining characteristics, but yield polytypic varieties. Note that the restriction to small-integer Mg/Al ratios suggests that there may well be long-range order within individual brucite-like layers, but if this is strictly two-dimensional, and does not propagate between layers, then it will produce at best streaks of diffuse scattering in diffraction patterns, and no sharp superlattice spots.

For hydrotalcite, with Mg/Al = 3, the only proven structural variation is the stacking of brucite layers in the same orientation to produce the 3R polytype, or rotated by 180° about  $z$  relative to their neighbours, giving the 2H structure, both with  $a \approx 3$  Å and  $c$  close to 2 × or 3 × 7.7 Å. Frondel (1941) suggested doubling of the  $a$  parameter for both polytypes and also of the  $c$  parameter for the 3R mineral, and the corresponding values are occasionally cited. However, Allmann (1968) stated that the doubling was not justified, and there seems to be no evidence that long-range order occurs in the 3R phase (in contrast to the erroneous statement in Mills *et al.*, 2012).

Quintinite, with Mg/Al = 2, shows a much greater tendency towards long-range order of Mg and Al. If we represent the ~3 Å  $a$  parameter of the subcell as  $a'$  and the ~7.7 Å layer spacing as  $c'$ , then the following varieties have been described: (1) a phase analogous to hydrotalcite-2H apart from the different Mg/Al ratio, with space group  $P6_3/mmc$ ,  $a = a'$  and  $c = 2c'$ ; from Kovdor, Russia (Zhitova *et al.*, 2010); (2) a phase analogous to hydrotalcite-3R (except for Mg/Al), with space group  $R\bar{3}m$ ,  $a = a'$  and  $c = 3c'$ ; recorded as a synthetic phase by Bellotto *et al.* (1996), while Allmann and Jepsen (1969) characterized a natural example and Zhitova *et al.* (2015) reported another; (3) a superstructure of the 2H phase with space group  $P\bar{6}2m$ ,  $a = \sqrt{3}a' \approx 5.3$  Å due to Mg–Al ordering,  $c = 2c'$ ; recorded from Jacupiranga, Brazil, by Arakcheeva *et al.* (1996), also, called ‘quintinite-2H-1c’ by Krivovichev *et al.* (2010a). Zhitova (2013), however, recently described this superstructure in  $P\bar{3}c1$ . (4) A more complex superstructure of the ‘2H-1c’ phase, with tripled  $c$  repeat due to systematic offset of the Al atoms from layer to layer, with space group  $R32$ ,  $a = \sqrt{3}a'$ ,  $c = 6c'$ ; recorded as ‘quintinite-2H-3c’ from Kovdor by Krivovichev *et al.* (2010a); (5) an analogue of hydrotalcite-3R, with all layers translationally equivalent. However, because the  $x$  axis is rotated 30° relative to its orientation in the  $a \approx 3$  Å structures, the interlayer stacking vector is no longer a potential rhombohedral lattice vector, and the structure is monoclinic  $C2/m$ ,  $a = \sqrt{3}a'$ ,  $b = 3a'$ ,  $c \sin\beta = c'$ ,  $c \cos\beta = -a/3$ , recorded as ‘quintinite-1M’ from Kovdor by Krivovichev *et al.* (2010b). This appears to be the most common structural variety of natural quintinite (Zhitova *et al.*, 2015); (6) ‘quintinite-2H’ from Jacupiranga of Chao and Gault (1997), with  $a$  doubled relative to that of Arakcheeva *et al.* (1996); space group  $P6_322$ ,  $a = \sqrt{12}a' \approx 10.6$  Å,  $c = 2c'$ ;

and (7) 'quintinite-3*T*' of Chao and Gault (1997), from Mont Saint-Hilaire, Québec; a superstructure of the 3*R* type with space group  $P3_112$ ,  $a = \sqrt{12}a' \approx 10.6 \text{ \AA}$ ,  $c = 3c'$ .

The rather subtle differences between these phases and the likelihood that more will be discovered both emphasize the importance of not relying on diffraction data to distinguish LDH species of the hydrotalcite group ( $M^{2+}/M^{3+} = 3$ ) from those of the quintinite group ( $M^{2+}/M^{3+} = 2$ ). Quantitative chemical analysis is required, and in its absence, it is possible that some 'hydrotalcite' or 'hydrotalcite-3*R*' occurrences described in the literature are actually examples of the quintinite-3*R* listed at (2) above, while some 'manasseite' or 'hydrotalcite-2*H*' is actually the disordered quintinite-2*H* of (1). The Jacupiranga quintinite was originally described as 'manasseite' by Menezes and Martins (1984), despite its superstructure. It is possible that the layer spacing obtained from XRD may provide some indication of composition: all the quintinite polytypes of Krivovichev *et al.* (2010*ab*) and Zhitova *et al.* (2010) have  $c' = 7.56\text{--}7.59 \text{ \AA}$  and that of Allmann and Jepsen (1969) has  $7.60 \text{ \AA}$ , while hydrotalcite has a larger spacing of  $7.67\text{--}7.69 \text{ \AA}$  (2*H* and 3*R* polytypes from Somerville, New York; Frondel, 1941),  $7.78 \text{ \AA}$  (Snarum; Zhitova *et al.*, 2015),  $7.79 \text{ \AA}$  (3*R* polytype from Snarum; the present study) and  $7.81 \text{ \AA}$  (2*H* polytype from Snarum; the present study).

## Conclusions

We have located specimens which were probably collected by the discoverer of hydrotalcite and are satisfied that they come from the discovery locality. We have shown them to have a chemical composition corresponding to hydrotalcite rather than to another species in the hydrotalcite supergroup, such as quintinite. Our proposal that these specimens be designated the neotypes of hydrotalcite has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (proposal 15-J). We note and correct some errors in the historical record and discuss the potential for confusion between hydrotalcite, quintinite and possibly other species if samples are not analysed quantitatively.

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