

# Secondary Zn and Cu minerals from the Oslo region, Norway: Addendum

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## Abstract

*The suggested formula  $Zn_7(CO_3)_3(OH)_8 \cdot H_2O$  for massive hydrozincite from Glomsrudkollen as compared to  $Zn_5(CO_3)_2(OH)_6$  for well-crystallized hydrozincite is tentatively explained in terms of the layered crystal structure of hydrozincite.*

*An unknown mineral from Sando quarry gives an X-ray powder pattern identical to that of the so-called "Lockenmineral" from Schwaz, Tirol. Indexing of the latter on a monoclinic cell gave  $a = 2.7584$ ,  $b = 9.4466$ ,  $c = 11.9616 \text{ \AA}$ ,  $\beta = 91.338^\circ$ . A preliminary chemical analysis of the Schwaz mineral is reported.*

## Sammendrag

*Den foreslåtte formelen  $Zn_7(CO_3)_3(OH)_8 \cdot H_2O$  for massiv hydrosinkitt fra Glomsrudkollen, sammenlignet med  $Zn_5(CO_3)_2(OH)_6$  for velkrystallisert hydrosinkitt, kan forsøksvis forklares på grunnlag av sjiktstrukturen hos hydrosinkitt.*

*Et ukjent mineral fra Sando pukkverk gir et røntgenpulverdiagram som er identisk med diagrammet for det såkalte "Lockenmineral" fra Schwaz, Tirol. Indicering av sistnevnte med en monoklin celle gav  $a = 2,7584$ ,  $b = 9,4466$ ,  $c = 11,9616 \text{ \AA}$ ,  $\beta = 91,338^\circ$ . En foreløpig kjemisk analyse av mineralet fra Schwaz rapporteres.*

## Introduction

Based on new information, two of the minerals treated in my previous article on the secondary Zn and Cu minerals from contact deposits of the Oslo region (Raade 1995) deserve some additional comments.

### Mineral closely related to hydrozincite

It was shown (Raade 1995) that X-ray powder films of hydrozincite could be divided into two groups: those of well-crystallized material and those of massive material, mainly occurring as coatings. The differences between the patterns of the two groups are subtle, but nevertheless distinct. It is not only a question of weaker and more diffuse reflections for the latter group, since differences in relative intensity and spacing could also be noted.

Also Jambor (1964) has described - based on slight differences in composition, temperature of endothermic effect, X-ray powder patterns, and infra-red absorptions in the OH stretching region - that natural hydrozincites could be classified into two categories: hydrozincite proper and a less common phase of hydrozincite referred to as the "Dorchester type".

Chemical analysis of a thick, porcelain-like coating of hydrozincite from Glomsrudkollen yielded a formula close to  $Zn_7(CO_3)_3(OH)_8 \cdot H_2O$  (Raade 1995). This is in contrast to  $Zn_5(CO_3)_2(OH)_6$  for well-crystallized hydrozincite. The oxide weight percentages for these two formulae are rather close, and the correctness of the former formula depends therefore on the analysis being very accurate, which I believe can be claimed.

It was erroneously stated in my article that the crystal structure of hydrozincite was not known. Indeed, the structure was described in 1964 by Ghose. When I checked the latest index of *Structure Reports* (Ferguson, 1993) before writing my previous article, I could not find the mineral name. The reason for this turns out to be that it was misspelled as "hydroxyzincite" in that index.

The crystal structure of hydrozincite was determined on material from Goodsprings, Nevada from multiple-film integrating Weissenberg photographs to  $R = 0.16$  for 284 observed *hkl* reflections (Ghose 1964). The structure is composed of Zn in both octahedral and tetrahedral coordination, in the ratio 3:2. The octahedral Zn atoms form sheets parallel to (100) with some vacant octahedral positions, Zn atoms in tetrahedral coordination occurring above and below these 'holes'. The carbonate groups are situated normal to the complex  $Zn_3(OH)_6O_2^{4-}$  sheets and bind them together in a three-dimensional network.

Ghose (1964) interpreted some natural hydrozincites, yielding few broad powder reflections - corresponding to the strongest powder reflections of well-crystallized hydrozincite - to be nothing but stacking-disordered phases, similar to synthetic  $CO_2$ -deficient disordered phases, which can be converted to the ordered phase by ageing with  $CO_2$ . He also commented that synthetic basic Zn carbonates always contain some water, part of which may be structural, and that water molecules may be "located in channels parallel to [001] in between rows of carbonate groups". Evidence based on a continuous variation in cell dimensions of synthetic hydrozincites and a gradual change in infra-red OH absorptions of natural hydrozincites indicates a series of hydrozincites with varying stacking-order and shows that it is not necessary to distinguish the "Dorchester type" as a separate mineral (Zabinski 1966; Jambor 1966).

As for the Glomsrudkollen mineral - provided that its chemical composition is correct - the extra molecule of water can be accommodated in channels between the sheets as explained by Ghose (1964). However,

this mineral is not CO<sub>2</sub>-deficient; it is instead deficient in Zn and OH relative to well-crystallized hydrozincite (Zn:CO<sub>2</sub>:OH is 2.33:1:2.67 versus 2.5:1:3). In addition to possible stacking-disorder, vacancies in some of the Zn and proton sites or extra carbonate between the sheets can be envisaged in order to explain this feature.

An attempt was made to verify the presence of an extra molecule of water in the massive hydrozincite from Glomsrudkollen from its infra-red spectrum. However, a very strong CO<sub>3</sub> absorption at 1512.3 cm<sup>-1</sup> completely masks any H<sub>2</sub>O bending vibration around 1600 cm<sup>-1</sup>. The atlas of infra-red spectra of carbonate minerals by Jones & Jackson (1993) includes two spectra of hydrozincite. One is for well-crystallized material from Goodsprings and shows a well-resolved spectrum; the other is for a coating from Wales and is less complex, but has the same overall pattern. Our spectrum of the Glomsrudkollen mineral is identical to the latter, which is referred to as the "Dorchester type".

### "Lockenmineral"

After my previous article was finished (Raade 1995), it was found that the X-ray powder pattern of the so-called "Lockenmineral" from Schwaz is identical to that of the unknown mineral from Sando quarry. As more material is available from the former locality, further investigations were made on that material.

Prof. Fjellvåg from Department of Chemistry, University of Oslo, kindly agreed to collect powder diffraction data on the Schwaz mineral at the synchrotron facility in Grenoble. He has been able to index the powder pattern on a monoclinic cell with  $a = 2.7584$ ,  $b = 9.4466$ ,  $c = 11.9616$  Å,  $\beta = 91.338^\circ$ ,  $V = 311.60$  Å<sup>3</sup>. These cell parameters are near to - but significantly different from - those of malachite and rosasite. We have so far not been able to solve the crystal structure of the "Lockenmineral", but work is in progress.

A new chemical analysis of the Schwaz mineral was inconclusive, due to a high analytical total and the presence of unexpectedly large amounts of CaO (indicating possible contamination by calcite). The raw data are as follows:

Weight loss at 105°C is 0.3%

CO<sub>2</sub> and H<sub>2</sub>O were determined with a Leco R-412 instrument on dried material:

CO<sub>2</sub> 21.65 and 20.45 wt.%

H<sub>2</sub>O 11.7 and 11.0 wt.%

The method was checked by analyzing malachite with theoretical values CO<sub>2</sub> 19.9 and H<sub>2</sub>O 8.2 wt.%. Duplicate analyses gave 20.41/19.90 and 9.76/9.86 wt.%, respectively. The water figures are thus slightly on the high side by this method. Metal oxides were determined by AAS on original (undried) material:

CuO 57.2 wt.%

ZnO 7.25

FeO 0.13

MgO 0.68

CaO 3.87

Rem. 0.5 (quartz)

These data can be compared with those published for the Schwaz mineral by Meixner & Paar (1975):

CuO 61.96, ZnO 4.11, FeO 0.21, MgO 0.79, CaO 1.25, CO<sub>2</sub> 21.80, H<sub>2</sub>O 10.00, sum 100.12 wt.%. The main differences are in the CuO, ZnO and CaO figures.

### Acknowledgements

Alf Olav Larsen provided the IR spectrum of hydrozincite from Glomsrudkollen. A fair amount of "Lockenmineral" from Schwaz was put at my disposal by Thilo Arlt. Alf Olav Larsen and Arne Åsheim contributed its chemical analysis. Special thanks to Helmer Fjellvåg for his willingness to embark upon a difficult problem in Grenoble. Brenda B. Jensen kindly corrected the English text.

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