

Proposal of a Microbial Route for the Synthesis of the Rare Tsumeb Mineral Sohngelite, Ga(OH)₃

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Abstract

Rare *Tsumeb* minerals such as sohngelite, Ga(OH)₃ respectively stottite, FeGe(OH)₆, could not be obtained synthetically as yet. We propose their synthesis via microbe activities. Such a synthesis route was recently offered for dioptase, Cu₆(Si₆O₁₈)·6H₂O, also a mineral of the *Tsumeb* paragenesis. It opens further technological applications by using thermally stable dehydrated dioptase or its nano-crystalline decomposition product CuSiO₃ (orthorhombic) as effective catalysts. Microbe activity possibly could explain the formation route of many rare minerals from the *Tsumeb* mine multi-metallic ore deposit.

Keywords: Mineral Synthesis via Microbes, Gallium, Germanium, Tsumeb Minerals, Sohngelite, Tsumgallite, Stottite, Dioptase, Dehydrated Dioptase, Catalysis, Microbial Gemstone Production.

1. Introduction

On March 3rd 2022 the inauguration of the renovated building of the historic mineralogy took place in *Tsumeb* on the old mine site. On this occasion I would like to write a small contribution. The *Tsumeb* mine in Namibia was operated between 1907 and 1996 and is the type-locality of 72 minerals. The worldwide unique paragenesis of rare germanium and gallium minerals from this mine triggered early activities for their synthesis, but with quite limited success. Already in 1968, *Otto* synthesized the rare *Tsumeb* minerals fleischerite, Pb₃Ge(OH)₆(SO₄)₂·3H₂O as well as schaurteite, Ca₃Ge(OH)₆(SO₄)₂·3H₂O [1]. Also the isotopic strontium compound was synthesized, which is unknown as a mineral. The crystal structure of fleischerite has been determined already in 1970 [2] [3].

The worldwide unique pure gallium mineral from the *Tsumeb* type-locality, sohngelite, Ga(OH)₃, was described in 1965 by *Strunz* and named after the well-known former chief-geologist of the *Tsumeb* mine, *Gerhard Söhngel* [4]. However, the first who knew about the uniqueness of this new compound was the present author as a former coworker of *Strunz*, who performed that time a spark spectroscopic analysis and a first X-ray powder pattern indicating the phase as being tetragonal pseudo-cubic due to observed line splitting of back reflections. *Strunz* suspected germanium as the main metallic component of the new mineral, but I confirmed to his surprise a pure gallium compound. However, all efforts to synthesize the

mineral failed that time. A synthesis of the mineral is not known since today. So we propose a new route to synthesize the rare mineral supported by microbes as was shown recently in the case of dioptase, also a secondary mineral from the *Tsumeb* poly-metallic Cu-Pb-Zn ore deposit.

2. Proposal of a Microbial Route for the Synthesis of Ga(OH)₃

It was as a surprise to the present author studying the remarkable and seminal work of a microbially supported synthesis of Cu₆(Si₆O₁₈)·6H₂O (dioptase) by *Rao* and *Krishna* by using only copper oxide (tenorite), quartz and microbes, even if important information and references are missing in this contribution [5]. Special microbes are obviously able to create the needed conditions of the mineral-bearing solutions such as an optimal *pH*. We succeeded before in the synthesis of germanate dioptase, Cu₆(Ge₆O₁₈)·6H₂O simply from solution and the partial replacement of Ge by Si towards pure dioptase, but could not even synthesize pure dioptase [6] [7] [8]. So the synthesis supported by microbes is a fine alternative for a large scale production with respect to the application of dehydrated dioptase as a catalyst [9] respectively its decomposition product orthorhombic CuSiO₃ [10] [11] [12] [13]. In contrast, the proposed synthesis of Ga(OH)₃ is only of academic interest for the time being, but research towards supercapacitor application could be useful.

Ga(OH)₃ forms by weathering of the primary Ga-containing sulfides sphalerite, ZnS, respectively gallite, CuGaS₂, within the second oxidation zone at depths of 900 to 1100 m. The acidic environment resulting from sulfide oxidation must be buffered. Here possibly microbes come into play creating the optimum *pH* for the Ga(OH)₃ formation, while otherwise only GaO(OH) would be formed. It is quite possible that surface water enriched with microbes can reach the site of sphalerite at the appropriate depth down the pipe-like ore body. One could try to detect such microbes there.

In this way it is recommended to decompose gallite, CuGaS₂ (tetragonal, chalcopyrite prototype), under ambient hydrothermal conditions in the presence of microbes. The same microbe mixture used by *Rao and Krishna* [5] could be applied: *Stenotrophomonas maltophilia*, *Psodomonas putila*, *Pseudomonas aeruginosa*, *Enterobacta cloacae*, *Staphylococcus sciuri*, *Acinetobacter calcloaceticus*, *Pantoeau agglomerans* and *Flavobacterium* spp. Whether the transformation of stable gallium oxide hydroxide, GaO(OH), into Ga(OH)₃ in the presence of microbes is possible should be investigated too. GaO(OH) was recently found as a new *Tsumeb* mineral, named tsumgallite [14]. Its discovery was only a matter of time. The naming tsumgallite is indeed inappropriate, since gallite is a sulfide, CuGaS₂. Names such as metasohngite or gallaspor, referring to the structural prototype diaspor, would be more meaningful. The microbially supported synthesis of the rare *Tsumeb* mineral stottite, FeGe(OH)₆ [15], should be considered, too.

Previously the Ga respectively O sites of Ga(OH)₃ are thought to be arranged in an orthorhombic-distorted ReO₃-type crystal structure with *Z* = 8 formula units in the unit cell [16], but recent investigations indicated polymorphism and proton-driven transformation behavior, based on a tetragonal unit-cell with *a* = 7.4546 Å and *c* = 7.3915 Å, space group *P4₂/nmc* or *P4₂/n* [17]. This is still a distorted ReO₃-type crystal structure!

The ore deposit of the *Tsumeb* mine is indeed extremely rich on rare minerals. However, the German Kupferschiefer, for instance, contains 54 chemical elements, and besides the metals Pb, Zn, Cu, Co, Fe, Ni, V, Ag, Au, Ge and Ga also Re and U were observed, which are absent in *Tsumeb*.

This contribution presents only synthesis proposals, because the present retired author no longer works experimentally. But if he would still do experiments, he would study the conditions under which a seed of gem quality dioptase would continue to grow in the environment of microbes, possibly paving the way for a microbial gemstone production.

3. Conclusion

This contribution focuses on the mineral synthesis via microbial activities and proposed the synthesis of rare minerals such as sohngeite, $\text{Ga}(\text{OH})_3$, respectively stottite, $\text{FeGe}(\text{OH})_6$, found exclusively in the oxidation zone of the *Tsumeb* mine, Namibia. A successful synthesis would help better understanding the extraordinary mineral paragenesis at *Tsumeb* mine. Special microbes are obviously able to create the needed conditions of the mineral-bearing solutions such as an optimal *pH*. The formation of dioptase, $\text{Cu}_6(\text{Si}_6\text{O}_{18}) \cdot 6\text{H}_2\text{O}$, via the activity of microbes, has large scale technological importance, because dehydrated dioptase, $\text{Cu}_6(\text{Si}_6\text{O}_{18})$ shows pronounced catalytic activities. This almost insoluble silicate compound with empty channels of sufficient opening of the hexamer silicate rings along the hexagonal axis is very stable at high temperatures. Also microbe-assisted gemstone production may be possible in future.

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