



## Georgeite: A rare copper mineral with important drinking water implications



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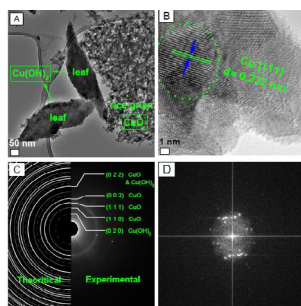
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### HIGHLIGHTS

- Georgeite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ) was conclusively identified as the solid.
- Understand the effect of water chemistry on the solubility and properties.
- Solids were X-ray amorphous, isotropic, and were light blue to blue.
- Georgeite is an extremely rare, amorphous malachite analog.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

Significant research has been conducted on copper corrosion and solubility in drinking water, including the establishment of the “cupric hydroxide model.” The model describes the temporal aging and associated solubility changes of copper minerals beginning with the most soluble solid, cupric hydroxide. Although the model explains copper levels in field observations well, there are model aspects that are not well understood, including a lack of evidence of the presence of cupric hydroxide in drinking water distribution systems. This study aimed to understand the effect of water chemistry on the solubility and properties of newly precipitated cupric solids, including mineral identification. Bench-scale copper precipitation tests were performed in water under a matrix of pH and dissolved inorganic carbon conditions. Copper solids were analyzed using a combination of materials analysis tools including XRD, FTIR, TGA and inorganic carbon analyses. Copper solids were X-ray amorphous, isotropic, and were light blue to blue. Based on the repeated analysis, georgeite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ) was conclusively identified as the solid at all test conditions. Georgeite is an extremely rare, amorphous malachite analog, and because of its rarity, very little has been reported on its presence in any environment.

### 1. Introduction

Elevated copper levels in consumers’ tap water can cause acute health problems at high concentrations, blue water, staining of sinks

and tubs, and clogging of filters. Because of potential health concerns, the U.S. Environmental Protection Agency’s (EPA) Lead and Copper Rule (LCR) established a copper action level (AL) of 1.3 mg/L in a 1 L first draw sample collected from the consumers’ tap [1–3]. The AL is

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health-based associated with stomach and intestinal distress, liver or kidney damage, and complications of Wilson's disease in genetically predisposed people, and considers total copper ingestion (i.e., soluble and particulate copper). Since the implementation of the LCR, a huge amount of research has been conducted on copper corrosion, solubility, and leaching from materials in drinking water distribution systems. Many of these research findings have improved the water industry's understanding of how water chemistry affects the solubility of copper minerals found in drinking water distribution systems, the role of stagnation time on copper leaching from copper pipes, and the use of corrosion inhibitors to reduce copper levels at the consumer's tap [4–9]. Additionally, new information on copper solubility in water has relevance to the drinking water premise plumbing (including buildings) treatment field. For example, the use of copper-silver ionization systems to control *Legionella* in the drinking water of large buildings (e.g., hospitals) has grown in interest [10–13] and by water chemistry and associated copper solubility control the applied copper dose.

A particularly important development was the establishment of the "cupric hydroxide model" [14]. As pipes age and passivating films build and become more thermodynamically stable, the associated copper solubility changes. For example, new copper piping is more cuprosolvent at equilibrium than old piping, though not necessarily corrosive toward copper [14–18]. As a result, some researchers [14,16,18] have noted that older methods for predicting Cu(II) solubility fail when applied to newer plumbing systems because these methods assume the formation of tenorite or malachite minerals that may or may not be present on the pipe surface. The cupric hydroxide model provides an important understanding of cuprosolvency, particularly the impact of solids-aging and water chemistry on soluble copper levels in water [14]. The model essentially proposes that copper solubility-controlling solids on the surface of copper plumbing change as they "age," from a relatively soluble copper solid to an insoluble one. The reliability of this model has been substantiated in many ways, including bench-scale and pilot-scale studies, field observations, and chemical equilibrium modeling simulations. Although cupric hydroxide solubility and model explain copper levels in field observations reasonably well [14,15] there are aspects of the model that are not well understood. For example, although the aging process is assumed, to begin with, cupric hydroxide, it is not readily formed in drinking water and rarely identified in drinking water distribution systems where its presence has been questioned [19].

There are many significant Cu(II) mineral corrosion by-products that have been identified on drinking water distribution materials, including tenorite (CuO), langite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ), posnjakite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$ ), malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ), cupric chloride ( $\text{CuCl}_2$ ), and brochantite ( $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ ) [6,14,20,21]. In addition to these solids, georgeite represents an extremely rare, amorphous copper hydroxy-carbonate hydrate mineral that exists in nature [22,23] and has been synthesized in a limited number of environments [24–26]. First reported in 1975, georgeite (properties are shown in Table S1) was discovered in the Carr Boyd Mine in Western Australia [22] and later reported to be found at the Britannia Mine in Snowdonia, Wales [23].

Georgeite is an X-ray amorphous analog of malachite having several reported chemical formulas:  $\text{Cu}_2\text{CO}_3(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  [23,27,28],  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$  [29] and  $\text{Cu}_5(\text{CO}_3)_3(\text{OH})_4 \cdot 6\text{H}_2\text{O}$  [22]. Georgeite is light, pale, or sky blue; non-crystalline or amorphous, and isotropic. Georgeite, as well as other copper hydroxy-carbonates, are of great interest to the chemical industry as they are widely used catalyst precursors [24,26,30,31]. Pollard et al. [24] synthesized georgeite in the laboratory by mixing 0.8 g (47 mmol) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  to 100 mL of a solution containing 5.3 g (50 mmol)  $\text{Na}_2\text{CO}_3$  at 25 °C. In later work, Pollard et al. [25] produced georgeite by mixing a 0.1 M aqueous solution of  $\text{CuSO}_4$  with 1 M aqueous  $\text{Na}_2\text{CO}_3$  solution at 60 °C. More recently, Kondrat et al. [26] synthesized georgeite using a supercritical anti-solvent precipitation process that uses carbon dioxide rather than sodium

carbonate as the carbonate source. Catalysts developed from a georgeite precursor were superior to those formed in  $\text{Na}_2\text{CO}_3$  [24] because the sodium, a potential catalyst poison, was eliminated and reduced from the catalyst precursors [26,32]. Due to its rarity, very little has been reported on its properties in any environment, including water where its solubility has yet to be determined. Georgeite has never been recognized by the drinking water industry and has never been reported in drinking water suspensions or drinking water distribution systems.

Although many significant developments have been made in controlling copper corrosion and reducing copper solubility in water, many questions remain. There remains a great need to better understand copper geochemistry in aqueous environments, including drinking water systems. Specifically, although the conceptual understanding of copper aging in water described by the cupric hydroxide model, cupric hydroxide is not identified in drinking water systems nor is it easily formed in aqueous environments. Increasing our understanding of copper behavior in drinking water will improve corrosion control, protection of public health, and *Legionella* treatment in buildings. This study aimed to examine the effect of water chemistry on the solubility and properties of newly precipitated copper solids. Most importantly, the primary objective of this work was to conclusively identify the copper mineral (s) that freshly form in water. Understanding the impact of water chemistry on the solubility and properties of newly precipitated copper solids is necessary for controlling copper in consumer's drinking water and protecting public health.

## 2. Experimental

### 2.1. Chemicals and reference standards

Unless otherwise specified, all chemicals used in this study were Analytical Reagent (AR) grade. Dilute 0.6 M HCl, and 0.5 N NaOH (Fisher Scientific; Fairlawn, NJ) were used to adjust pH. Sodium bicarbonate (Fisher Scientific; Fair Lawn, NJ) was added to adjust DIC concentration. Copper was added as cupric perchlorate ( $\text{Cu}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ) (GFS Chemicals; Columbus, OH).

Copper reference materials were obtained to compare against the experimentally synthesized precipitates. Cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) was purchased from Alfa Aesar (Haverhill, MA). Azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) was a geological mineral specimen from the Morenci Mine in Morenci, Arizona. Copper (II) carbonate basic ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) was obtained from Sigma-Aldrich (St. Louis, MO). Malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ) was obtained from a precipitate formed in copper corrosion research experiments [33]. Lastly, georgeite was obtained as a geological mineral specimen and reference material from the Carr Boyd Nickel mine in Kalgoorlie, W.A. Australia.

### 2.2. General experimental design

Cu(II) solubility and particle formation experiments were conducted in a 3 L glass beaker. The beaker top contained ports for acid and base injection, sample collection, pH electrode, dissolved oxygen/temperature probe, mechanical stirrer, and a gas feed tube.

Experiments were initiated by adding 2 L of double deionized (DDI) water to the beaker located on a stir plate set at 200 rpm. DDI water was prepared by passing distilled water through a deionized water system (Milli-Q Plus, Millipore Corporation; Belford, MA) having a resistivity 18.2 M $\Omega$ ·cm. An appropriate amount of sodium bicarbonate was then added to the water to achieve target DIC concentrations of 10, 50, and 100 mg C/L.

After DIC addition to the reaction vessel, the treatment water was titrated to the desired pH and after that maintained during the experiment using the Jensen Systems Multi-T 2.2™ software (Jenson Systems; Hamburg, Germany) and Schott Titronic Universal dual auto-titrators (Schott Geräte; Germany). The pH was maintained by rapidly adding small increments of 0.6 N hydrochloric acid (HCl) or 0.6 N

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