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TECHNICAL ARTICLE

Silicified Microorganisms and Microorganism-Like Particles in the Groundwater of an Abandoned Coal Mine

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Abstract
Relatively little research has been conducted on the preservation of microorganisms and microbial particles in the groundwater of abandoned mines (GAM). In this study, silicified microorganism-like particles, 50–450 nm in diameter, were found to commonly occur outside microbes and their associated extracellular polymers. These particles comprise a cellular core surrounded by a cortex essentially of silica and are similar in morphology to certainly known microorganisms. The studied samples suggest the preservation of micro-organisms through silicification and add to understanding about how microorganisms in natural water systems undergo biomineralization. Finally, the silicified microorganism-like particles were surrounded by many silica nanoparticles. This study identified a new mode of silica transport in the GAM.

Keywords Silica · Biomineralization · Microbe preservation · Cell

Introduction

Abandoned mine sites affect 240,000 km^2 globally and pose a significant risk to humans and the environment (Wolkersdorfer 2008). In particular, abandoned underground mines can change the surface and groundwater by changing water levels, recharge, and groundwater flow paths (Cederstrom 1971; Hawkins 2004; Stoner 1983), groundwater-surface water interactions (Sidle et al. 2000), and stream flows (Sidle et al. 2000). In turn, these can cause problems at the regional level, such as drought and flood risks, and can affect the availability of freshwater (Dvořáček et al. 2004).

Previous research regarding the ecological influence of groundwater of abandoned mines (GAM) primarily focused on the toxicity of acidic mine water as well as its impact on surface water, groundwater, soil, and plants (Avril and Barten 2007; Foley et al. 2005). As such, studies on GAM were predominantly limited to the water's physical (such as pH and redox potential) and chemical composition [e.g. Si, Na, Al, Ca, Mg, Fe, C (as organic or $CaCO_3$) and S as SO_4^{2-}]. Mines that remain unflooded are usually exposed to the atmosphere, i.e. they have access to oxygen (McDonough et al. 2005; Watzlaf 1992; Younger 2000). As a result, unflooded mines frequently produce acidic water with high sulfate and iron contents, in large part due to the activity of iron-oxidizing bacteria.

There is a high probability of microorganism preservation by mineralization in GAMs, which can be attributed to high quantities of Fe, Ca, or Si facilitating the fossilization of resident microbes (Wolkersdorfer 2008). Evidence of microbe preservation includes mineralized microbes discovered in acidic mine drainage systems and experiments conducted in the laboratory (Fowler et al. 2001; Laidler and Stedman 2010; Orange et al. 2011). However, naturally silicified microbes are rarely found in GAMs and there is presently only limited knowledge of their preservation, plausible preservation techniques, and whether or not they are recognizable once silicified in natural settings.

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The present study demonstrates the preservation of microorganism-like particles through silicification in GAM from the Lingzi coal mine, and that microorganisms can be preserved while encased outside the cells of their host. The results also reveal a characteristic form of nano-silica particles in the GAM.

Materials and Methods

Site Description and Sample Collection

The Lingzi coal mine, which closed in 2010, is located in the middle of Zibo city, Shandong Province, in eastern China (Fig. 1). The mine area is 33.5 km^2 and the ore reserves total ≈ 20 million tons. The exposed strata in the mining area included Ordovician dolomitic limestone, dolomite, thick limestone mixed with marl, Carboniferous-Permian sandstone, sandy shale, shale, clay shale, thin limestone, Triassic thick variegated shale mixed with fine sandstone, Jurassic conglomerate or sandy conglomerate and Quaternary deposits (Fig. 2). The coal deposit is mainly located in the Carboniferous-Permian strata.

The aquifers in the Lingzi coal mine comprised a Quaternary gravel layer aquifer, a Jurassic sandy aquifer, a Permian sandy aquifer, a Carboniferous limestone and sandy aquifer, as well as an Ordovician limestone aquifer. According to the mine's statistics, the net water inflow of the mine averaged 810 m^3/h, with a maximum of 950 m^3/h. Within the mining area, there were 44 coal mines including the Lingzi mine that had accumulated water. The amount of accumulated water in this mine pool was season-dependent. The ponding, in the form of fracture leakage or seepage furnished a continuous supply to the aquifers in the coal measures, thereby providing an additional water supply to the dynamic reserves of the mine. Finally, the surrounding coal mines were mined by each other.

Water samples were collected in December 2021 in 50 mL sterile Falcon tubes from the source waters of the Lingzi coal mine (Fig. 3). Samples of water were passed through 0.45 μm membrane filters and collected in clean wax-sealed polyvinyl fluoride bottles. In addition, samples were collected in duplicate, with one preserved in 2% (v/v) glutaraldehyde. An additional 10 samples were obtained and passed through a 0.2 μm cellulose acetate syringe filter (Sarturius) prior to chemical analysis. During fieldwork, the samples were stored in a cooler, and subsequently refrigerated prior to analysis. The water pH was measured directly in the field using a pH meter (Hanna HI9828, USA). This pH meter is automatically calibrated, with five calibration points with options for 1, 2, or 3 standard point calibration.

Water Chemistry

Chemical analysis of samples was conducted in laboratories at the Shandong Provincial Geo-mineral Engineering Exploration Institute and the Qingdao Geo-Engineering Survering Institute, China. The water samples were analyzed for the existence and quantification of SiO_2, Mg, Fe, Al, and Mn by inductively coupled plasma optical emission spectrometry (ICP-OES Optima 2100 DV, the lower limit of 0.01 mg L^{-1}). The samples were heating and acidolysis with nitric acid on an electric heating plate. Repeated analyses demonstrated reproducibility within 2%. HCO_3^- analysis

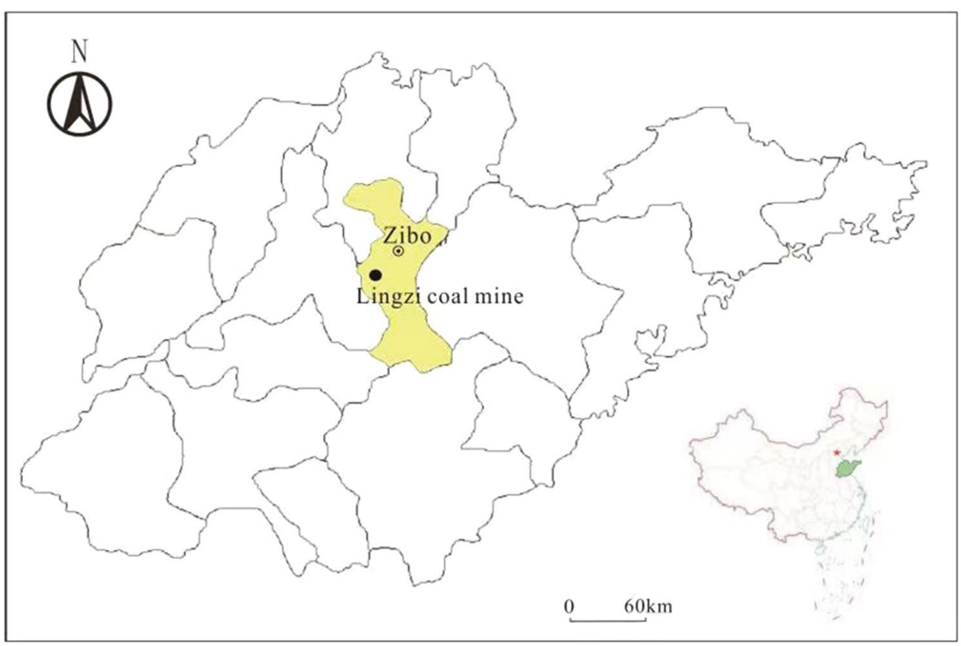

Fig. 1 Location of the Lingzi coal mine

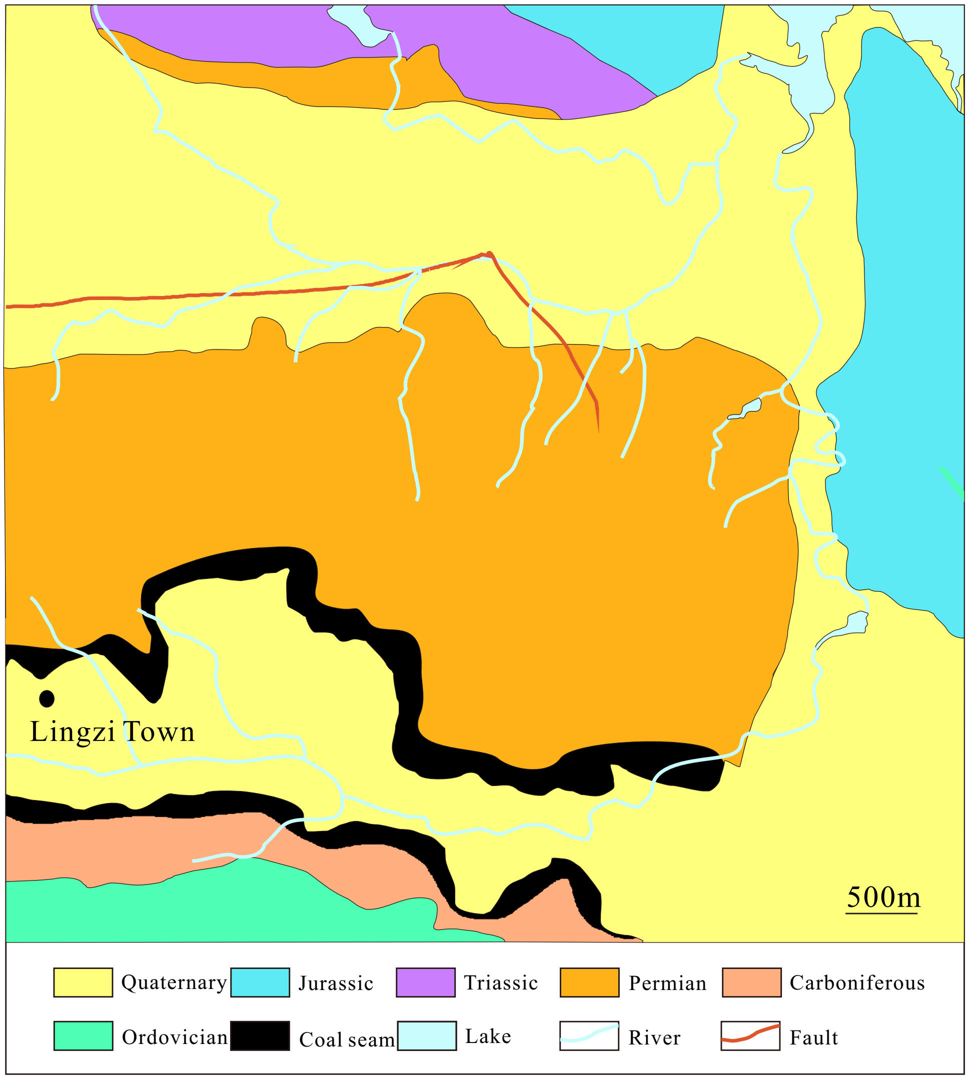

Fig. 2 Geological diagram of the Lingzi coal mine

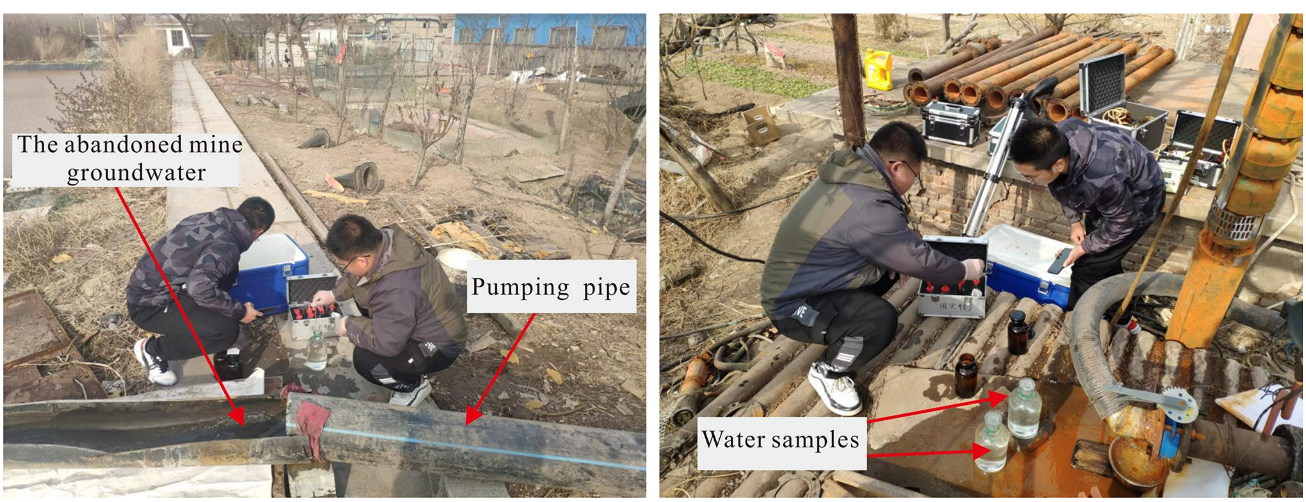

Fig. 3 The abandoned mine groundwater and water samples in the Lingzi coal mine

was carried out using the acid titration method; Cl^- concentration was measured by the $AgNO_3$ titration method. The SO_4^{2-} concentrations were estimated by the $BaCl_3$ turbidity method using a spectrophotometer (UV 1600 PC). Na^+ and K^+ were analyzed using flame photometer (AFP 100, Hamburg, Germany), where Ca^{2+} was analyzed by titration. The analytical precision and measurement reproducibility was within 2%. The ionic balance error for investigated ions was within ± 5%.

Transmission Electron Microscopy (TEM)

Prior to TEM analysis, the GAM samples were pre-treated as described by Li et al. (2016). The collected water samples were transferred onto a TEM grid with a pipette, after which the bottles were lightly shaken to remove any uneven dispersion of nanoparticles within an aqueous solution, with the process being repeated four to five times. Nanoparticles were placed onto the TEM grids after preprocessing. Grid samples were assessed at the Sinoma Institute of Materials Research (Guangzhou) Co., Ltd where a FEI Talos F200X transmission electron microscope (TEM) operated at 200 kV was used to conduct TEM analyses. A TEM energy-dispersive spectrometer (EDS) was used to analyze 200 kV. Acquisition of EDS maps was achieved in the STEM DF mode, using a focused electron beam (1 nm). Since the TEM grid is composed of carbon-coated copper, both the C and Cu concentrations were subtracted from the analysis in our study. In the EDS spectral analyses, the leftmost pick represents C, and the two rightmost picks represent Cu. Mineral structures in the regions of interest were determined using TEM according to selected-area electron diffraction (SAED). TEM was also conducted on a Tecnai G2F20 field emission electron microscope operated at 200 kV.

Results

Water Chemistry

The groundwater chemistry of the Lingzi coal mine is show in Table 1. Saturation indices (SI) were identified using the PHREEQC software (Parkhurst and Appelo 1999) (supplemental Table S-1), with values approximately equal to 0 for amorphous SiO_2 (− 1.4), chalcedony (− 0.5), and quartz (− 0.1) (Table 1). These values suggest the virtual impossibility of solid-phase silica deposition in the analyzed water.

Table 1 A summary of the hydrochemical properties of the Lingzi abandoned mine groundwater

pH	6.3
SiO_2 (mg L^{-1})	10.1
Na (mg L^{-1})	215
K (mg L^{-1})	10.6
Ca (mg L^{-1})	418
Mg	156
Fe	0.1
Al	< 0.1
Mn	2.1
SO_4 (mg L^{-1})	1358
HCO_3 (mg L^{-1})	410
Cl (mg L^{-1})	226
SI	
Amorphous SiO_2	− 1.4
Chalcedony	− 0.5
Quartz	− 0.1

Identification of Silicified Microorganism-Related Particles

TEM analysis demonstrated a diverse array of particles in the GAM with microorganism-like characteristics. Most of these were shaped like spheres or droplets, with or without tails (Fig. 4). The diameters of these microorganism-like particles in the GAM ranged from ≈ 50 to 450 nm, most of them measuring ≈200 nm in diameter. Their size and morphology were similar to the microorganisms that have been commonly detected in many acidic mine drainage environments (Table 2). Iron and S, which are biophilic elements, were also detected by element mapping and EDS (Figs. 5 and 6).

In addition, TEM images from the Lingzi GAM showed numerous silica nanoparticles on the outside of microbes and associated extracellular polymeric substances (Fig. 7). While these nanoparticles had variable morphologies, their sizes ranged from 10 to 100 nm, and they surrounded the microorganism-like particles with a SiO_2 cortex. The TEM images showed a sharp boundary between the microorganism-like particles and the cortex, particularly since the SiO_2 cortex was lighter in color than the associated core (Fig. 7). Element mapping (Fig. 8) and EDS analyses (Fig. 9a) further demonstrated that the silica nanoparticles were formed from Si and O, with selected-area electron diffraction (SAED) patterns having characteristic diffuse halos confirming the existence of non-crystalline SiO_2 (Fig. 9b). Compared to the associated cortices, the cores had a lower Si and O content (Fig. 8).

Discussion

Origin of Silicified Microorganism-Like Nanoparticles

The pH of the GAM in the Lingzi coal mine was 6.3, with notable amounts of sulfate and iron present in the water

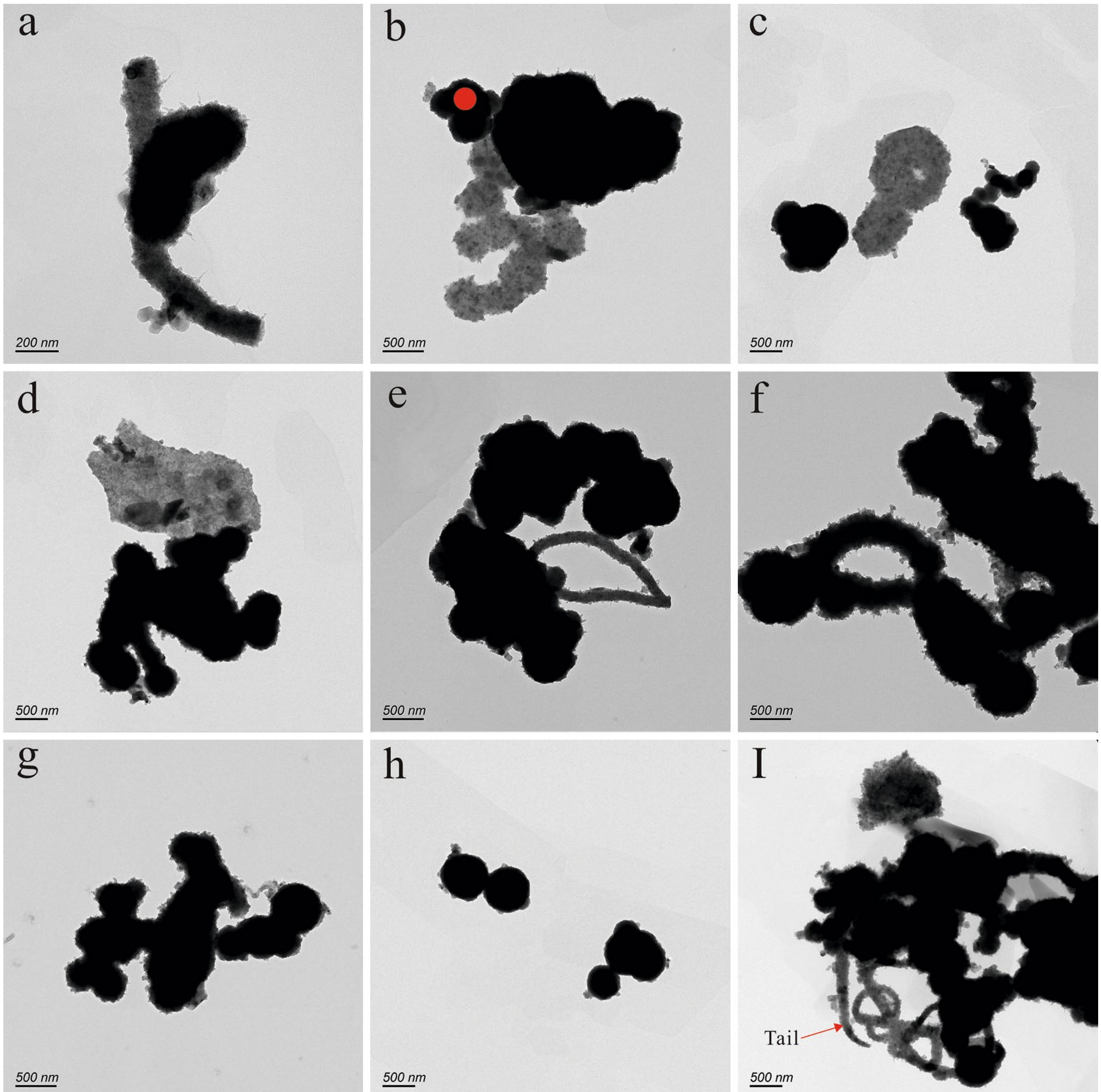

Fig. 4 Microorganism-like particles of different sizes and morphologies in groundwater from the Lingzi abandoned mine: (**a**–**h**) Microorganism-like particles without the tail. (i) Microorganism-like particles with a tail. The red dot in (**b**) shows the precise position of EDS analyses

Table 2 Common morphologies of microorganisms reported in water environments

Morphology	Family/genus	Representative	Size	References
Spherical	Globulaviridae	PSV1	≈100 nm in diameter	Haring et al. (2004)
		TTSV1	≈70 nm in diameter	Ahn et al. (2006)
		Nameless	≈30 nm in diameter	Rice et al. (2001)

system. Therefore, the GAM in the Lingzi coal mine was favorable for the existence of microbes. In addition, the silicified nanoparticles were spherical microorganism-like particles 250 nm in diameter and were associated with extracellular polymeric substances. The sizes of the cores were consistent with those of various microorganisms (e.g. Ahn et al. 2006; Häring et al. 2004; Peng et al. 2013; Rice et al. 2001). The nearly conventional nanoparticle-size division and cores in the coated nanoparticles were consistent with those of biological origin (cf. Ferris and Magalhaes 2008). Meanwhile, the association of silicified nanoparticles with biophile elements (e.g. Fe and S) suggest that the cores are of biogenic origin. Therefore, it is likely that the silica nanoparticles associated with extracellular polymeric substances could have been silicified

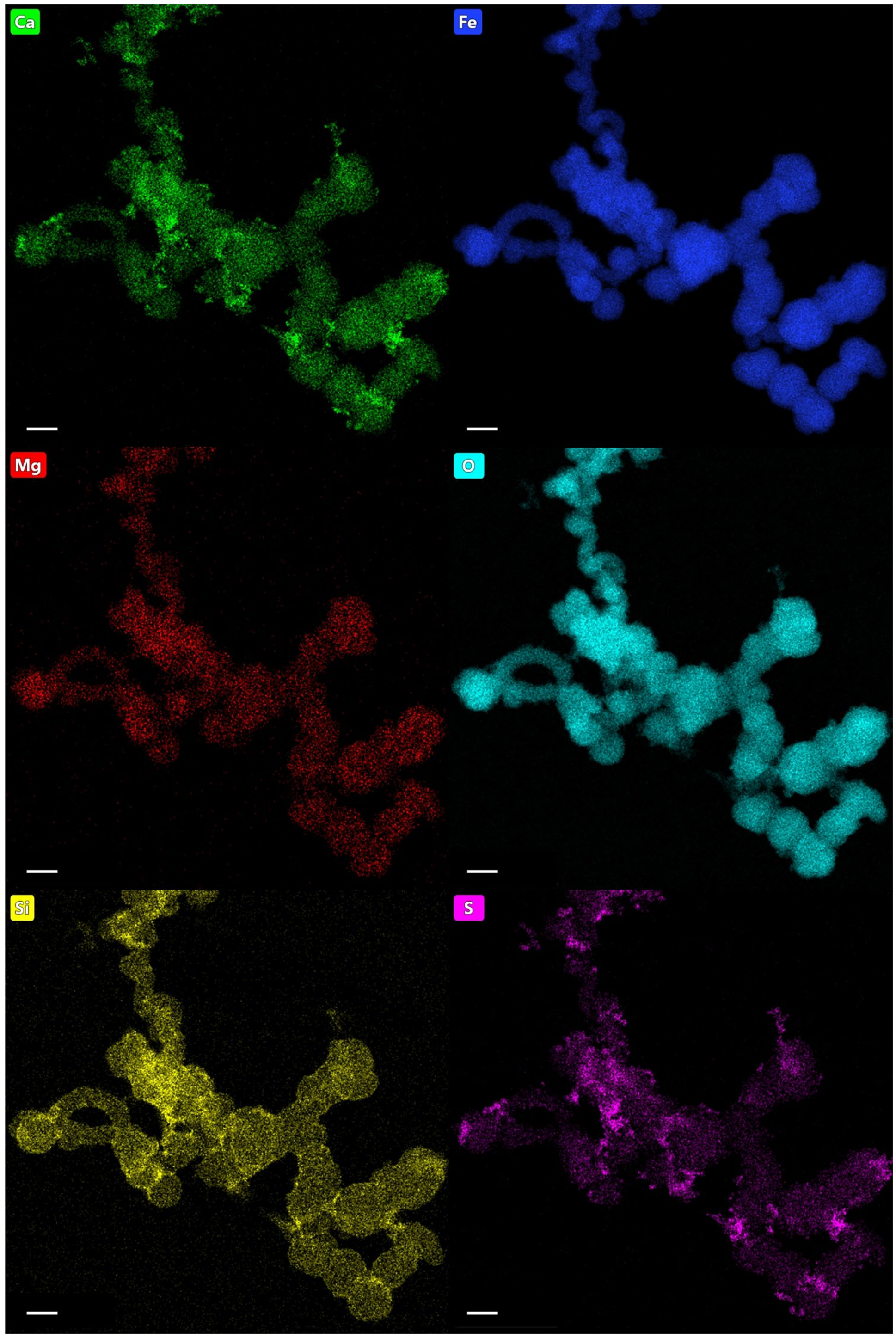

Fig. 5 Chemical composition of the microorganism-like particles shown in Fig. 4f, indicating that this particle in the GAM was composed of O, Fe, Si, S, Mg and Ca. Scale bar = 50 nm

microorganisms or cell detritus (small bits of protein) produced during the microorganism preservation process.

Possible Mechanisms Under Which Microorganisms-Like Particles Undergo Silicification

Orange et al. (2011) and Laidler and Stedman (2010) used a series of experiments to show that microorganisms (e.g. viruses) could be silicified in the laboratory. Moreover, Peng et al. (2013) have reported that microorganisms can also be silicified in natural settings, such as in a hot spring. In our GAM, the SI for SiO_2 was nearly negative (Table 1), indicating that SiO_2 cannot precipitate physically in this system. Therefore, there must be some other mechanisms regulating the formation of SiO_2, i.e. biomineralization. Microbial reproduction can occur via a lytic or lysogenic

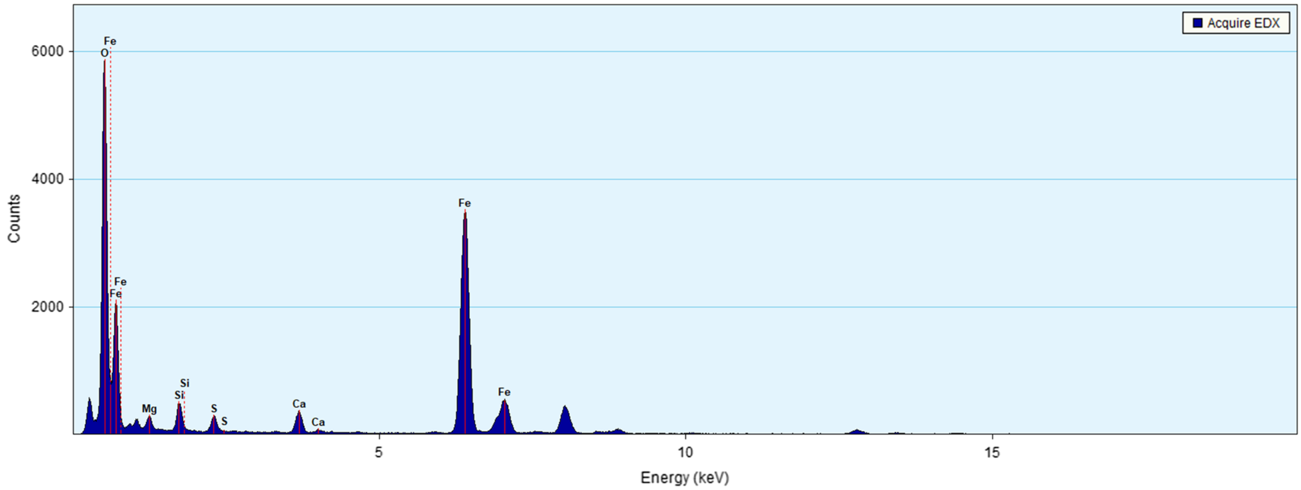

Fig. 6 Chemical composition of the microorganism-like particle shown in Fig. 4b, indicating that this particle in the GAM was composed of O, Fe, Si, S, Mg and Ca

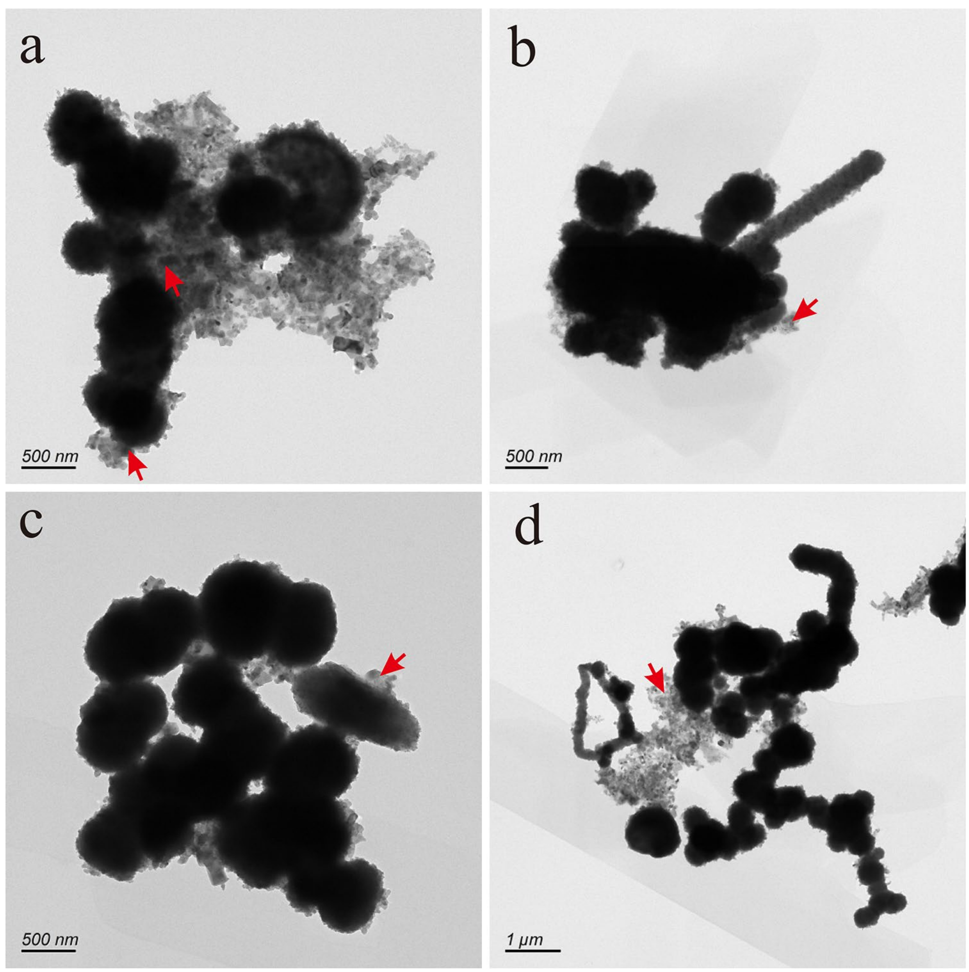

Fig. 7 Silica nanoparticles (red arrows) of different sizes and morphologies concentrated outside the microorganism-like particles in the groundwater of the Lingzi abandoned mine

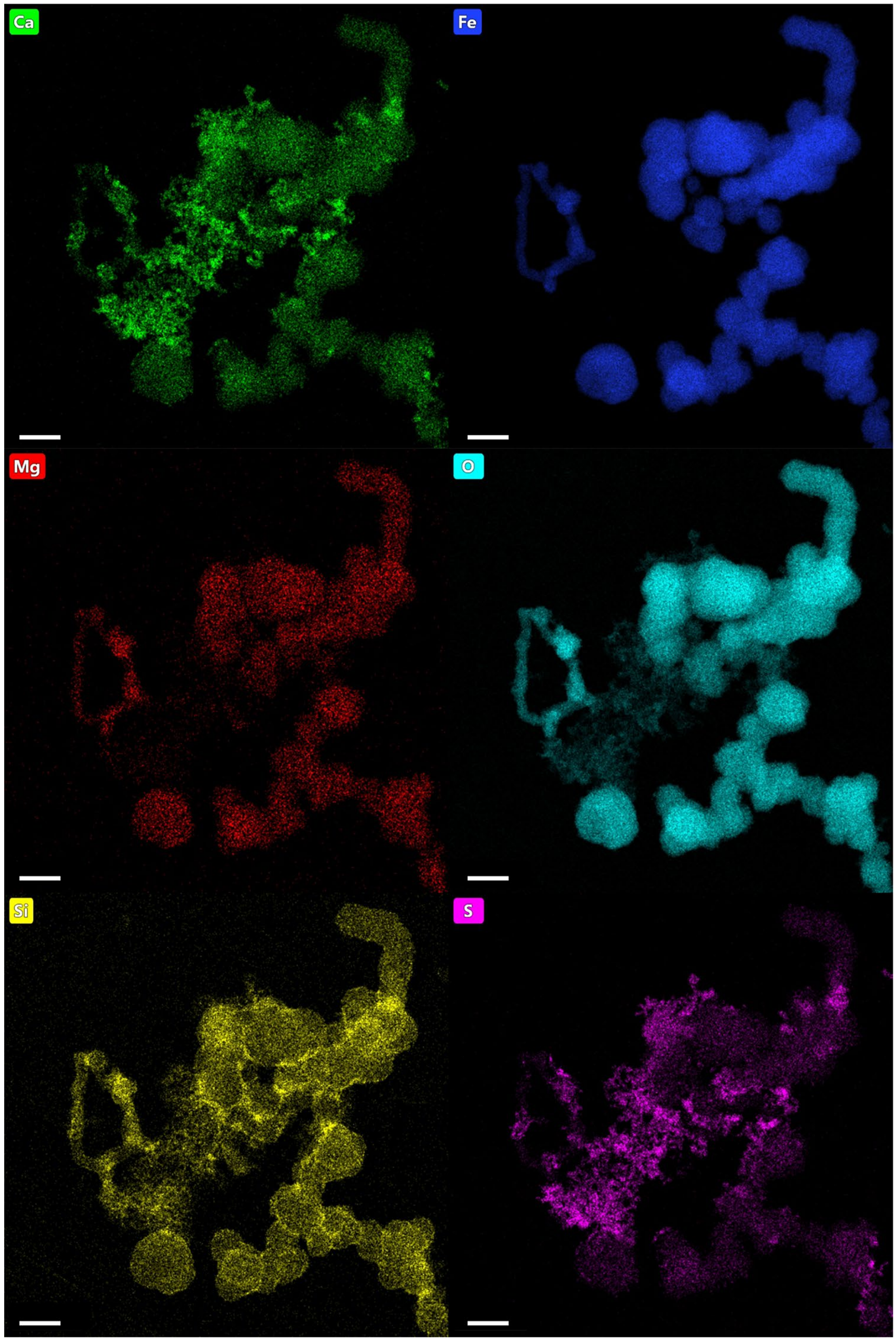

Fig. 8 Chemical composition of the silica nanoparticles shown in Fig. 7d, indicating that they were composed of O, Fe, Mg, Si, S and Ca. Scale bar = 50 nm

cycle. In the latter case, the nucleic acid of a microorganism is integrated into the chromosome of the host or exists as extrachromosomal plasmids within the cytoplasm of the host. The transmittance of the prophage to the daughter cells may take place during subsequent host cell division. In contrast, during the lytic cycle, microorganisms can be dispersed by the generation of individual lytic viruses that can survive outside host cells and can infect other cells. In addition, most microorganisms remain balanced in host cells as prophages and adhere to the lysogenic cycle. Consequently, lysed microbiological particles are not found inside infected cells. Silicified microorganisms-like nanoparticles found outside host cells in the GAM suggest silicification of the microorganisms during the lytic cycle rather than the lysogenic cycle.

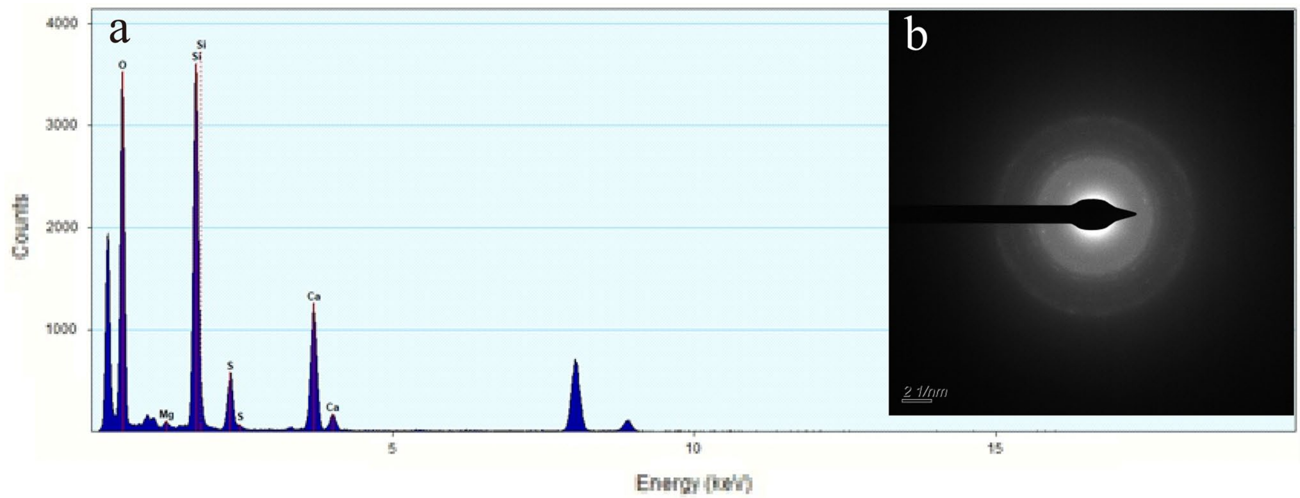

Fig. 9 Chemical composition of the silica nanoparticles shown in Fig. 6c, indicating that they were composed of O, Fe, Mg, Si, S, and Ca. **b** Selected-area electron diffraction patterns of the silica-coated nanoparticles indicating their non-crystallinity

Microorganism-like, round, silicified nanoparticles were exclusively observed in the Lingzi GAM. The predominance of these spherical forms presumably reflects the dominance of spherical microorganisms in the GAM and/or greater potential for the preservation of spherical particles than filamentous microorganisms. In this context, Orange et al. (2011) suggested that the preservation potential of microorganisms (e.g. viruses) depends on their structure, morphology, and/or chemical components.

If silicification of microorganisms had occurred in modern GAM, it would have been evident for a long time. The observation of microorganism-like silica nanoparticles in GAM indicated that GAM systems might supply targets for recording the process of microorganism biomineralization in a natural water environment. The typical measures for identification of spherical, silicified microorganisms as well as the process of microorganism biomineralization in natural water environment can include: (i) diameter, typically < 200 nm, (ii) distinct cores representing the original microorganism, (iii) levels of microorganism-like silica nanoparticles inside host cells, (iv) chemical biosignatures, such as Fe and S (Laidler and Stedman 2010), similar to those observed in some microfossils (House et al. 2000; Schopf et al. 2002).

A New Transport Form of Si in the Silicon Biogeochemical Cycle

Silicon biologically and geochemically interacts with other globally important biogeochemical elements (Struyf and Conley 2009). In addition, silicon is an essential nutrient for the growth of many microorganisms (e.g. diatoms). Microorganisms play an important role in the biogeochemical cycle of silicon in natural and manmade environments (Prentice et al. 2001; Ragueneau et al. 2006; Treguer et al. 1995). Others have noted how microorganisms and diatoms in mine water can take up silicon to build their siliceous cell wall or "frustule" (Douglas et al. 1998; Ohimain 2003; Perrin et al. 1992; Rohwerder et al. 2003). However, previous research revealed that the main form of silicon in the environment is dissolved silicate, i.e. ortho-silicic acid (H_4SiO_4), and it has been inferred that this form could be of prime importance in terms of silicon transport in the environment (Meybeck 1994).

In this study, amorphous silica nanoparticles were observed in the GAM settings, suggesting their occurrence in the natural water environments as well as their transport in the form of nanoparticles. Silica nanoparticles have been found in other natural media, such as soil aerosols (Liu et al. 2021), and could be important in transporting natural silica. In addition, research suggests that both aerosols and natural silica nanoparticles suspended in water can cause adverse health effects in animals, including humans (Ambrosone et al. 2014; Hirai et al. 2012; Nabeshi et al. 2011, 2012; Yamashita et al. 2011; Yoshida et al. 2011). Therefore, amorphous silica nanoparticles in the GAM settings could adversely affect aqueous environments.

Future Considerations

At present, the GAM at the Lingzi mine is being used for energy storage, via the mutual transformation of electrical energy and potential energy. However, fouling and scaling by silica can greatly decrease the performance of industrial facilities and equipment, especially their water treatment systems (Gunnarsson and Arnorsson 2005). Therefore, the potential effect of silica nanoparticles on the Lingzi coal mine water treatment system and pumped-storage processes should be investigated.

Conclusion

We investigated the nature and composition of silicified microorganism-related particles in the GAM. These particles, which were predominantly spherical, were first observed by TEM-mapping and were found to range between 50 and 450 nm in size. Furthermore, the silicified microorganism-like particles were found to contain Fe and S and to be amorphous in nature. These results suggest a biogenetic origin for the silicified microorganism-like particles. The novel nature of microbiological silicification implied that the silicified nanoparticles were presumably formed outside of the host cell before being released into the ambient environment. The results also indicated that microorganisms can be silicified in a mine water system, demonstrating a new form of silica transport in GAM and potentially affecting the quality of the aqueous environment.

Precipitation of amorphous silica in the immediate vicinity of microorganism cells and associated extracellular polymeric substances has been recognized in many natural systems but has not been well studied in the GAM. We anticipate that future research will be conducted areas such as the genetic sequencing of the microbes present, biomolecular investigations to determine the nature and presence of biosilicifying enzymes, encapsulation as a survival strategy in toxic environments, and the potential use of encapsulation to improve AMD bioremediation.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10230-023-00945-3.

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Data availability The data that support the findings of this study are available, upon reasonable request.

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