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Weathering of a mined quartz-carbonate, galena-sphalerite ore and release and transport of nanophase zinc carbonate in circumneutral drainage

Jeff B. Langman[a,*], James G. Moberly[b]

[a] Department of Geological Sciences, University of Idaho, Moscow, ID, USA
[b] Department of Chemical and Materials Engineering, University of Idaho, Moscow, ID, USA

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ABSTRACT

The formation and transport of geogenic metal nanoparticles in mining-impacted environments is a developing concern because of their potential for greater distribution compared to larger particles. Discharge from the abandoned Gem Mine in the Coeur d'Alene Mining District of northern Idaho was examined for the presence of metal nanoparticles from weathering of an ore body of galena [PbS] and sphalerite [(Zn,Fe)S] with associated carbonate zones of siderite [$FeCO_3$] and ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$] in intruded quartz veins. Analysis of this circumneutral discharge from the abandoned mine and groundwater in the receiving shallow aquifer indicate poor-quality mine drainage containing nanophase Zn-CO_3 form(s) that dissociate into smaller particles or ions with release into the new geochemical environment of the aquifer. The nanoparticles were identified through acid titrations and dynamic light scattering analysis of 450-nm-filtered mine water. The stability of the nanoparticles was estimated through ζ potential analysis of mine water and groundwater, which indicated limited stability of the nanoparticles that was sufficient for transport in the mine drainage but insufficient for transport in the aquifer. The release of the nanophase Zn-CO_3 form(s) likely occurs through weathering of secondary carbonate minerals in the mined areas of the Gem-Gold Hunter deposit through water-rock interaction → crystal repulsion → particle detachment → solution entrainment → and limited dissociation during transport as opposed to crystal formation in solution with mineral-phase saturation.

1. Introduction

The impact of legacy mines is a global issue and has resulted in extensive metal contamination of natural environments such as the Coeur d'Alene Mining District (District) of northern Idaho, also known as the Silver Valley. The District sustained considerable metal contamination because of legacy mining practices (Balistrieri et al., 2010; National Research Council, 2005; Reece et al., 1978; Sprenke et al., 2000), and this legacy impact continues to produce poor quality mine drainage that discharges substantial metal loads to surface- and groundwater systems (Balistrieri et al., 2010; Clark and Mebane, 2014; National Research Council, 2005). Entrance of oxygenated water into the District's abandoned mines results in weathering of metal-sulfide and metal-carbonate minerals and release of metals into the environment with subsequent mine discharge (Balistrieri et al., 2010; Box et al., 2001; Clark and Mebane, 2014; National Research Council, 2005). The form (ion to nanoparticle and ligand association) of the dissolved (< 450 nm) metals discharging directly from the mines is unknown but should be contingent on source minerals, seasonal weathering, transport processes, and environmental conditions (Boujelben et al., 2009; Cornell, 1991; Galán et al., 2003; Kretzschmar and Schäfer, 2005; Salvador et al., 2007; Stolpe et al., 2013).

The goal of this study was to identify the presence and composition of metal nanoparticles (< 450 nm = dissolved phase particles) in discharge from an abandoned mine and evaluate the persistence of these nanoparticles in the receiving shallow alluvial aquifer. The input of oxygenated water into abandoned mines may allow for the release and transport of metals as free ions or inorganic nano- to micro-scale particles (Balistrieri and Blank, 2008; Hochella et al., 2005; Hochella et al., 2008; Hoffmann et al., 2007; Plathe et al., 2013; Wigginton et al., 2007). The formation of transportable, inorganic metal nanoparticles with weathering of mined ore bodies poses substantial risks to water resources because of their potential for greater mobility and bioavailability compared to suspended particles (Delay and Frimmel, 2011; Ju-Nam and Lead, 2008; Keller et al., 2010). Metal nanoparticles formed in mining-impacted environments have shown selective persistence and transport as nanophase minerals or combined with other metals as inorganic multi-metal nanoparticles (Delay and Frimmel, 2011; Haus

* Corresponding author at: University of Idaho, Department of Geological Sciences, 875 Perimeter Drive, Moscow, ID 83844-3022, USA.
E-mail address: jlangman@uidaho.edu (J.B. Langman).

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et al., 2008; Hochella et al., 2008; Kretzschmar and Schäfer, 2005; Plathe et al., 2013; Wigginton et al., 2007).

The persistence of a transportable, mining-derived metal nanoparticle would depend on the process of nanoparticle formation and particle characteristics that would influence stability within the aqueous solution (Bostick et al., 2001; Guo and Barnard, 2012; Keller et al., 2010). Typically, nanophase minerals in solution are associated with mineral-phase saturation, but recent studies have found the ejection of nano- to micro-scale metal-carbonate particles into solution from mineral surfaces because of grain-scale repulsive forces that enhance surface retreat (Emmanuel et al., 2015; Levenson and Emmanuel, 2017). Weathering of carbonate minerals has traditionally assumed to occur through chemical dissolution, but the identification of a mechanical force that enhances weathering alters the perception of the release and transport of carbonate metals (Levenson and Emmanuel, 2016).

2. Study area and methods

The field site for this study is located in the District's Burke Canyon, which contains an abandoned mine discharge that infiltrates to the local alluvial aquifer. The District and Burke Canyon (Fig. 1) are located in the upper Coeur d'Alene River Basin, which is bounded by the Coeur d'Alene Mountains that are part of the Bitterroot Range of the Northern Rocky Mountains. The Coeur d'Alene Mountains are composed of the quartzite, siltite, and argillite of the Precambrian Belt Supergroup, which contain the ore-bearing formations that have been mined for Ag, Pb, and Zn since the 1880s (National Research Council, 2005). The ore primarily consists of argentiferous galena [PbS] and sphalerite [(Zn,Fe)S] in thin (< 1–2 m) quartz veins. Associated with the sulfidic ore are carbonate zones consisting primarily of siderite [$FeCO_3$] and ankerite [$Ca(Fe,Mg,Mn)(CO_3)_2$]. Within Burke Canyon is the abandoned Gem Mine that targeted the Gem-Gold Hunter mineral belt within the Burke and Prichard formations of the Belt Supergroup (Criss and Eaton, 1998; Leach et al., 1988). The Gem Mine operated from 1889 to 1967 and produced 2.5 Mt. of ore from which 191 t of Ag was extracted from an ore body located about 1000 m below land surface (Long, 1998; Mitchell and Bennett, 1983).

Burke Canyon was a focal point of mining in the District and contained the region's first silver mine (1884). Mining ceased in the canyon in 1981 with closure of the last active mine (Star Mine—the deepest mine in North America at 2470 m upon its closure). Today, the canyon contains numerous abandoned mines, and infiltrating water weathers the exposed carbonate-sulfide veins of the submerged adits below the canyon floodplain. At Gem Mine, the long travel path of the mine water (ore body around 1000 m deep) returns circumneutral, metal-laden water to the surface through the mine portal where mine water is collected and discharged to the alluvial floodplain of Canyon Creek (Fig. 2). At the discharge apron, mine water velocity is slowed and oxygen is introduced, which allows for precipitation of metals, growth of microbial flocs, and infiltration of the water to the shallow groundwater (Fig. 3). The Gem Mine discharge is the largest contributor to metals being transported in the shallow alluvial aquifer beneath Canyon Creek (CH2MHILL, 2007), and an ideal location to evaluate the formation and transport of geogenic metal nanoparticles derived from weathering of the mined quartz-carbonate, galena-sphalerite ore body.

Burke Canyon is a high gradient, V-shaped, deeply incised canyon of approximately 60 km^2. The study area (Fig. 2) is near the upper portion of the Lower Burke Canyon Waste Rock Repository, approximately 4 km upstream of Canyon Creek's discharge to the South Fork of the Coeur d'Alene River. The shallow alluvial aquifer beneath the Canyon Creek floodplain consists of unconsolidated alluvium. This aquifer has a thickness ranging from 3 to 15 m and is about 4–5 m thick in the study area (CH2MHILL, 2007). Near the Gem Mine discharge are an upgradient well and a downgradient well (Fig. 2) screened in the shallow alluvium at 1–5 m below land surface. Beneath the shallow alluvium is a leaky aquitard composed of clayey deposits or argillite with clayey deposits (CH2MHILL, 2007). Discharges from the mines and natural drainages feed Canyon Creek and the associated alluvial aquifer. The downgradient well reflects groundwater representative of the upgradient groundwater mixed with infiltrated Gem Mine discharge. There are no other surface water inputs between the two wells, and it is unlikely there are additional groundwater inputs between the wells because of the shape and geology of the canyon.

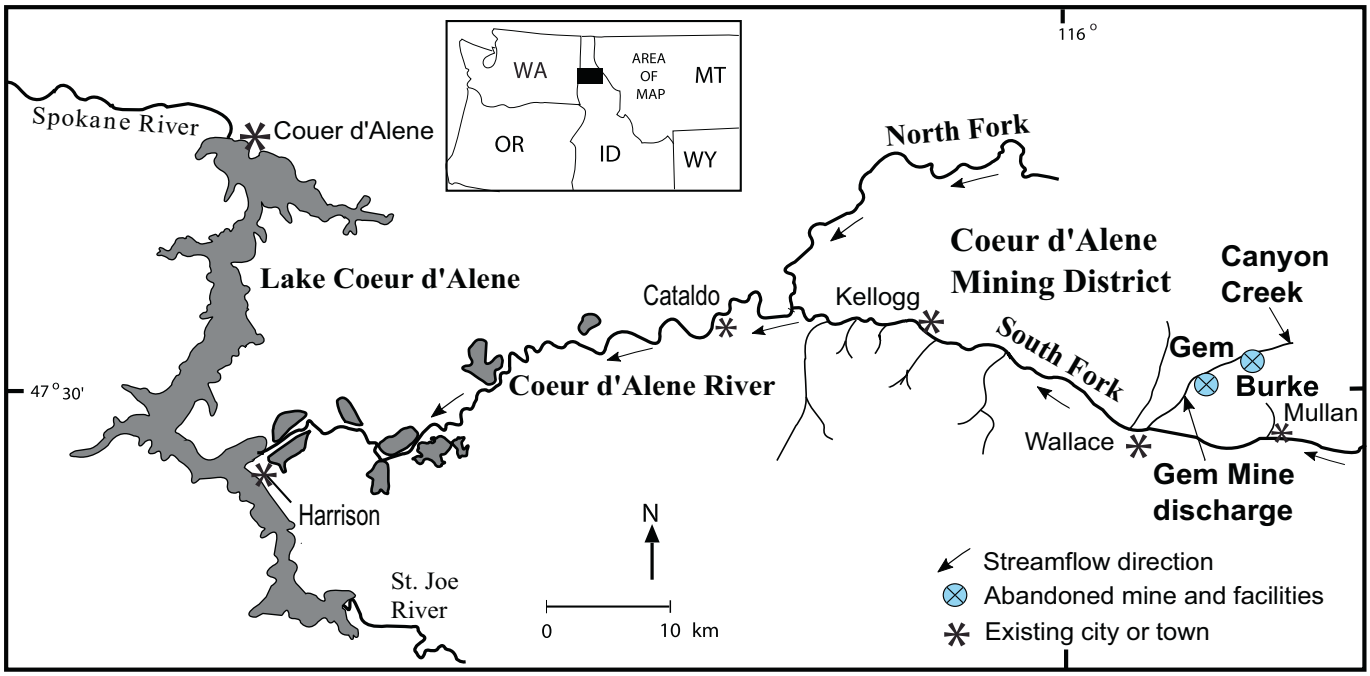

Fig. 1. Location of the Coeur d'Alene Mining District and Gem Mine discharge to Canyon Creek in Burke Canyon, Coeur d'Alene River Basin, Idaho.