Nitrogen stable isotope composition and the origins of cupric nitrate mineralization

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ABSTRACT

Cupric nitrate minerals are rare, but when present may record evidence of past biological activity. The cupric nitrate minerals we examined from localities around the world are broadly divided into four main groups based upon their inferred conditions of formation and $\delta^{15}N$ values. These groups, named for their probable source of nitrogen, include: 1) termite, 2) bat, 3) atmospheric and 4) coal mine fires and natural gas. It is clear that in three of these categories, the role of past or present biological activity is critical for formation of cupric nitrate minerals. For cupric nitrate minerals associated with an atmospheric source of nitrogen the link is not clear, though a microbial source is possible. Nitrogen isotope analyses of gerhardtite and buttgenbachite mineral pairs from two localities suggest fractionation between these two minerals at ambient temperatures is 1.1‰ (Australia) to 0.8‰ (Democratic Republic of Congo). Similarly, differences between $\delta^{15}N$ values of sal ammoniac and gerhardtite pairs suggest fractionation between these minerals at higher temperatures in coal bed fires is 1.9‰ (Pennsylvania, USA) to 1.7‰ (Germany).

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1. Introduction

Cupric nitrate minerals are rarely observed in the oxidized zone of copper deposits. Recognized species include gerhardtite ($Cu_2[NO_3|(OH)_3]$), buttgenbachite ($Cu_{19}[Cl_4|(NO_3)_2|(OH)_{32}] \cdot 2H_2O$), likasite ($Cu_3[NO_3|(OH)_5] \cdot 2H_2O$), and rouaite ($Cu_2[(OH)_3|NO_3]$). The uncommon occurrence of these minerals reflects the usual dominance of other dissolved anionic species (e.g. HCO_3, SO_4, Cl) relative to aqueous nitrogen species in natural waters. For cupric nitrate minerals to develop, aqueous nitrogen, usually speciated as nitrate (NO_3^-), must be locally present at levels that make it the dominant anion available for copper mineral deposition.

Gerhardtite is perhaps the most widespread of the cupric nitrate species. Gerhardtite forms orthorhombic crystals of emerald- to turquoise-blue color. It was first described as a natural occurrence by Wells and Penfield (1885) and named in honor of French chemist Charles Frederic Gerhardt (1816–1856) (Anthony et al., 2003). The type locality for gerhardtite is the United Verde Mine at Jerome, Arizona, USA (Wells and Penfield, 1885), though the mineral occurs at four other localities in the USA (e.g., Lindgren and Hillebrand, 1904; Lindgren, 1905; Williams, 1961; Rosemeyer, 1990). Gerhardtite has also been confirmed in France (Sarp et al., 2001), Germany (Wittern, 2001; Kolitsch et al., 2010), Spain (Viñals et al., 2010), Italy (Franzini and Perchiazzi, 1992), Ukraine (SSSR, 1969), Democratic Republic of Congo (Oswald, 1961), and Kazakhstan (Voloshin et al., 1988). A relatively recent discovery of gerhardtite at the Great Australia deposit in Cloncurry, Queensland, Australia has produced some of the most spectacular and rich specimens known to date, with crystal aggregates up to 2 cm (Wallace and Pring, 1990). Gerhardtite is also reported by personal communication through www.mindat.org for Chile at the Los Azules Mine (Terry Szenics) and the Quebrada Blanco Mine (Bob Jenkins), and in the Rudabányai Mountains of Hungary (G. Koller).

Buttgenbachite is a deep-blue translucent mineral. It is named for Belgian mineralogist Henri Buttgenbach (1874–1964) and was first described at the Likasi (Panda) Mine, Democratic Republic of Congo (Schoep, 1925; Anthony et al., 2003). It is also reported for Queensland, Australia (Anthony et al., 2003); Cornwall, England (Anthony et al., 2003); three locations in Arizona (Williams, 1963; Hibbs et al., 2006), Nevada (Castor and Ferdock, 2003), and Michigan (Heinrich and Robinson, 2004).

This study presents nitrogen isotope data for these rare copper nitrate minerals, in an attempt to explore the unusual conditions under which they form. Nitrogen isotope data for nitrate mineral pairs are also presented to quantify $\Delta^{15}N$ values. Understanding these paleo-environmental conditions, nitrogen fractionation behavior between nitrate minerals, and the highly variable sourcing of nitrogen for these minerals may have application to mineralogists and biogeochemists wishing to differentiate biological vs. abiological nitrogen sources in paleoenvironments.

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2. Methods

Twenty one samples of cupric nitrate minerals and three samples of copper-stained sal ammoniac (NH_4Cl) were collected from 11 locations representing diverse depositional environment conditions around the world (Fig. 1, Table 1), and analyzed for $\delta^{15}N$ values. Sample pedigree is provided here to document the degree of reliability for true origins of these exceedingly rare samples. At the Bisbee Mine, Arizona locality several specimens from the buttgenbachite ($Cu_{19}[Cl_4|(NO_3)_2]|(OH)_{32}] \cdot 2H_2O$)–connellite ($Cu_{19}[Cl_4|(SO_4)|(OH)_{32}] \cdot 3H_2O$) solid solution were obtained from Bisbee mine geologist Dick Graeme, and from specimens collected in 1992 by the lead author and Mike Schern. These specimens of radiating acicular crystals on cuprite were tentatively identified as buttgenbachite (nitrate-dominant) rather than connellite (sulfate-dominant), based upon broad-spectrum EDS analyses where $SO_4^{2-} < NO_3^-$ (e.g., Hibbs et al., 2002, 2003a, 2003b). Samples of gerhardtite on metabasalt from the Caledonia Mine, Michigan were obtained from the collections of mine owner Richard Whiteman, and Tim Rose. The samples from the Likasi (Panda) Mine, Democratic Republic of Congo (D.R.C.) were obtained from the Mineralogical Research Company and Excalibur Minerals. The Dzhezkazgan Mine, Kazakhstan samples came from Peter Williams and Excalibur Minerals. While employed by Phelps Dodge Corporation between 1990 and 1993, the lead author collected the specimens of gerhardtite from the Morenci Mine, Arizona near Copper Mountain and the Stargo area. Gerhardtite and buttgenbachite–connellite samples on cuprite from the Great Australia Deposit, Queensland, Australia were collected in 1997 by the lead author, Peter Williams, Jim Sharpe, and Bernie Day. The lead author and Eduardo Campos collected gerhardtite from the Zaldivar and Lomas Bayas Mines, Chile in 2008. The Zaldivar Mine samples were collected on the 2990 m level within the top of the oxide zone at the conglomerate/bedrock contact. The samples from the Lomas Bayas Mine were collected from the conglomerate/bedrock contact exposed in the top benches at two places several hundred meters apart on the 1600 m level. Gerhardtite and melanterite overgrowths on massive sabieite and sal ammoniac from Lichtenberg Absetzer Mine, Thuringia, Germany were obtained from Dave Shannon Minerals in 1995. Gerhardtite, atacamite, and sal ammoniac growths on copper wire scraps were collected by the lead author in 1999 at a vent site in the town of Centralia, Pennsylvania. Copper-stained Letovicite from the Kukhi-Malik area of Tajikistan was obtained from Dave Shannon Minerals in 1995.

A high-purity concentrate of the copper nitrate mineral from each location was prepared by handpicking small (<2 mm) cleavage fragments and crusts from a coarsely crushed sample. Mineral separates were ground to −200 mesh and mixed thoroughly by 10 passes through a micro-splitter to maximize homogeneity. Purity was checked by EDS analysis and element mapping, optical examination, and confirmed by powder X-ray diffraction (XRD) analysis and the consistent stoichiometric nitrogen gas yield from combustion for isotope analyses. The XRD analyses were performed on a Philips X-Pert diffractometer. A Philips Electronics Instruments Silicon Powder Standard (Type N: 52131) and an alpha quartz sample from Hot Springs, Arkansas were run as XRD standards. Centroid peak errors on the standards were +/− 0.002 2θ. These mineral specimens were analyzed by combustion using a ThermoFinnigan Deltaplus in-line element analyzer and stable isotope ratio mass spectrometer at the Environmental Isotope Laboratory at University of Waterloo, Canada. Replicate analyses were performed by combustion using an in-line element analyzer and ThermoFinnigan Deltaplus stable isotope ratio mass spectrometer at the University of California Riverside Facility for Isotope Ratio Mass Spectrometry (FIRMS) and at University of Waterloo, and by standard off-line combustion methods (e.g., Silva et al., 2000) with analysis by ThermoFinnigan Deltaplus Advantage stable isotope ratio mass spectrometer with multi-port inlet at the Geochemistry Laboratory at California State University, San Bernardino. All analyses were calibrated to in-house standards. Statistical uncertainty is assumed to represent total uncertainty. Systematic biases related to sample preparation are presumed to be minimal, due to uniform sample handling, fine grinding, and mixing. Nitrogen isotope analyses are reported in the usual manner, as δ notation ‰ deviations from the AIR standard. Standard deviation for duplicate $\delta^{15}N$ analysis is better than ±0.33‰ for mineral samples.

3. Results

Results of stable isotope analyses are presented in Table 1 and Fig. 2. $\delta^{15}N$ values were dominantly positive, with values for cupric nitrate minerals ranging from −1.0 to +16.6‰ (Table 1). The $\delta^{15}N$ values for individual localities are remarkably consistent and relatively unique with respect to other localities, suggesting that our samples from

Fig. 1. Map of cupric nitrate localities analyzed as part of this study. UTM locations of sample collection points are provided in Table 1.