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Copper and arsenic (enargite) contamination of soils along a toposequence in Chinkuashih, northern Taiwan

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ABSTRACT

This study investigates the species of Cu and As (enargite) residues present in soils of the Chinkuashih area, northern Taiwan. Two pedons, on the shoulder and footslope along a toposequence, were examined for their metal partitioning and geochemical origins. The bulk soils were analyzed by sequential extraction combined with mineralogical analyses, including X-ray diffraction (XRD) and scanning electron microscopy / energy dispersive spectrometer (SEM / EDS) analyses. Soil pH ranged from 4.23 to 4.91 with low base saturation, and the soils can be classified as fine, mixed, thermic, Typic Kandiudults. Mineralogical study indicated that enargite and pyrite particles mainly coexisted in silt and sand fractions, particularly in lower soil horizons of the footslope, showing high contents of Cu and As. Kaolinite and illite were dominant minerals in clay fractions. The footslope accumulated more total Cu and As than that of shoulder pedon. The sequential extraction experiments resulted in high proportions of Cu remaining in residual fractions, while the most of As was bound in amorphous Fe and Al oxyhydroxide fraction. The risk analyses of Cu and As (enargite) contamination in soils of the Chinkuashih area merits further study.

1. Introduction

Enargite is a copper arsenic sulfide with formula of Cu_3AsS_4. It is found in some orebodies associated with other sulfides such as pyrite, sphalerite, bornite, galena, and chalcocite. Significant amounts are found in the so-called 'high sulfidation' volcanic-hosted epithermal deposits (Sasaki et al., 2010a). With respect to potential environmental issues, there is an obvious threat represented by release of toxic elements (copper and arsenic) and acidity. This is especially true for acidic soils affected by intensive precipitation and with a lower adsorption capacity.

However, most published papers about enargite are concerned with the leaching process, mineralogy and geology. For example, Curreli et al. (2009) reported that using alkaline Na_2S solutions, 98% arsenic could be leached from enargite–luzonite minerals, while copper in enargite was converted into a new species with chemical formula $Cu_{1.5}S$. Sasaki et al. (2010a) found that amorphous ferric arsenate was formed in the bioleaching of enargite by *Acidithiobacillus ferrooxidans*. Padilla et al. (2010) further noted that the rate of dissolution of copper from enargite in the mixed sulfidized concentrate was faster than dissolution rate of copper from pure enargite concentrate, due to a galvanic couple with pyrite or indirect leaching by ferric ions. Moreover, Oyarzun et al. (2006) showed that long-term continuous natural erosion of As–Cu rich sulfide ores (including the important presence of enargite) and their mineral deposit, led to important and widespread metal dispersion along the Elqui watershed (northern Chile). But as previously stated, less information is available for mineral constituents and the potential environmental risk of metals (Cu and As) in the soils derived from the parent materials containing enargite.

The topographical position of a location is the most important factor in controlling trends in metals and minerals distribution in hilly region. Cheng et al. (2011) reported that footslope accumulated more total Cr and Ni than shoulder and backslope in serpentine soils. This is attributed to soil on the footslope receiving more effective precipitation as runoff from the upslope and there potentially being more leached than soils of the other topographies. In contrast, Hseu (2006) reported that the total Cr and Ni of the pedons along a serpentinitic toposequence were in the following order: summit≥shoulder>backslope≥footslope. Cornu et al. (2005) noted that along a Planosol toposequence developed in metamorphic parent material at a slope, Fe and Cu were found to accumulate in the middle of the slope, while Pb and Mn accumulated at the base. This was related to the water dynamics and hydromorphic conditions prevailing along slope. But, few pedologic studies have provided detailed information about the mineralogy, fractions of metals (Cu and As) and the influence of topography on their distributions in enargite soils. Therefore, this study aimed to (i) clarify the topographic effect on the

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distribution of minerals, (ii) partition Cu and As into different fractions in enargite soil profile along a northern Taiwan toposequence, and (iii) explore some enargite soil properties and pedogenic processes related to mobility of Cu and As.

2. Materials and methods

2.1. Study site description and sampling

The study area is located in the Chinkuashih hilly region (25° 07' N, 121° 51' E) on the Pacific coastal range of northern Taiwan (Fig. 1A). Epithermal high-sulfidation enargite (Cu_3AsS_4)–gold deposits at the Chinkuashih area occurred both within Pleistocene andesite and Miocene sedimentary rocks (Wang, 2010). The major ore minerals in the Chinkuashih area are enargite, pyrite, luzonite and silver-bearing gold, along with a few other accessory metallic minerals (Fang et al., 2004). The common gangue minerals include quartz, barite, alunite, sericite, clay minerals, as well as local accessory sulfur, diaspore, and limonite (Chen et al., 2001). Information about minerals and parent materials at the Chinkuashih can help to explain metals distribution in soils.

The annual precipitation is 5000 mm, with the Chinkuashih experiencing more than 200 rainy days a year. Its temperatures are generally 3–10 °C in the winter and 32–38 °C in the summer. In contrast with other parts of Taiwan, vegetation of the Chinkuashih hilly region is characterized by the predominance of evergreen shrubs, including *Dicranopteris pedata* and *Rhizoma Phragmitis*.

Two pedons were selected to represent the degree of soil development in different topographical positions along the hillslopes. Pedon 1, on the shoulder, is located at latitude 25° 07' 02" N and longitude 121° 51' 26" E, at an elevation of 270 m and average slope of 45%, with well drainage. Pedon 2, on the flat footslope, is located at latitude 25° 07' 08" N and longitude 121° 51' 38" E, at an elevation of 89 m and average slope of 18%, with poor drainage (Fig. 1B). These two pedons were exposed by excavating pits to the depth of the C horizon. Pedon 1 was divided into five horizons, namely 0–3 (A), 3–10 (AB), 10–18 (Bt_1), 18–34 (Bt_2) and 34–43 cm (Bt_3), and pedon 2 into seven horizons of 0–5 (A), 5–15 (AB), 15–25 (Bt_1), 25–35 (Bt_2), 35–50 (Bt_3), 50–65 (Bt_4) and 65–80 cm (Bt_5). Both pedons were east facing. Soil samples were collected from each horizon to determine their physical and chemical properties varying with depth (Table 1). The soil samples were air-dried and crushed to pass through a 2-mm sieve for subsequent laboratory analyses.

2.2. Soil analyses

Organic matter was removed with 30% H_2O_2 solution by heating on a hot plate. The particle-size distribution was determined by pipette method (for clay and silt), and silt was separated from sand by wet sieving (sieve 53 μm) techniques (Gee and Bauder, 1986). Size fractions obtained were then classified as clay (<2 μm), silt (2–50 μm) and sand (50–2000 μm). Clay fractions were dialyzed against distilled water and freeze-dried (Jackson, 1979). Soil pH was determined with a pH meter (Mettler-Toledo EL20K) in 2:1 water/soil suspensions (Thomas, 1996). Total organic carbon (TOC), total nitrogen (TN) and total sulfur (TS) contents were measured by automated dry combustion gas chromatography using a Carlo-Erba NA-1500 elemental analyzer (Carlo-Erba, Milan, Italy). Soil cation-exchangeable capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}) were extracted with 1 mol L^{-1} ammonium acetate buffered at pH 7.0 (Rhoades, 1982), and concentrations determined by inductively coupled plasma-optical emission spectrometry (ICP-OES, Perkin–Elmer, Model Optima 2000 DV). Free Al- and Fe-oxides (Al_d and Fe_d) in soils were extracted by dithionite–citrate–bicarbonate (DCB) solution and determined by ICP-OES (Mehra and Jackson, 1960).

To identify the sequential fractions for Cu and As, a metal analyses of soils was conducted by a method modified from Wenzel et al. (2001) or Yolcubal and Akyol (2008). One gram of air-dried soil sample (<2 mm) was placed in 50 mL centrifugation tubes and 25 mL of extracted solutions were added sequentially. The soil metal fractions determined by this sequential-extraction method were as follows: (1) nonspecific bound easily exchangeable fraction (F1), extracted with 50 mmol L^{-1} $(NH_4)_2SO_4$ solution (shaking 4 h, 20 °C); (2) strongly bound inner-sphere complexes fraction (F2), extracted with 50 mmol L^{-1} $(NH_4)_2H_2PO_4$ solution (shaking 16 h, 20 °C) from the residue of (1); (3) bound to carbonate fraction (F3), the residue from (2) was extracted with 1 mol L^{-1}, pH 5 of NaOAc/HOAc buffer solution shaking at 20 °C for 6 h; (4) bound to Mn oxyhydroxides fraction (F4), extracted with pH 6 of 100 mmol L^{-1} $NH_2OH \cdot HCl + 1$ mol L^{-1} NH_4OAc solution (shaking 30 min, 20 °C) from the residue of (3); (5) bound to amorphous Fe and Al oxyhydroxides fraction (F5), the residue from (4) was extracted with pH 3.25, 200 mmol L^{-1} of NH_4-oxalate buffer solution shaking 4 h in the dark at 20 °C, wash step with pH 3.25, 200 m mol L^{-1} NH_4-oxalate buffer solution, shaking at 20 °C for 10 min. (6) bound to sulfides and organic matter fraction (F6), the residue from (5) was extracted with 15 mL, 30% H_2O_2 and 3 mL, 20 mmol L^{-1} HNO_3 (shaking 2 h, 85 °C), and 5 mL, 3.2 mol L^{-1} NaOAc solution (shaking 3 h, 85 °C). Between each successive extraction step, the solution was separated from the solid phase by centrifugation (5000 rpm, 10 min), and then filtered through 0.45 μm filter paper (Whatman 42). The total fraction of each soil metal was determined by digestion with aqua regia solution (US Environmental Protection Agency, 2007). In all solutions, Cu and As were measured by ICP-OES. (7) The residual fractions (F7) were calculated from total Cu and As subtracted from $F1+F2+F3+F4+F5+F6$.

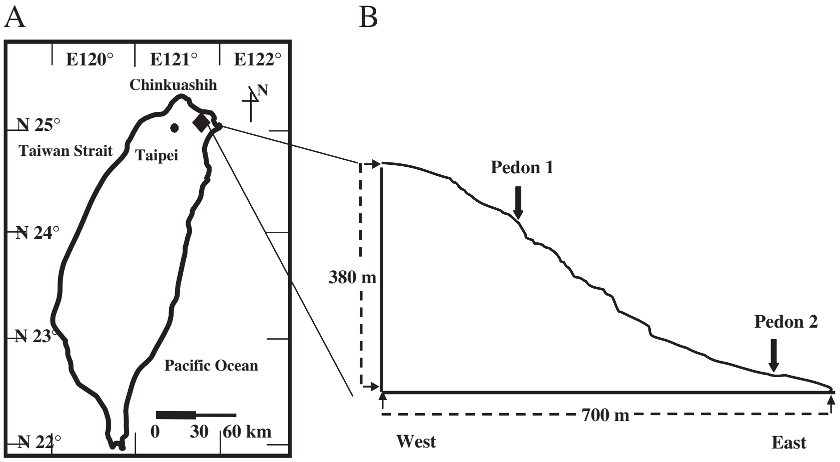

Fig. 1. (A) Location of the study area in northern Taiwan and (B) elevation of two pedons.