Corderoite, First Natural Occurrence of α-Hg$_3$S$_2$Cl$_2$, from the Cordero Mercury Deposit, Humboldt County, Nevada

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Abstract

Corderoite, Hg$_3$S$_2$Cl$_2$, (isometric; space group $I2_13$, $a_0 = 8.94$ Å, $Z = 4$, $d_{calc} = 6.85$ gm cm^{-3}), a new mineral from the Cordero mine in Humboldt County, Nevada, occurs in late Miocene playa sediments in association with montmorillonite, α-quartz, α-cristobalite, and cinnabar. It is also found, along with cinnabar, within the "opalite" layer, which consists of silicified rhyolitic tuffs and sediments at the base of the lake beds, and within altered basement volcanics below the opalite layer. In all cases corderoite replaces cinnabar.

The powder diffraction pattern and chemical composition for corderoite are analogous to those for the material synthesized and described by Puff and coworkers (1962) and are the same as for α-Hg$_3$S$_2$Cl$_2$ synthesized by Carlson (1967) and described by Frueh and Grey (1968).

Fresh corderoite is light orange pink (5YR 8/2) but upon exposure to artificial light or sunlight becomes light gray to black (N6 to N2). Grain size is less than 2 μm in diameter for the natural corderoite specimens. Because the grains are so small, crystals of α-Hg$_3$S$_2$Cl$_2$ were synthesized by Carlson's (1967) method. For these synthetic crystals, refractive index $n > 25$. Reflectances in air are $R_{650\,nm} = 15.1$; $R_{589\,nm} = 15.1$; $R_{546\,nm} = 15.5$, and $R_{470\,nm} = 16.7$ percent VHN$_{15}$. Vickers hardness numbers for 15 and 25 g loads are: VHN$_{15} = 35$-58 with a mean of 45; VHN$_{25} = 28$-61, mean 48. Optical properties are: isotropic and colorless-pale yellowish white.

Introduction

Corderoite, Hg$_3$S$_2$Cl$_2$, found by Foord in February 1973 in samples of mercury ore from the playa sediments adjoining the Cordero mercury deposit, Humboldt County, Nevada, has been synthesized previously (Puff and Kohlschmidt, 1962; Carlson, 1967), but this marks the first description of the natural material.

The name corderoite has been submitted to and approved by the Commission on New Mineral Names of the International Mineralogical Association, and is taken from the name of the major mercury mine (Cordero mine) in what is known as the Opalite Mining District. The name cordero is derived from the Basque language, meaning 'little lamb,' after the original discovery of ore specimens by Basque prospectors during the lambing season.

This paper describes the occurrence, genesis, and physical characteristics of corderoite.

Mode of Occurrence

Corderoite, with or without cinnabar, occurs predominantly in Upper Miocene playa sediments within an approximately 5–7 meter thick zone subparallel to bedding or as irregularly distributed discontinuous masses. This mineralized zone increases in depth away from the surface exposures of volcanic basement rocks on which the lake sediments were deposited (see Figure 1). The lake sediments consist of clays (altered tuff and ash) with lesser amounts of agglomerate and small lenses of chalcedony. The associated ore zone minerals are mainly pale-green-to-buff-colored montmorillonite, α-quartz, α-cristobalite, alkali feldspar, and plagioclase feldspar. Corderoite occurs in this zone as separate masses or as replacements and rims for cinnabar.

The corderoite-bearing zone locally includes the top of the "opalite" layer at the base of the lake beds and above the volcanic basement. The "opalite"

zone consists of rhyolitic tuffs and overlying sediments which are silicified and replaced by α-quartz and α-cristobalite. Corderoite and cinnabar also occur within hydrothermally altered rhyolitic breccia in the main Cordero mine and nearby underground workings and surface pits.

In all cases, the material is less than 2 μm in diameter. In excess of several hundred tons of corderoite exist within the mineralized zone. The corderoite is light orange pink (5YR 8/2), but becomes light gray to black (N2–N6) upon exposure to artificial light or sunlight. Other photosensitive mercury minerals such as the oxychlorides have been described by Ford (1932).

Possible Genesis of the Corderoite

Attempts to synthesize crystals large enough for measurement of microhardness, reflectance, and other optical properties will be described first, followed by a series of experiments designed to explore the possible mode of formation of corderoite in nature.

Synthetic corderoite formed by heating stoichiometric mixtures of red HgS and $HgCl_2$ in evacuated glass tubes at temperatures of 140°C to 155°C was too fine-grained (less than 5 μm) to be of much use (Puff and Kohlschmidt, 1962). The material formed at 140°C was light orange pink (5YR 8/2), whereas that formed at 155°C was very light gray (N8).

Crystals large enough (up to 1 mm long) for optical studies and microhardness and reflectance measurements were synthesized in the cool end of a gradient furnace (410°C–300°C) by reacting HCl gas with solid red HgS (Carlson, 1967). Metacinnabar-cinnabar grew in the temperature region of 375°C–345°C, and α-$Hg_3S_2Cl_2$ below 345°C. No γ-$Hg_3S_2Cl_2$ was observed, which is in contrast to Carlson's findings.

Decomposition experiments using evacuated pyrex glass tubes (about 45 cm in length, 5 mm I.D.) in a gradient furnace (400°C–100°C) were carried out on both natural and synthetic corderoite. The material placed in the hot end of the furnace showed characteristic decomposition products at definite temperature intervals. Within each temperature interval more and larger crystals grew at the highest temperatures and tapered off gradually towards the cool end. At the finish of each experiment only metacinnabar remained at the high temperature end (400°C) of the tube. Cinnabar grew in the tempera-
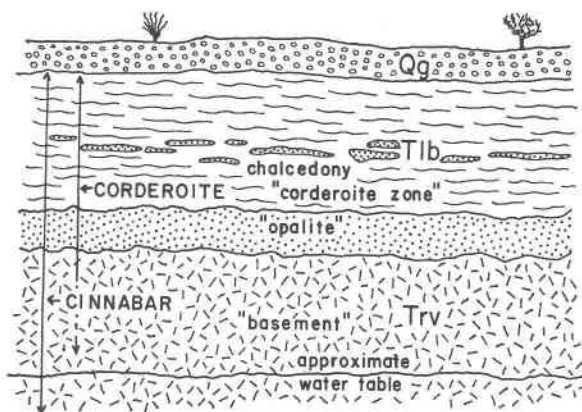

FIG. 1. Idealized cross section of corderoite-bearing rocks in proximity to the Cordero Mine, Humboldt County, Nevada (not drawn to scale). Qg = Quaternary gravel, Tlb = Tertiary lake beds, Trv = Tertiary rhyolite volcanics.

ture region of 340°C–325°C, at which point corderoite appeared and persisted down to about 280°C. Upon removal from the furnace the corderoite crystals were transparent straw yellow, but with subsequent cooling they turned a pale greenish white, which was identified as α-$Hg_3S_2Cl_2$. The straw yellow crystals were not X rayed, but judging from their color and habit only, the possibility exists that they were the metastable form, known as γ-$Hg_3S_2Cl_2$ (Carlson, 1967). Two more products were identified. At a temperature of about 120°C, HgCl (calomel) was precipitated, and at a slightly lower temperature, $HgCl_2$ appeared. The control for the last two temperatures is not as good as for the others.

The occurrence of corderoite in the deposit suggests that it is of low temperature and/or supergene origin. At room or slightly elevated temperatures, attempts were made to alter cinnabar to corderoite in the presence of ions common in natural waters, especially those associated with thermal springs.

Cinnabar was allowed to react with concentrated HCl (37–38 wt percent) at room temperature. Within a few days, very fine grained (less than 5 μm in diameter) pale greenish gray corderoite crystals formed. In the next set of experiments seven solutions (100 ml each) were prepared containing 0.5 g red HgS and varying amounts of NaCl (0.5–8.0 wt percent). The pH of the solutions was controlled by addition of H_2SO_4 and varied from pH = 1 to pH = 3. Within a week, a black coating formed on the HgS, the most prominent coating developed in the solution having the lowest pH (1) and the highest NaCl concentration (8 wt percent). The

same experiment was initiated in the absence of light. After a week, no obvious coating on the red HgS was visible. Subsequent exposure to light produced rapid darkening. A solution containing 0.2N HCl and 5 wt percent NaCl was allowed to react at room temperature with red HgS, and again a black coating formed within a week on the red HgS.

A combination of the amount and the grain size of the material formed made it impossible to separate the black coating from the red HgS, and X-ray diffraction did not prove the existence of a new phase. However, after filtering and repeated washing, microprobe analysis showed that the mixture contained Hg, S, and Cl as the only detectable elements. Knowing that corderoite is photosensitive, and that Hg, S, and Cl are the only major ions in the material, it is believed that small quantities of poorly crystalline corderoite were formed.

To test if corderoite would readily form in an alkaline environment, red HgS was added to a solution containing NaOH (pH = 12) and 5 wt percent NaCl. After three weeks no reaction had taken place.

The relative ease with which corderoite is formed under acid conditions, the presence of Cl ion as a common constituent of hot spring or groundwaters, and the relationships observed in the field suggest that corderoite is indeed a low temperature supergene mineral.

X-ray Data

Natural corderoite yields a diffraction pattern nearly identical to that of α-$Hg_3S_2Cl_2$ (Carlson, 1967). Powder camera (Guinier deWolff) films were made of the natural material using Cu$K\alpha$ radiation and LiF as an internal standard, covering the region 0°–90° 2θ. The space group and crystal structure of corderoite was initially worked out by Puff and Kuster (1962) and confirmed and refined by Frueh and Gray (1968). Our data compare very favorably with that of Frueh and Gray: $a_0 = 8.940 \pm 0.005$ Å vs 8.949 ± 0.002 Å, $D_c = 6.845$ vs $D_c = 6.83$, $Z = 4$. D_m (Carlson, 1967; Frueh and Gray, 1968) = 6.895 ± 0.007.

Chemical Composition

Because of the exceedingly fine grain size (less than 2 μm) of the natural material, it is difficult to obtain pure corderoite for quantitative work. However, qualitative electron microprobe (ARL-EMX-SM)

analysis indicated Hg, S, and Cl as the only significant constituents. Quantitative analysis of synthetic crystals, grown using the method of Carlson (1967), indicated a formula of $Hg_3S_2Cl_2$. Cinnabar and calomel were used as standards.

Physical and Optical Properties

Using 15 and 25 gram loads Vickers hardness numbers (VHN_{15} and VHN_{25}) were measured with a Leitz Miniload Microhardness Tester on polished grain mounts of synthetic material prepared by the method of Carlson (1967). For twenty hardness determinations made on 10 grains at each load, VHN_{15} ranged from 35 to 58 (mean value, 45), VHN_{25} from 28 to 61 (mean value, 48). Mean hardness was 15 gram load-45 and 25 gram load-48.

Reflectance was measured in air for wavelengths 470 nm, 546 nm, 589 nm, and 650 nm, using a Zeiss continuous interference-filter monochromator and a Zeiss MPM microscope photometer. The silicon carbide standard used has a reflectance of 20.9, 20.3, 20.0 and 19.65 percent in air for the respective wavelengths. Five measurements of reflectance (on as many grains) were made for each of the four wavelengths. Resultant values were 470 nm, 16.7 percent; 546 nm, 15.5 percent; 589 nm, 15.1 percent; and 650 nm, 15.1 percent.

Refractive index was determined by use of S-Se melts to be greater than 2.5. Because of the extremely fine grain size of the natural material, under transmitted light only an isotropic powder is observed. Artificial corderoite is isotropic, and colorless to pale yellowish white. In reflected light, synthetic corderoite is pale yellowish white in color, and possesses no detectable bireflectance or anisotropy. Internal reflections are very pale yellow or absent.

Type Specimen Material

A few grams of purified corderoite are kept in the mineralogy collection at Stanford University, along with several kg of high-grade ore material. Similar material has been deposited with the San Francisco office of Placer Amex, Inc.

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