Mineralium Deposita (2000) 35: 796–798

LETTER

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The darkening of cinnabar in sunlight

Received: 6 April 2000 / Accepted: 28 July 2000

Abstract Most cinnabar is brilliant red and remains so under sunlight. However, some cinnabar is photosensitive and irreversibly blackens during exposure to sunlight. Electron microprobe analyses of cinnabar from several occurrences show that photosensitive cinnabar contains noteworthy concentrations of chlorine, whereas non-photosensitive cinnabar does not. Experimental evidence shows that non-photosensitive cinnabar becomes photosensitive after exposure to halogens. The darkening of cinnabar in sunlight is caused by the presence of contained chlorine or other halogens.

Introduction

Cinnabar (hexagonal HgS), the most important source for mercury, is normally brilliant red and has been used throughout history as a pigment for paints and clothing. However, cinnabar from some localities is photosensitive and permanently blackens during a few hours of exposure to sunlight. The cause of cinnabar photosensitivity has been suggested to be related to physical and chemical mechanisms, such as photo-oxidation and changes in atomic structure. Dreyer (1939) studied the darkening of cinnabar and concluded that minute impurities in cinnabar may cause the behavior. It has been suggested that cinnabar transforms to the black polymorph metacinnabar (cubic HgS) during exposure to sunlight, but there is no evidence to support this. Dickson and Tunell (1959) showed that pure cinnabar inverts to metacinnabar at 1 bar at 344 °C, and reverts to cinnabar below 344 °C. They showed from textural evidence that metacinnabar typically is hypogene and earlier than cinnabar, and not an alteration product of cinnabar. It has been suggested that all cinnabar will eventually darken if left in sunlight, but this is contradicted by the many historical uses of the mineral as a pigment that have remained brilliant red. Dreyer (1939) noted that most cinnabar is not sensitive to sunlight. Additionally, reagent grade red HgS left exposed to sunlight for years does not darken, indicating that pure cinnabar is not photosensitive. Potter and Barnes (1971) investigated the reflectivity of infrared light from HgS as a function of temperature and composition and found that it decreased with decreasing mercury content. This may well apply to natural light observation of color variations between cinnabar specimens, but does not explain the rapid color change of photosensitive cinnabar, or why certain cinnabar specimens are photosensitive whereas others are not.

Editorial handling: R. J. Goldfarb

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Natural materials

Photosensitive cinnabar has been reported from several localities, and is perhaps best known from its occurrences at Steamboat Springs, Nevada, and the Opalite deposit, Oregon. Electron microprobe analyses were made of photosensitive cinnabar from the Steamboat Springs (Washoe Co., NV), Opalite (Malheur Co., OR), Silver Cloud (Elko Co., NV), Clementine (Elko Co., NV), Buckskin Peak (Humboldt Co., NV), Goldbanks (Pershing Co., NV), B and B (Esmerelda Co., NV) and Santa Barbara (Huancavelica district, Peru) deposits. Analyses of non-photosensitive cinnabar from the Almaden (Spain), Monte Amiata (Italy), New Almaden (Santa Clara Co., CA), New Idria (San Benito Co., CA), Redbird (Pershing Co., NV), and Cahill (Humboldt Co., NV) deposits were also made. Analyses were conducted using a three spectrometer Cameca (CAMEBAX) wavelength-dispersion microprobe analyzer at the Mackay School of Mines, operating at an accelerating potential of 15 kV and a beam current of 15 nA, with a beam diameter of 1 μm. A number of elements were initially evaluated, but only Hg, S and Cl proved to be of significant concentration. Reagent HgS and PbCl were used as standards, and a ZAF correction was performed with Cameca software.

Concentrations of Hg and S did not depart from stoichiometric HgS (Hg 86.2, S 13.8 wt%) outside of the accuracy limits of the probe (Hg $\pm 0.97\%$; S $\pm 0.05\%$, Cl $\pm 0.01\%$), except when chlorine concentrations were above ~ 1 wt%; a general inverse relationship between sulfur and chlorine was then noted. Results for chlorine are summarized in Table 1, and show that photosensitive cinnabar contains a significant concentration of chlorine, whereas non-photosensitive cinnabar does not.

Photosensitive cinnabar is commonly spatially associated with mercury halide minerals, as at the Opalite deposit where this study identified terlinguaite (Hg_2OCl), calomel (Hg_2Cl_2), and a Hg–S–Cl mineral, possibly corderoite (α-$Hg_3S_2Cl_2$). Photosensitive cinnabar is found in association with terlinguaite, calomel, kleinite [$Hg_2N(Cl, SO_4) \cdot nH_2O$], eglestonite ($Hg_4Cl_2O$), comancheite [$Hg_{13}(Cl, Br)_8O_9$, and mosesite ($Hg_2$ N(SO_4, MoO_4, Cl] H_2O) in deposits of the Terlingua district (Brewster Co., TX), where exposed ores were black, and red cinnabar could be seen only on freshly broken surfaces (Turner 1900). At the McDermitt deposit (Humboldt Co, NV), photosensitive cinnabar occurs with corderoite, radtkeite (Hg_3S_2 ClI), kenhsuite (γ-$Hg_3S_2Cl_2$), calomel, kleinite, and eglestonite.

Table 1 Electron microprobe analyses of chlorine in cinnabar (±0.01 wt%)

Deposit	Photosensitive	Average Cl wt%	Range Cl wt%
Steamboat Springs	Yes	0.96	0.05–4.96
Opalite	Yes	0.17	0.01–3.21
Silver Cloud	Yes	0.10	0.05–0.15
Clementine	Yes	0.33	0.04–1.96
Buckskin	Yes	0.16	0.07–0.25
Goldbanks	Yes	0.04	0.01–0.12
B + B	Yes	0.05	0.02–0.10
Santa Barbara	Yes	0.25	0.07–0.59
Almaden	No	<0.01	<0.01
Monte Amiata	No	<0.01	<0.01
New Almaden	No	<0.01	<0.01
New Idria	No	<0.01	<0.01
Redbird	No	<0.01	<0.01
Cahill	No	<0.01	<0.01

Reconnaissance experimental studies

A number of reconnaissance experimental studies have been conducted that further establish a relationship between the presence of halogens and the photosensitivity of cinnabar. McCormack et al. (1991) noted that rapidly darkening photosensitive coatings develop on cinnabar after long exposure to high concentrations of halogens in solution. Crystals of non-photosensitive cinnabar from the Cahill deposit were kept in contact with KI- and KCl-saturated brine, in the dark and at room temperature, for 2 years. The cinnabar retained its red color, but, after washing and drying, turned black on exposure to sunlight within 1 h. The effect was surficial; the red color returned when the darkened crystals were pulverized, and did not darken when again exposed to sunlight. The darkening was probably caused by the presence of a volumetrically insignificant, thin surface coating of an unknown photosensitive compound, possibly synthetic corderoite or radtkeite.

In this study, photosensitive cinnabar was produced by other reactions, including brief contact of cinnabar with concentrated HCl at room temperature, and with dilute halogen solutions at elevated temperatures in Parr bombs. Cinnabar in contact with a slightly saline (NaCl) solution blackens while the solution is evaporated under sunlight, but not when evaporated to dryness in the dark and then exposed to sunlight. Davidson and Willsher (1981) noted similar results in an experiment wherein red HgS powder suspended in potassium iodide solutions darkened during exposure to a 125-W lamp.

Photosensitive red mercury sulfide was produced by reaction of reagent-grade HgS powder with NaCl–KI solutions kept at room temperature in the dark for nearly 3 years. An unexposed sample of this material yielded a normal cinnabar X-ray diffraction pattern, and was placed in sunlight until darkened and radiographed again, without disturbing the X-ray mounting. The pattern of cinnabar alone was again obtained from the blackened material, but with significantly reduced intensities (~−10%). The darkened material is not metacinnabar. It may be an amorphous phase, or blackened HgS may more strongly absorb X-rays.

Discussion

The only other mineral to have been appreciably utilized as a mercury ore is corderoite [α-$Hg_3S_2Cl_2$; Foord et al. (1974)], which constituted ~25% of the ore at the McDermitt mercury mine. Corderoite is remarkably photosensitive, and is salmon pink on freshly exposed surfaces and blackens rapidly in sunlight. At McDermitt, corderoite was determined to be a hypogene replacement of cinnabar, and its formation is likely dependent on the presence of a relatively high activity of chloride in hydrothermal solutions (McCormack 1986).

Corderoite can be synthesized with relative ease. In the present study pure HgS reacted with concentrated HCl at room temperature for 80 min produced mixtures of corderoite and cinnabar. These mixtures are initially vivid red, but blacken rapidly on exposure to sunlight. Other photosensitive mercury sulfur-halide minerals and phases, such as kenhsuite (γ-$Hg_3S_2Cl_2$), radtkeite (Hg_3S_2ClI), grechischevite [$Hg_3S_2(Cl, Br, I)_2$], lavrentievite [$Hg_3S_2(Cl, Br)_2$], arzakite [$Hg_3S_2(Br, Cl)_2$], $Hg_3S_2Br_2$, and $Hg_3S_2I_2$ also form readily in closed tubes by reacting HgS with Hg-halides at elevated temperatures (McCormack 1997; McCormack and Dickson 1998). Observed photosensitivity of natural cinnabar may be caused by the presence of corderoite or other photosensitive mercury halide minerals within or on it.

Exceptionally high chlorine concentrations were determined from a few cinnabar samples that may represent cinnabar that has been partially replaced by corderoite or another mercury chloride mineral. Chlorine contents >7 wt% were determined in two cinnabar grains from Steamboat Springs, and >6 wt% in one from the Opalite deposit. As these grains might be halide minerals rather than simply chlorinated cinnabar, and because their inclusion would unnecessarily skew the average chlorine values above that typical for these deposits, their analyses were excluded from Table 1.

Photosensitivity of cinnabar is produced by the same mechanisms as fluorescence and phosphorescence. Photo-reactions begin with absorption of light energy, which forces electrons from low energy orbitals to higher energy orbitals. It may follow that electrons return from the excited state to ground state, accompanied by the emission of light (Balzani and Maestri 1993). Visible light emission is termed luminescence; it is termed fluorescence when it occurs during exposure to light, or phosphorescence if it continues after exposure. Absorption is not necessarily followed by emission, and the shifting of electrons can cause changes in color.

The perceived color of an opaque solid is the color of that portion of incident light that is reflected from it, with the remaining light being absorbed (Phillips 1971). It is likely that the color of normal cinnabar is caused by the reflectance of red light alone, with all other wavelengths being absorbed, but for photosensitive cinnabar, red wavelengths are also absorbed after photo-reactions have taken place.

Conclusions

Photosensitive cinnabar contains chlorine and possibly other halogens, and non-photosensitive cinnabar does not. Non-photosensitive cinnabar and reagent HgS become photosensitive after exposure to halogens. Numerous photosensitive mercury sulfur-halide minerals and phases form readily by reaction of HgS with halogens, and form as thin surface coatings on and as partial to complete replacements of HgS. Most natural photosensitive cinnabar is fine-grained (typically tens of microns or finer), with large relative surface areas that facilitate reactions. Photosensitive cinnabar results from its exposure to high concentrations of halogens for short times, or to lower halogen concentration for longer exposure times, and indicates that halogens are present in the mineral as impurities or as mercury halide minerals.

Acknowledgments I am grateful to Dr. Frank Dickson for direction, support and encouragement in this and innumerable other projects. He also provided insightful review of this manuscript, as did Howard McCarthy, US Geological Survey, Reno Field Office, Greg Arehart and Mae Gustin of the University of Nevada, Reno, and Richard Goldfarb and an anonymous reviewer for *Mineralium Deposita*. I am indebted to Andrew Floyd and the late Dr. Tom Lugaski of the W.H. Keck Museum, Mackay School of Mines for providing cinnabar specimens.

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