

CARPATHITE AND IDRIALITE: ORGANIC (HYDROCARBON) MINERALS ASSOCIATED WITH MERCURY DEPOSITS IN CALIFORNIA

Gail E. Dunning
773 Durshire Way
Sunnyvale, California 94087

Ted A. Hadley
907 Anaconda Way
Sunnyvale, California 94087

Bay Area Mineralogists Report

INTRODUCTION:

Two prominent California mining areas rich in mercury mineralization also host two polycyclic aromatic hydrocarbon (PAH) minerals, carpathite and idrialite. The regions hosting these minerals are separated by over one hundred eighty airline miles. The first, the New Idria Serpentine Body, is located in what is known as the Southern Diablo Range and is confined to San Benito County. The second area, The Mayacmas District, is centered in Lake County, but includes mines in Sonoma, Napa and Yolo counties.

Our interest in these two organic minerals was prompted by the fact that carpathite is found exclusive in at least five mercury mines in the Southern Diablo Range area just south of Clear Creek, Picacho Peak area, San Benito County, while idrialite is confined to at least six mines in the Mayacmas District of the north bay area, Skaggs Springs and Culver Baer mines being the most interesting. It is the object of this study to determine what geochemical differences, if any, in source material, thermal stability and origin, existed between the two areas that resulted in the individual formation of carpathite and idrialite in their respective areas. It is known that both of these localities occur near fault zones and in addition, the Mayacmas District is within an active geothermal zone.

LOCALITY OF MINES:

Southern Diablo Range

Carpathite occurs in the mercury mines of the Southern Diablo Range, San Benito County, which include the Picacho, Andy Johnson, Fourth of July, Cowboy and a single unnamed claim along a small tributary of Clear Creek adjacent to the Victor claim (Cooper et al. 2003).

Mayacmas District

The mines within the Mayacmas District occur in the counties of Lake, Napa, Sonoma and Yolo. In Lake county, idrialite has been identified from the Abbot mercury mine as a solid yellow fracture filling; also it occurs with cinnabar at the Mirabel and Great Western mines and at the Helen and Research mines about four miles northwest of the Great Western mine. In Napa County, idrialite occurs at the old Knoxville mercury mine. In Sonoma County, idrialite has been found with realgar, metacinnabar and opal at the Skaggs Springs mine and with cinnabar at the Culver Baer mine. In Yolo County, idrialite has been found at the Reed mine at the northern tip of the Knoxville District associated with cinnabar and heavy black oil.

No reported occurrences exist for either mineral outside its specific area either in California or the rest of North America.

GEOLOGY:

Southern Diablo Range

The geological features of the southern Diablo Range serpentinite body are summarized by Dunning et al. (2005). This large, elongate, tectonically emplaced body intrudes parts of the Pinoche Formation (Upper Cretaceous) and the Franciscan Complex (late Mesozoic to early Tertiary), and forms the core of a large anticline that lies between the San Andreas fault and Coast Ranges to the west and the Great Valley to the east. The structural position of the New Idria serpentinite body suggests that it may represent serpentinitized peridotites that originally made up part of the Late Jurassic-aged Pacific oceanic crust. Post Jurassic-aged subduction of the peridotites emplaced them under the growing Franciscan accretionary wedge. Following serpentinitization, a northwest-southeast fault formed within the serpentinite at depth. This fault zone, which now lies nearly parallel to the boundary of the western edge of the serpentinite body with the Franciscan Complex, was then silicified by fluids along a trend from what is now the Clear Creek mine at the northern end to the Picacho mine at the southern end. These fluids are considered to be the method by which the mercury-bearing fluids penetrated the host formation along with organic-rich fluids.

Mayacmas District

The mercury deposits in the Skaggs Springs area lie within a block of interbedded sandstone and shale of Cretaceous age (Everhart 1950). This block is bounded by two northwest-trending faults separating it from rocks of the Franciscan group of Upper Jurassic age. In general, the Mayacmas Mountains of northern Sonoma County are underlain by rocks of the Jurassic-Cretaceous Franciscan Formation and Great Valley sequence. These consist primarily of marine sedimentary and volcanic rocks and include graywackes, shales, spilistic basalt and serpentine. They have been folded and faulted into a series of rugged, northwest-trending ridges and valleys. The geological features of the area have been summarized by Dunning and Cooper, (1993). The region within the Mayacmas Mountains is still active with numerous hot springs and earthquake activity. Upwelling fluids rich in mercury have invaded the region's rock formation resulting in deposits of cinnabar and in many cases, organic material. The geothermal activity nearby at The Geysers confirms the underlying heat source and upwelling of steam and mineralized fluids (Dunning and Cooper 1993).

BASIC MINERAL DATA:

Carpathite ($C_{24}H_{12}$) is lite yellow to yellowish-brown and greenish-yellow, monoclinic, $P2_1/c$. Crystals are acicular, thin tabular parallel [001] showing {001}, {100}, {201} plus other forms. The habit is typically bladed groups and fibrous radiating aggregates, and rarely as individual crystals with terminations. The mineral shows intense blue-white fluorescence in both long-and short-wave ultraviolet light (Anthony et al., 2003). The type locality is Olenevo, Svalyavskiy Region, Zakaarpats'ka Oblast', Ukraine (Piotrovsky

1955). Other world localities include France, Slovakia, Slovenia and Russia. Chemically, carpathite is coronene, and has the following chemical formula and structure:

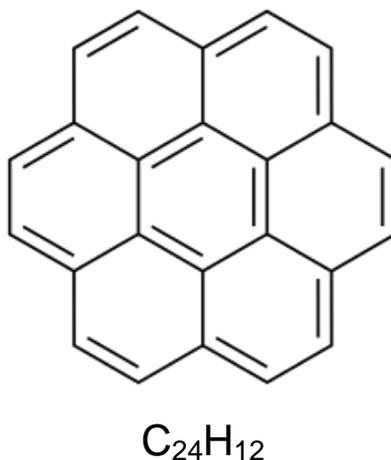


Figure 1. Chemical diagram of coronene showing the connectivity of the individual hexagonal benzene rings.

Coronene is soluble in benzene, toluene, and other organic solvents. Synthetically, it is a byproduct of the hydrocracking process used in petroleum refining. It is thermally very stable, having melting and boiling points of 473.3°C and 525°C, respectively. Coronene has been rumored to be carcinogenic, though no objective confirmation could be found for this report. The authors recommend it be handled with care.

Idrialite ($C_{22}H_{14}$), also originally called curtisite (Wright and Allen 1930; Geissman et al. 1967), was named and first described by Dumas (1832) from the Idrija mercury deposit in Slovenia. The mineral is greenish-yellow, orthorhombic, no space group; also, tabular crystals are precipitated from a chloroform extraction of cinnabar ore. The mineral shows intense pale blue to blue-green to white fluorescence in both long and short-wave ultraviolet light. The mineral has a perfect {001} cleavage and a poor {100} one. The fracture is conchoidal with a vitreous to adamantine luster. In natural light it is pale brown to pale greenish yellow (Anthony et al., 2003).

Chemically, idrialite is a mixture of variable composition of PAHs shown by the chemical structures below.

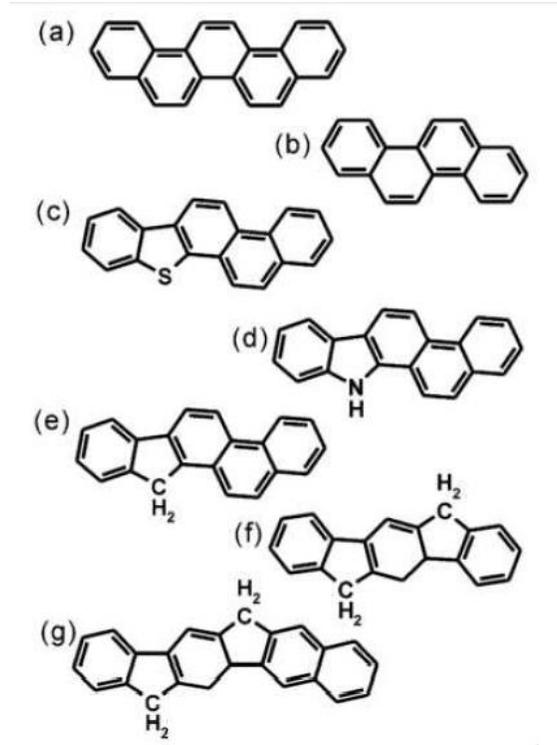


Figure 2. Molecular structures of PAHs contained in idrialite from Skaggs Springs. Approximate abundance of their components is shown in square brackets: (a) picene [40%], (b) chrysene [7%], (c) benzo-phenanthro-thiophene [10%], (d) dibenzo-carbazole [trace], (e) dibenzo-fluorene [33%], (f) indeno-fluorene [7%], and (g) benzo-indeno-fluorene [4%]. After Wise et al. 1986.

Whereas coronene is a ring of six benzene rings, idrialite is composed of chains of benzene rings of various lengths and including some substitution of sulfur, ammonia, and unsaturated hydrocarbon. When the mineral is formed, layers of these PAHs stack like sheets of paper to build the gross structure. Since the mineral is a mixture, its chemical and physical properties are slightly variable depending upon the specific amounts and stacking order of each PAH present.

Because idrialite is a mixture, it is not technically a mineral and today would not be accepted by the IMA as such. Since it was originally published ca. 1832, it is grandfathered.

LOCALITY PHOTOS:

The following [ingine](#) site photos, although not complete, illustrate the terrain hosting several mines rich in cinnabar and associated minerals. Collecting can be difficult at times because of the steep faces of the mine workings. Most of the exposed mineralized rock can be quite hard to break. Mineralization often followed fractures in the host rock and consisted of mercury-rich fluids, silica and organic phases.



Figure 3. View from above the Culver-Baer mercury mine looking down on the steep mine face workings and surrounding topography.



Figure 4. View of the lower area of the Culver-Baer mercury mine showing the steep terrain and the exposed rocks.



Figure 5. Photo of the Culver-Baer mercury mine, Sonoma County showing the steep face of the workings and boarded adit near the top.



Figure 6. Working face of the Culver-Baer Mine showing John Magnasco (L) and Len Pisciotta (R) collecting idrialite and cinnabar.



Figure 7. McLaughlin mine (old Manhattan mine), Napa County, California showing the extensive benchwork. Gary Moss photo, 1996.



Figure 8. View of the working face of the Picacho mine where mercury ore was mined and where carpathite was found at the base.

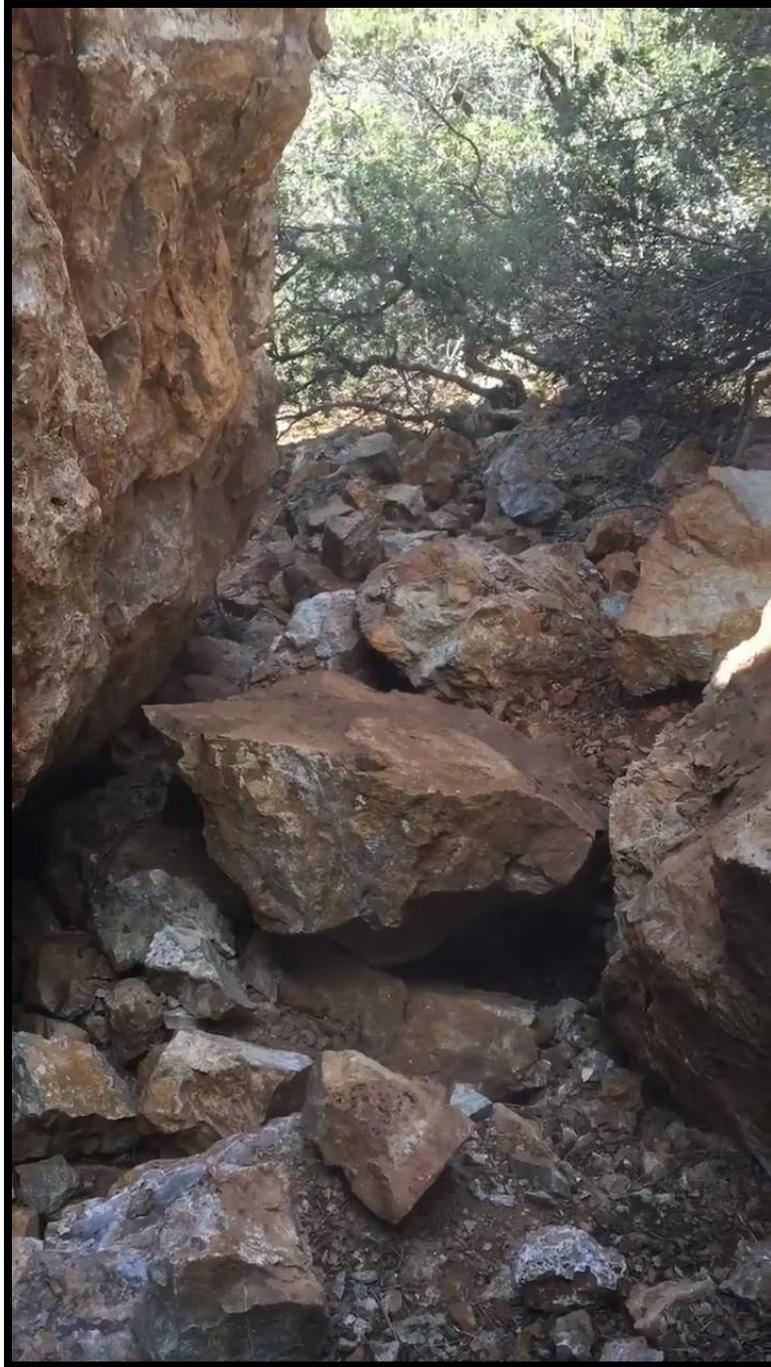


Figure 9. Collecting area at the Cowboy claims, San Benito Co., California where excellent samples of carpathite were collected. Dan Evanich photo.

SPECIMEN FIGURES:

Carpathite

Carpathite from the Clear Creek area occurs in good prismatic crystals along seams in the altered silica carbonate host rock. The carpathite from the Andy Johnson mine, located along the main road to the upper Picacho workings, occurs associated with cinnabar and make some very nice samples.



Figure 10. Light yellow covering of prismatic carpathite with red cinnabar along a fracture surface. Andy Johnson mine, San Benito County. FOV = 50 mm.



Figure 11. A good coverage of intergrown prismatic carpathite crystals associated with cinnabar along a fracture surface. Andy Johnson mine, San Benito County. FOV = 25 mm.



Figure 12. An association of red cinnabar and light yellow carpathite from the Andy Johnson mine, San Benito County. FOV = 25 mm.



Figure 13. Typical coverage of carpathite crystals on silica carbonate rock from the Picacho mine. FOV = 10 cm.



Figure 14. Naturally terminated crystals of carpathite in a vug from the Picacho mine. Ted Hadley specimen and photo. FOV = 5 mm.



Figure 15. Sample of lite yellow carpathite with silica from the Cowboy claims. FOV = 8 cm.

Idrialite



Figure 16. Idrialite (yellow) on quartz and bitumen (black). McLaughlin mine (old Manhattan mine), Napa Co., CA. Ted Hadley specimen, Dan Evanich photo.



Figure 17. Bright yellow idrialite with minor cinnabar and quartz along a fracture seam. [CulvarCulver](#)-Baer mine, Sonoma County. FOV = 40 mm. Photo courtesy of Tom Loomis, Dakota Matrix.



Figure 18. Bright yellow vein of idrialite with minor red cinnabar along a vein of quartz. [CulvarCulver](#)-Baer mine, Sonoma County. FOV = 35 mm. Photo courtesy of Tom Loomis, Dakota Matrix.



Figure 19. Yellow vein of idrialite in silica associated with red cinnabar in a brown weathered rock, Culver-Baer mine. FOV = 30 mm. Photo courtesy of Tom Loomis, Dakota Matrix.



Figure 20. Idrialite, Culver-Baer mine, photographed in visible light. Dan Evanich collection and photo. FOV = 3 cm.

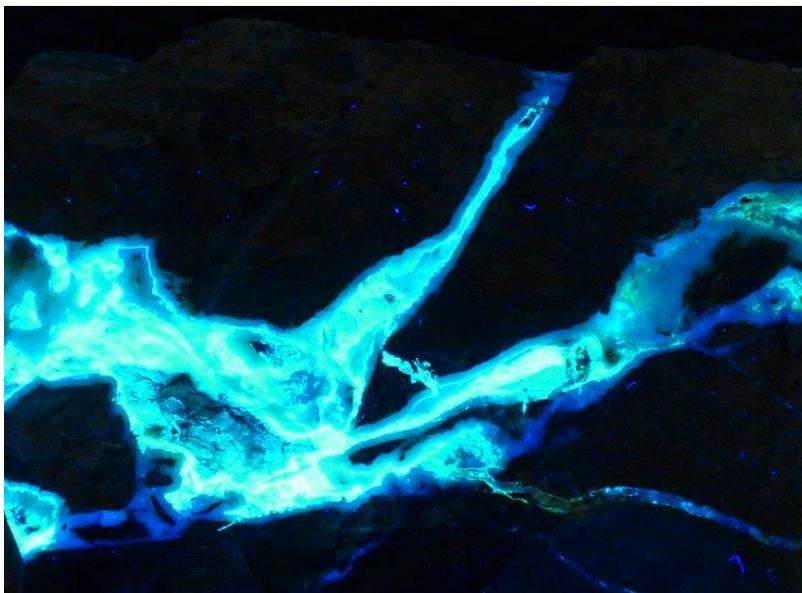


Figure 21. The above idrialite specimen photographed in shortwave ultraviolet light. Dan Evanich collection and photo.

ANALYTICAL METHODS AND RESULTS:

In their study of carpathite and idrialite, Echigo et al. (2007, 2009), employed a series of analytical methods to better characterized these two polycyclic aromatic hydrocarbon (PAH) minerals. These include Raman spectrographic, single crystal X-ray diffraction, micro infrared spectrographic, electron microprobe, thermal, and carbon isotopic analyses. The combination of these tests acquired data that was used to characterize the individual PAH minerals from two specific localities, namely the Picacho mine of San Benito County and from the Skaggs Springs mine, Sonoma County.

Idrialite

Carbon isotopic compositions for idrialite from Skaggs Springs was determined to be -24.429‰. This $\delta^{13}\text{C}$ value is typical of sedimentary organic matter of plant origin (Deines 1980; Galimov 1995). Thus the PAH molecules composing the present idrialite are inferred to have originated from sedimentary organic plant matter present in the underlying rocks.

Micro X-ray diffraction patterns for the yellow and brown phases of idrialite and picene were compared. The yellow phase was identified as idrialite while the brown phase consists of both amorphous and crystalline components.

Electron microprobe analysis showed no significant chemical zoning and the line analysis disclosed the homogeneous distributions of sulfur. Thus, the BSE image and line analyses indicate that S-bearing PAH (SPA) molecules such as benzo-phenanthro-thiophene are homogeneously distributed in the crystal structure of idrialite. Nitrogen-bearing (NPAH) molecules such as dibenzo-carbazole in idrialite crystals are below the detection limit of the analysis.

After TG and DTA analysis, the idrialite samples were completely volatilized up to 740°C, whereas other types of natural organic matter in solid states leave carbonaceous residues on the thermal analyses up to 1000°C (Martinez-Alonso et al. 1992; Guillen et al. 1996). It is known that there remains no residue when natural organic matter in liquid states is completely combusted up to 640°C. The idrialite samples studied

by Echigo et al. (2009) are more similar to liquid organic matter in thermal behavior and left no solid residue. Hence, the thermal analysis suggests that the PAH mineral was crystallized from fluid phases.

Amorphous organic matters co-existing with idrialite are reported only in the present specimens from Skaggs Springs. No amorphous component is associated with idrialite from Idrija mercury deposit (Strunz and Contag 1965), the type locality, which suggests that small PAHs are completely removed from hydrothermal fluids in the latter locality. Idrialite from Idrija contains more 6-ring PAHs than from Skaggs Springs (Wise et al. 1986). The melting point and thermodynamic stability of PAHs are increased with the number of benzene rings (Echigo et al. 2009). One inference from the above observations might be that idrialite from Idrija was crystallized at higher temperatures than that from Skaggs Springs.

Carpathite:

The BSE image of the Picacho mine carpathite reveals that neither other hydrocarbons nor any other compounds were observed within the distinct boundary between carpathite and quartz. An associated mineral found in the vugs in cinnabar in minuscule amounts was found to be only carpathite. Three infrared absorption spectra of the carpathite and a synthetic crystal of pure coronene showed both to be identical. Raman scattering spectra of carpathite and synthetic coronene showed that other hydrocarbons were not coexistent with natural carpathite. A comparison between TG and DTA data also showed no discernable difference between natural carpathite and coronene.

For carpathite from the Picacho mine, the isotopic composition of carbon yielded a $\delta^{13}\text{C}$ value of -22.39‰, which is similar to carbon isotopic compositions of sedimentary organic matter in the far-reaching tectonic regions. This organic matter may be considered to have converted to coronene molecules by hydrothermal fluids leading to the formation of carpathite (Echigo et al. 2007).

The Picacho Peak area is along the San Andreas Fault in the West Coast. Hydrothermal activities associated with seafloor spreading were reviewed by Rona (1984, 1988) and Rona and Scott (1993). It was evident that hydrothermal alteration of organic matter generated PAHs such as naphthalene (C_{10}H_8), phenanthrene ($\text{C}_{14}\text{H}_{10}$) and coronene ($\text{C}_{24}\text{H}_{12}$) (Simoneit, 2000). Coronene molecules were reported in the hydrothermal petroleum, occurring in the seafloor hydrothermal systems, namely the Excanaba Trough and Guaymas Basin (Simoneit and Shoell 1995; Simoneit et al. 1997). Both of them are hydrothermal vent systems at sediment-covered ridges and along the San Andreas Fault.

PARAGENETIC CONSIDERATIONS:

Echigo et al. (2007, 2009) give analytical and observational data for the probable paragenetic relationships for both carpathite and idrialite at the two localities studied. Both carpathite and idrialite have essentially the same paragenetic relationship to both quartz and mercury mineralization, especially cinnabar. With respect to carpathite from the Picacho mine, San Benito County, textural relationships indicate that after the strong concentration of coronene molecules in the hydrothermal fluids, carpathite growth postdates both hydrothermal quartz precipitation, and subsequent cinnabar formation.

With respect to idrialite from Skaggs Springs, Sonoma County, both the yellow part (idrialite) and the brown part (amorphous organic matter) occur on the coexisting minerals (opalline silica, metacinnabar, and siderite): the textural relationship indicates that the organic matter precipitated after crystallization of the associated mercury minerals. Thus, it is suggested that the organic molecules were migrated by hydrothermal fluids and then separated into hydrophobic (idrialite) and hydrophilic (amorphous organic matter) molecules during the cooling process. Following the formation of silica phases and mercury minerals (cinnabar and metacinnabar), idrialite crystallized and then the amorphous organic matter precipitated at the final cooling stage of the hydrothermal activity.

The $\delta^{13}\text{C}$ value and occurrence of the Picacho mine carpathite may derive its origin from both sedimentary kerogen and the subsequent conversion into coronene molecules by hydrothermal fluids. An interpretation that the hydrothermal fluids led to the formation of cinnabar supports the suggestion by

Studemeister (1984) that the retrograde metamorphism of Mesozoic-aged sediments released mercury-bearing fluids to form mercury-bearing minerals in the New Idria District. The sedimentary kerogen contains various organic compounds (Hayes et al. 1983), whereas carpathite consist of nearly pure coronene. The formation of carpathite must result from specific purification to avoid mixing of other PAHs and at a higher temperature than that for idrialite from Skaggs Springs, which is believed to have precipitated at a lower temperature and allowed additional organic molecules to co-exist with the main constituent of primary idrialite.

DISCUSSION:

Carpathite is a natural crystalline analog of the synthetic hydrocarbon coronene, which is a well-investigated material. The properties of these two phases are in good agreement with each other and it is almost impossible to distinguish carpathite from ultrapure coronene (Wise et al. 1986) by infrared absorption, Raman scattering, and differential thermal analyses. The absence of other PAHs in carpathite may be attributed to the high degree of aromaticity of coronene molecules (Krygowski and Cyranski, 2001). In comparison, idrialite consists of picene molecules ($C_{22}H_{14}$), however many other organic compounds are present such as $C_{20}H_{14}$ and $C_{19}H_{12}S$ (Wise et al. 1986). Picene molecules are conjugated hydrocarbon compounds and also have the high degree of aromaticity (Krygowski, 1993), as well as coronene molecules in carpathite. However, picene molecules have overcrowded H atoms whose H-H distances are much shorter than the accepted van der Waals contacts. This overcrowding gives rise to intramolecular distortion which may facilitate mixing various PAHs in idrialite. In contrast, coronene molecules have neither overcrowded H atoms or intramolecular distortions, which explains the high purity of carpathite with respect to idrialite.

CONCLUSIONS:

In conclusion, the works of Echigo et al. (2007, 2009) indicate that there are significant differences in the formation criteria for both carpathite and idrialite from their respective localities. Both minerals have derived their chemical composition from underlying organic matter that has been hydrothermally altered to produce PAH molecules. The specific sub oceanic location, the Guaymas Basin, is believed to be the source of the petroleum that was hydrothermally altered to yield the coronene. The carbon 13 isotopic values of the coronene in the hydrothermal petroleum is a close match to the carpathite from the Picacho mine material. A higher temperature and purification at depth would cause a single phase to be transported into the host rock formation together with fluids rich in mercury. Lower temperature PAH phases, such as benzene, naphthalene and phenanthrene, would be depleted from the higher temperature fluids because of their lower thermodynamic stability. This would leave the remaining higher stable phase, coronene, to be deposited as the mineral carpathite in the host rocks surrounding the Picacho Peak area. The coronene molecule is recognized as the most thermodynamically stable isomer of all $C_{24}H_{12}$ isomers (Stein and Fahr 1985).

In contrast, the existence of idrialite from Skaggs Springs (and other mines in the area) has been shown by carbon 13 values to be consistent with that of the organic matter derived from plants of sedimentary origin. Higher plant terpenoids commonly contain pentacyclic aromatic hydrocarbons such as taraxerol and β -amyrin (Wang and Simoneit 1990; Killips and Killips 2005). It is known that these hydrocarbons undergo aromatization during diagenesis and convert to picene, which is the main component of idrialite. The fact that idrialite is not a single organic compound but a combination of several PAHs gives credibility to the lower temperature of the hydrothermal fluids which upwelled along a fracture system into the region along with fluids rich in mercury.

Thus, it can be concluded from the results of Echigo et al. (2007, 2009) that the difference in organic mineralization between the southern Diablo Range (Picacho mine carpathite) and the Mayacmas District (Skaggs Springs mine idrialite) can be related to differences in (1) at depth hydrothermal temperature of source material, (2) source and type of primary organic matter, and (3) thermodynamic stability of PAHs in the hydrothermal fluids. The carbon 13 values of the individual organic minerals from each location are consistent with these conclusions.

ACKNOWLEDGMENTS:

The authors sincerely thank the following individuals for use of their photos and information. Mr. Gary Moss, Mr. Dan Evanich, Mr. Tom Loomis, Dakota Matrix, Mrs. Sharon Cisneros.

REFERENCES:

- ANTHONY, J. W., BIDEAUX, R. A., BLADH, K. W. and NICHOLS, M. C. (2003) Handbook of Mineralogy, Volume V, Mineral Data Publishing, Tucson, Arizona, 813 pp.
- BLUMER, M. (1975) Curtisite, idrialite and pendletonite, polycyclic aromatic hydrocarbon minerals: Their composition and origin. *Chemical Geology*, **16**, 245–256.
- COOPER, J. F., JR, DUNNING, G. E. and HADLEY, T. (2003) Mineralogy of the Victor Claim, Clear Creek area, San Benito County, California. *Baymin Journal*, **4**, No. 1, www.baymin.org.
- DEINES, P. (1980) The isotopic composition of reduced organic carbon. In P. Fritz and J. C. Fontes, Eds., Handbook of Environmental Isotope Geochemistry, I, The Terrestrial Environment, A, 329-406. Elsevier, Amsterdam.
- DUMAS, J. (1832) Recherches sur les combinaisons de l'hydrogène et du carbone. *Annales de Chimie et de Physique*, **50**, 182-197.
- DUNNING, G. E. and COOPER, J. F., JR. (1993) History and minerals of The Geysers, Sonoma County, California. *Mineralogical Record*, **24**, 339-354.
- DUNNING, G. E., HADLEY, T. A., MAGNASCO, J., CHRISTY, A. G. and COOPER, J. F. JR. (2005) The Clear Creek mine, San Benito County, California: A Unique Mercury Locality. *Mineralogical Record*, **36**, 337-363.
- ECHIGO, T, KIMATA, M. MURUOKA, T. and NISHIDA, N. (2009) The crystal structure, origin, and formation of idrialite (C₂₂H₁₄): Inferences from the microbeam and bulk analysis. *American Mineralogist*, **94**, 1325-1332.
- ECHIGO, T. KIMATA, M., and MARUOKA, T. (2007) Crystal-chemical and carbon-isotopic characteristics of karpatite (C₂₄H₁₂) from the Picacho Peak Area, San Benito County, California: Evidences for the hydrothermal formation. *American Mineralogist*, **92**, 1262-1269.
- EVERHART, D. L. (1950) Skaggs Springs quicksilver mine, Sonoma County, California. *California Journal of Mines and Geology*, **46**, 385-394.
- FRANK-KAMENETSKI, V. A., FILATOV, S. K., and GILLER, Y. A. (1967) The crystal structure and chemical formula of carpathite. *Mineral. Sbornic L'vov Gos University*, **21**, 275-278.
- GALIMOV, E. M. (1995) Fractionation of carbon isotopes on the way from living to fossil organic matter. In E. Wada, T. Yonegawa, M. Minagawa, T. Ando and B. D. Fry, Eds., Stable Isotopes in the Biosphere, 133-170. Kyoto University Press, Japan.
- GEISSMAN, T. A., SUN, K. Y. and MURDOCH, J. (1967) Organic minerals. Picine and chrysene as constituents of the mineral Curtisite (idrialite). *Experientia*: **23**: 793-794.
- GUILLEN, M. D., DOMINGUEZ, A., IGLESIAS, J. J., FUENTE, E., and BLANCO, C. G. (1996) Analysis of coal tar pitch: relations between thermal behaviour and composition. *Fuel*, **75**, 1101-1107.
- HAYES, J. M., KAPLAN, I. R. and WEDEKING, K. W. (1983) Precambrian organic geochemistry, preservation of the record, In J. W. Schoft, Ed., Origin and Evolution of the Earth's Earliest Biosphere, p. 93-134. Princeton university Press, New Jersey.

KILLOPS, S. and KILLOPS, V. (2005) Introduction to Organic Geochemistry, 2nd edition, p. 393. Blackwell Publishing, Oxford.

KRYGOWSKI, T. M. (1993) Crystallographic studies of inter- and intra-molecular interactions reflected in aromatic character of σ -electron systems. *Journal of Chemical Information and Computer Science*, **33**, 70-78.

KRYGOWSKI, T. M. and CYRANSKI, M. K. (2001) Structure aspects of aromaticity, *Chemical Reviews*, **101**, 1385-1419.

MARTINEZ-ALONSO, A., BERMEJO, J. and TASCÓN, J. M. D. (1992) Thermoanalytical studies of pitch pyrolysis comparison with polycyclic aromatic hydrocarbons. *Journal of Thermal Analysis*, **38**, 811-820.

MURDOCH, J. and GIESSMAN, T. A. (1967) Pendletonite, a new hydrocarbon mineral from California. *American Mineralogist*, **52**, 611-616.

PEMBERTON, H. E. (1983) Minerals of California. Van Nostrand Reinhold Company, New York, Cincinnati, Toronto, London, Melbourne, 589 pp.

PIOTROVSKY, G. L. (1955) Karpatite – a new organic mineral from Transcarpathia. *L'vovskoe geol. Obshch., Mineral. Sbornik*, **9**, 120-127.

RONA, P. (1984) Hydrothermal mineralization at seafloor spreading centers. *Earth Science Reviews*, **20**, 1-104.

RONA, P. A. (1988) Hydrothermal mineralization at ocean ridges. *Canadian Mineralogist*, **26**, 431-465.

RONA, P. A. and SCOTT, S. D. (1993) Preface to special issue on sea-floor hydrothermal mineralization: new perspectives. *Economic Geology*, **88**, 1933-1976.

SIMONEIT, B. R. T. (2000) Alternation and migration of organic matter in hydrothermal systems and implications for metallogenesis. In M. Glikson and M. Mastalertz, Eds., *Organic Matter and Mineralization*, p. 13-37. Kluwer Academic Publishers, Great Britain.

SIMONEIT, B. R. T. and SCHOELL, M. (1995) Carbon isotope systematics of individual hydrocarbons in hydrothermal petroleum from the Guaymas Basin, Gulf of California. *Organic Geochemistry*, **23**, 857-863.

SIMONEIT, B. R. T., SCHOELL, M. and KVENVOLDEN, K. A. (1997) Carbon isotope systematics of individual hydrocarbons in hydrothermal petroleum from Escanaba Trough, Northeastern Pacific Ocean. *Organic Geochemistry*, **26**, 511-515.

STEIN, S. E. and FAHR, A. (1985) High-temperature stabilities of hydrocarbons. *Journal of Physical Chemistry*, **89**, 3714-3725.

STRUNZ, H. and CONTAG, B. (1965) Evkenit, Flagstaffit, Idrialin und Reficit. *Neues Jahrbuch für Mineralogie, Monatshefte*, **1**, 19-25.

STUDEMEISTER, P. A. (1984) Mercury deposits of western California: an overview. *Mineralium Deposita*, **19**, 202-207.

WANG, T. G. and SIMONEIT, B. R. T. (1990) Organic geochemistry and coal petrology of Tertiary brown coal in Zhoujing Mine, Baise Basin, South China: 2. Biomarker assemblage and significance, *Fuel*, **69**, 12-20.

WISE, S. A., CAMPBELL, R. M., WEST, W.R., LEE, M. L., and BARTLE, K. D. (1986) Characterization of polycyclic aromatic hydrocarbon minerals, curtisite, idrialite and pendletonite using high-performance liquid chromatography, gas chromatography, mass spectrometry, and nuclear magnetic resonance spectroscopy. *Chemical Geology*: **54**, 339–357.

WRIGHT, F. E. and ALLEN, E. T. (1930) Curtisite, a new organic mineral from Skaggs Springs, Sonoma County, California. *American Mineralogist*, **15**, 169-173.

APPENDIX

BITUMEN IN MERCURY DEPOSITS

Ted A. Hadley
907 Anaconda Way
Sunnyvale, California 94087

INTRODUCTION:

An organic material commonly found in the mercury deposits of California is bitumen, also called tar, pitch, oil, petroleum, etc. This report shows the material to be a broad mixture of hydrocarbons but having a composition significantly different from natural petroleum, and how that petroleum came to exist in ore veins.

BASIC DATA:

Bitumen is black, quite viscous to solid, and the solid material is brittle or very weakly plastic. It is isotropic and shows no preferred parting. No fluorescence is observed. It is completely amorphous and not a mineral.

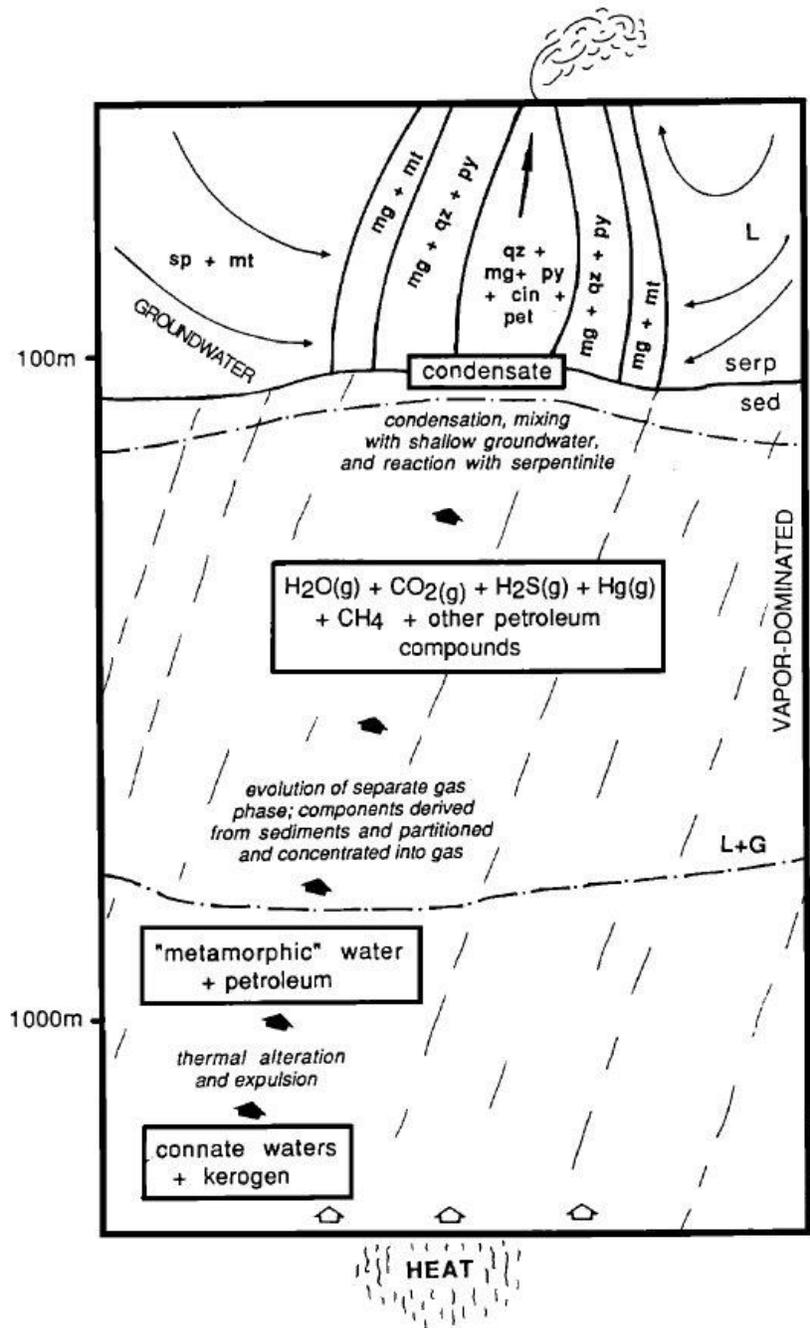
CALIFORNIA LOCALITIES:

The main localities for bitumen are the New Almaden mine complex and the Mayacmas District. The Picacho mine area in the New Idria Serpentine Body has small amounts of hardened bitumen. At the New Almaden mine, large seeps and drips can be seen in some of the adits. In addition, the bitumen occurs in spherical drops sealed in quartz and/or dolomite. These droplets existed within the mineralizing fluids and were trapped during crystallization of the minerals. The Culver-Baer mine is probably the most studied locality for ore bearing bitumen. Its occurrence is similar to the Picacho mine: relatively rare, solid, and brittle. At the Picacho mine, the bitumen occurs with carpathite, while at the Culver-Baer it occurs with cinnabar and idrialite.

GEOLOGY:

The geochemistry of petroleum in silica carbonate hosted cinnabar deposits is analyzed by Peabody and Einaudi (1992). Their work on the Culver-Baer mine indicates the chemical makeup of the petroleum is largely PAHs (rings of 6 carbon atoms), whereas conventional petroleum is mainly composed of aliphatic hydrocarbons (chains of carbon atoms). Using oxygen-18 and carbon-13 isotope comparisons, they have shown the source of the petroleum is hydrothermal. Furthermore, the origin of the hydrocarbons is believed to be organic kerogen, which was swept up in the deposit at depth as the mercury bearing fluids were transported. Petroleum transports easily in vapor phase and would likely accompany the mercury in such a situation.

Substantial amounts of mercury can be transported as a dissolved phase in the hydrocarbons. Miedaner, *et al.* (2005) show the solubility of mercury in different hydrocarbons and at different temperatures. This supports the vapor phase transport model for the mercury deposit.



Model for genesis of the mercury deposit at the Culver-Baer mine. For discussion, see text. G = gas, L = liquid; cin = cinnabar, mg = magnesite, mt = magnetite, pet = petroleum, py = pyrite, qz = quartz, sed = sediment, serp = serpentinite, sp = serpentine.

Figure A1. After Peabody and Einaudi (1992).



Figure A2. Bitumen dripping from the ceiling of the Santa Rita Drift of the New Almaden mine Santa Clara County. Photo: Mike Cox, 1979.



Figure A3. Bitumen fully enclosed in shells of dolomite and/or quartz, sealed within a mineralized vein. New Almaden mine, Dan Evanich collection and photo. FOV = 1 cm.



Figure A4. Bitumen from a quartz lined vug associated with cinnabar. Culver-Baer mine, Dan Evanich Collection and photo. FOV = 1.4 cm.

In Figure A1 Peabody and Einaudi (1992) show a schematic of a typical mercury deposit, where the mercury and organic matter are swept into the fluid channel. In the center of the channel, hydrocarbons aid in the transport of the mercury upward, where it is eventually condensed in the deposit.

The abundance of bitumen in some localities is shown in Figure A2. The photographer has dozens of similar photos. In Figure A3, the nature of the bitumen in somewhat spherical droplets completely covered with mineralization is seen. Though less dramatic, the bitumen of Figure A4 shows the same physical structure of a drop of bitumen surrounded by quartz.

CONCLUSIONS:

Much of the bitumen found in the deposits is likely remnants of the vapor phase transport, which were condensed with the mercury. It is for that reason it is found in the fluid passages and enclosed by other minerals in sealed capsules. The origin of the bitumen is not petroleum from nearby shales, as shown by the composition of the oils. This supports the theory that organics were incorporated in the mercury deposit at depth.

ACKNOWLEDGMENTS:

The author thanks Dan Evanich of San Jose, CA, and Mike Cox of Soquel, CA, for use of their photos. In addition, Mike Cox provided many references from his library, without which this report would not have been possible.

REFERENCES:

FEIN, J. B. and WILLIAMS-JONES, A. E. (1997) The Role of Mercury-Organic Interactions in the Hydrothermal Transport of Mercury. *Economic Geology* **92**, 20-28.

MIEDANER, M. M., MIGDISOV, A. A. and WILLIAMS-JONES, A. E. (2005) Solubility of metallic mercury in octane, dodecane, and toluene at temperatures between 100°C and 200°C. *Geochemica et Cosmochemica Acta*, **69**, No. 23, 5511-5516.

PEABODY, E. C. and EINAUDI, M. T. (1992) Origin of Petroleum and Mercury in the Culver-Baer Cinnabar Deposit, Mayacmas District, California. *Economic Geology* **87**, 1078-1103.